This is to certify that the

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Catalytic Upgrading of Succinates to Itaconic Acid

presented by

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has been accepted towards fulfillment
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CATALYTIC UPGRADING OF SUCCINATES TO ITACONIC ACID

By

Dushyant Shekhawat

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ABSTRACT

CATALYTIC UPGRADING OF SUCCINATES TO ITACONIC ACID

By

Dushyant Shekhawat

A novel process and catalysts to produce itaconic acid via condensation of succinic acid or its derivatives and formaldehyde were comprehensively studied.

The nature of sites on the support played an important role in the formation of citraconates in the vapor phase reaction. Neither highly acidic nor basic sites on the support favored the reaction. The highly acidic supports were found to be very active for cracking succinates into carbon dioxide, but not for condensation to citraconic anhydride. The basic supports gave little citraconic anhydride but catalyzed the Cannizzaro reaction of formaldehyde to methanol and formic acid, thus preventing formaldehyde from participating in the desired condensation. In contrast, γ-alumina, a mildly acidic support, without any salt added showed significant activity for the formation of citraconates from succinates. Results from different feedstocks over γ-alumina at the base case (standard) conditions are summarized in Table below.

Summary of Results from Different Feedstocks over γ-Alumina

S.N.	Feedstock	Yield of citraconates (%)	Conv of succinates (%)	Selectivity (%)
1	DMS + trioxane	35	48	73
2	SAN + trioxane	44	67	66
3	MMS + trioxane	26	40	78
4	DMS + Formalin	29	42	70
5	DMS + Formcel	34	56	61

The decay in catalyst activity was much slower with Formalin. Yields of citraconic anhydride and conversion of DMS dropped off very slowly over time for reaction times out to five hours. Coking on the catalyst was also much less with Formalin, likely because the water present steam-cleaned the catalyst during the reaction. Coking involves both the succinate species and formaldehyde. Citraconic anhydride yield stabilizes following acid site deactivation. Upon deactivation, the alumina catalyst was regenerated by exposure to air at 500 °C for five hours. The yields of citraconic anhydride were identical before and after the regeneration process, which demonstrated the robust nature of the oxide catalysts and their ability to be regenerated.

Yield of citraconic anhydride increased with increasing reaction temperature, but selectivity lowered due to more cracking of DMS at elevated temperatures. Citraconic anhydride yields were highest at 380 °C. Higher formaldehyde to DMS molar ratios gave better yields and selectivities of citraconic anhydride. The yield of citraconic anhydride decreased with increasing liquid feed flow rate, but selectivity remained unchanged. Citraconic anhydride yields were increased with increasing catalyst bed length, but the selectivities decreased. The condensation reaction of DMS with Formalin over intermediate surface area alumina is not mass transfer limited.

The subsequent process steps for separation of citraconic acid from unreacted succinates and isomerization of citraconic acid to itaconic acid have also been studied. A maximum 99.5% of purity of itaconic acid was observed. Finally, a process concept for itaconic acid production from succinates and formaldehyde is proposed. The calculated feedcost is $0.50/lb itaconic acid produced (base case results) for a 20-MM lb itaconic acid/yr capacity plant.

I dedicate this work to:

My parents, Icharaj Kanwar and Inder Singh Shekhawat

&

My aunt and uncle, Sarala and Fateh Singh Bika

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TABLE OF CONTENTS

32

33

Ma

34

35

Chapter 4

41

42

43

44

Chapter 6.

Solutions to

6.1

6.2

6.3

6.4

6.5

6.6

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1. Background

A number of chemicals are obtained from petroleum, natural gas, coal, and other fossil carbonaceous materials. But, biomass-derived feedstocks offer a potential alternative for producing variety of chemicals which are produced traditionally from fossils. There are several reasons for increased interest in biomass derived feedstocks. Nature puts a limit on traditional resources, so it is necessary to find alternate carbon sources for the production of basic feedstocks, shifting from a fossil to a renewable carbon base. The escalation of the cost of petroleum and natural gas and uncertainties in the long-range supply have triggered our attention towards biomass feedstocks. The use of biomass would reduce residues and wastes of the agriculture and forestry industries and will also boost our agriculture industry. It is also known that biomass conversion is more environmentally benign then petrochemical conversion. The complicated biomass refining is not complicated anymore because of recent advances in separation methods. Finally, the rapid growth in biogenetic engineering has made easier the commercial production of specific and complex materials from biomass.

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The focus of this research project is on the production of industrial commodities and specialty chemicals from biomass-derived (renewable) succinates. Some of the possible reaction pathways from succinic acid are illustrated in Figure 1.1. Succinic acid, also known as 1,4-butanedioic acid, and its alkyl esters are very valuable compounds in producing a variety of specialty chemicals. Succinic acid, containing two carboxylic acid groups and two reactive methylene groups, undergoes many chemical transformations to specialty chemicals and commodities. Among some of the known reactions are the Stobbe condensation (condensation of alkyl esters of succinic acid with aldehydes and ketones), reaction with amino compounds (making succinimides), esterification, hydrogenation (γ-butyrolactone, tetrahydrofuran, and 1,4-butanediol) and many more. The high cost of producing succinic acid ($2.72/lb)(1) via petroleum-based routes has prevented its commercial application. The fermentation process of producing succinic acid from biomass seems promising over the present petroleum process. Some pundits in this industry are projecting its market price as low as $0.20/lb. So, it is desirable to reconsider the above described chemical transformations as potential chemical processes.

1.2. Succinic Acid and Succinic Anhydride

Succinic acid (1,4-butanedioic acid), $C_4H_6O_4$, is a constituent of almost all plants and animal tissues. It was first prepared as the distillate from amber (Latin, *succinum*) for which it was named. Succinic anhydride (3,4-dihydro-2,5-furandione), $C_4H_4O_3$, was first obtained by dehydration of succinic acid. Succinic acid is used in the food, pharmaceutical, cosmetics, agriculture, textile, and polymer industries. Physical properties of succinic acid and its anhydride are summarized in Table 1.1.

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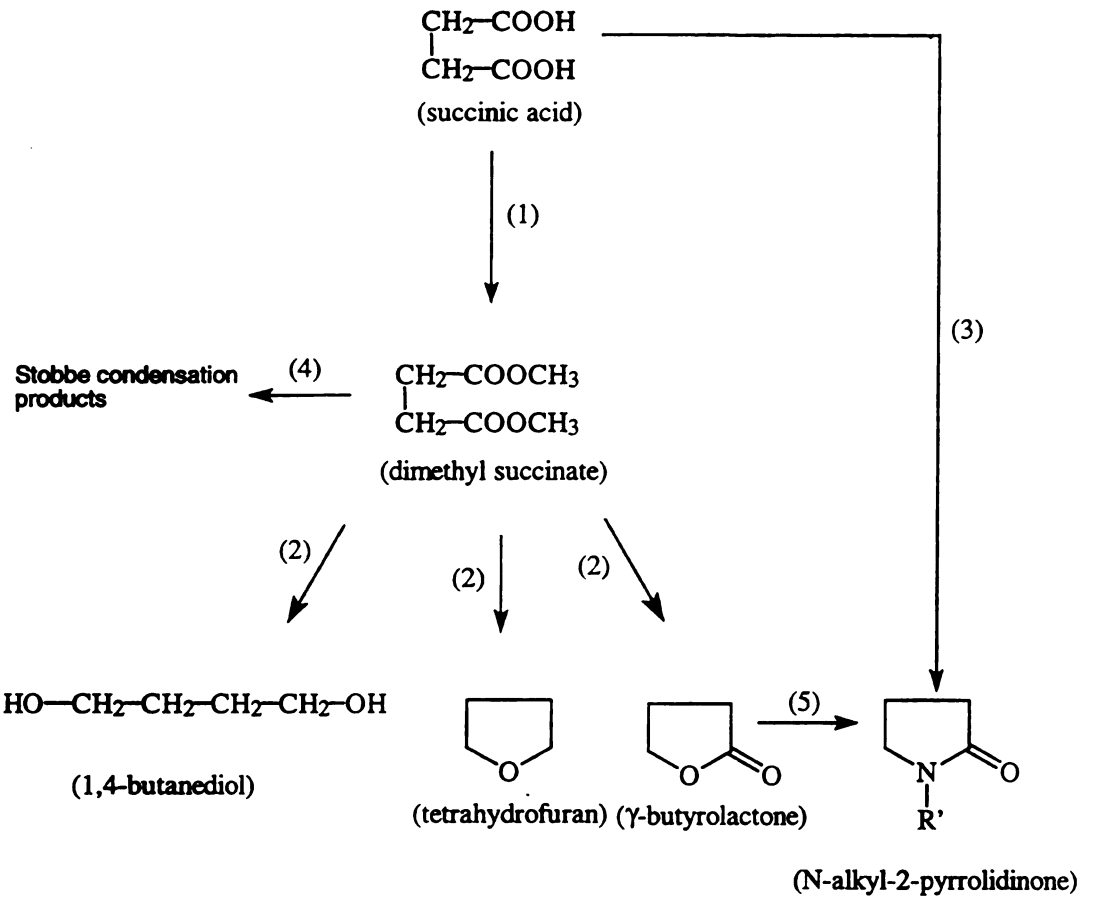


(1) Esterification process with methanol

(2) Catalytic hydrogenation over copper chromite, copper, or copper-chromium-manganese

(3) Hydrogenation of solution of succinic acid and $R'NH_2$ where, R' = H (ammonia) or an alkyl group (alkyl amine)

(4) Condensation with aldehydes or ketones and metal alkoxide

(5) Condensation of γ-butyrolactone with $R'NH_2$, an alkyl amine

Figure 1.1. Reaction Pathways from Succinic Acid (2)

Table 1.1. Physical properties of succinates under study[1]

Properties	Succinic acid	Succinic Anhydride	Dimethyl succinate	Diethyl succinate
Mol. wt.	118	100	146	174
MP (°C)	188	119	19	-21
BP (°C)	235 (dehy)	261	197	216
Density (g/ml)	1.572	1.234	1.120	1.010
Solubility in water (g/100 g solvent)	7.7 121@100 °C	Insoluble	6.8	1.8
Solubility in ethanol (g/100 g solvent)	8.0	Insoluble	23.2	Miscible
Enthalpy of formation (gas) (kJ/mol)	-822.9	-524.1		-851.0

[1]Properties at 25 °C, unless otherwise indicated.

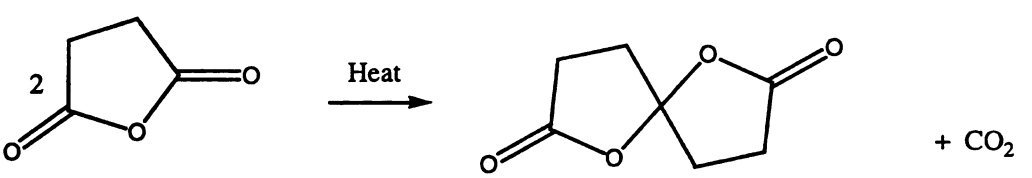
Succinic anhydride is currently manufactured by catalytic hydrogenation of maleic anhydride (2). Maleic anhydride is produced from the vapor phase oxidation of hydrocarbons or benzene over a solid catalyst. Maleic anhydride is very inexpensive ($0.44/lb) (1). Raney nickel, nickel, or palladium on different carriers are used as the catalyst for hydrogenation process (2). The reaction is carried out in liquid phase at a temperature of 120-180 °C and at moderate pressures (72-580 psi). The yield of the hydrogenation reaction is virtually theoretical. Succinic anhydride is dissolved in hot water to yield succinic acid, which is separated as crystals upon cooling, filtered and dried.

The preparation of succinic acid by fermentation has been studied extensively. Yields of succinic acid from glucose as high as >100% (CO_2 is incorporated) based on glucose charged have been reported (3). Historically, acetic acid as a co-product reduced yields of succinic acid, but recent advances have nearly eliminated acetate formation. But, the fermentation processes are not commercially acceptable yet, because of an inexpensive petroleum feedstock available. Process economics and hence the market

price of succinic acid is based mostly on separation methods employed to remove the acid from the product mixture. The fermentation technology for the production of succinic acid is gaining momentum with new innovations in process technology (4-8). This would lead to a definite drop in the price of the acid as a raw material. Succinic acid is also obtained in large amounts as a by-product in the production of adipic acid (2).

Worldwide consumption of succinic acid and succinic anhydride is the range of 18,000-20,000 tons/year (2). Mostly it is consumed and produced in Japan (Kawasaki Kasei, Nippon Shokubai, Takedo Chemical, Kyowa Hakko, and New Japan Chemicals). Buffalo Color is main producer in the US (500 tons/year) (2). Succinic acid currently is priced at $2.72/lb (1) and succinic anhydride at $1.71/lb (1).

Heating of succinic anhydride above 200 °C causes decarboxylation and the formation of the dilactone of gamma ketopimelic acid (1,6-dioxaspiro[4.4]nonane-2,7-dione) (2, 9-10):



Succinic anhydride

Dilactone of gamma kitopimelic acid

The above reaction takes place at lower temperatures in the presence of alkali. Succinic anhydride undergoes thermal decomposition in the gas phase to give carbon monoxide and carbon dioxide (11-13). Succinic anhydride can be decomposed even in the liquid phase at low temperature (13). Succinic acid is stabilized against the

deteriorative effects of heat by the addition of small amounts (0.5 wt%) of boric acid (12).

1.3. Alkyl Esters of Succinic Acid

Esterification is a very common, well-understood process (14-15). Succinic acid readily undergoes esterification to alkyl esters upon mixing and heating with the appropriate alcohol in the presence of small amounts of sulfuric acid (2).

$$R\text{-}COOH + R'OH = R\text{-}COO\text{-}R' + H_2O$$

Esterification generally proceeds rapidly, but in many cases the yield of ester is limited by equilibrium constraints. Because of this, most commercial processes either use a large excess of alcohol or constantly remove one of the reaction products to drive the reaction to completion. Excess amount of alcohol is used to minimize the yield of monoester of succinic acid. In a laboratory study, yields of 85% and 95% were reported for methyl and ethyl succinates, respectively, from succinic acid (16) via this pathway. Several patents describe the esterification of succinic acid as part of its recovery from the aqueous waste streams of adipic acid formation processes (17-22).

Esters of succinic acid can be made by routes other than direct succinic acid esterification. According to the Davey-McKee technology (23-24), maleic anhydride is first hydrolyzed and esterified to dialkyl maleate and then hydrogenated over a metal catalyst to the esters of succinic acid. Physical properties of dimethyl succinate and diethyl succinate are given in Table 1.1.

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1.4. 1,4-Butanediol, γ-Butyrolactone, and Tetrahydrofuran

The catalytic reduction of succinic acid or ester yields 1,4-butanediol (BDO), γ-butyrolactone (GBL), tetrahydrofuran (THF), or a mixture of these compounds, depending upon the catalyst and reaction conditions (25-26). The chemical structures of 1,4-butanediol, γ-butyrolactone, and tetrahydrofuran are given in Figure 1.1. Demand for 1,4-butanediol and γ-butyrolactone has been steadily increasing these past years. The largest uses of 1,4-butanediol are internal consumption in manufacturing of tetrahydrofuran and γ-butyrolactone (26). But demand for 1,4-butanediol has steadily increased owing to its use in the manufacture of polytetramethylene glycol (PTMEG) and polybutylene terephthalate (PBT) resin, along with a steady increase in the use of polyurethane (26). Butyrolactone is principally consumed by the manufactures by reaction with methylamine or ammonia to produce N-methyl-2-pyrrolidinone and 2-pyrrolidinone, respectively.

A review of current technologies used by the industry shows that the Reppe process is still the method being followed by the majority of manufacturing companies for production of 1,4-butanediol, but maleic anhydride based routes are the only ones in new plants being built. The low cost of acetylene as a raw material offsets any other alternative routes such as succinic acid or esters. Gas-phase catalytic hydrogenation of succinate to form 1,4-butanediol, γ-butyrolactone, or tetrahydrofuran is gaining momentum as the recent development of efficient fermentation technologies promises to lower succinic acid costs. Catalysts mentioned in the literature for the hydrogenation of succinates include copper chromites with various additives, copper-zinc oxides with promoters, silica-supported metal catalysts, and many others (25-26).

1.5. Stobbe Condensation

1.5.1. Introduction

One important reaction that is specific to esters of succinic acid is the Stobbe condensation. Ethyl, methyl, or t-butyl esters of succinic acid are used in Stobbe condensation with aldehyde or ketone compounds. This condensation reaction has led to the preparation of a variety of unsaturated and saturated substituted derivatives of succinic acid.

The reaction of carbonyl group (aldehydes or ketones) with esters of succinic acids to form alkylidenesuccinic acid (substituted itaconic acids) or a tautomer is called the Stobbe condensation. Hans Stobbe performed this reaction first in 1893 using a mixture of acetone and diethyl succinate in sodium ethoxide (27). One mole of a metal alkoxide per mole of succinate and aldehyde or ketone is required for the Stobbe condensation. The salt of the half ester is the primary product of the reaction.

Sometimes dialkylidenesuccinic acid is also formed from the condensation of two molecules of aldehyde with one molecule of ester (28). The yield of mono- or di-substituted products depends to a considerable extent upon the reaction conditions with low temperatures favoring the formation of di-substituted product (28). A variety of carbonyl groups e.g. aliphatic, aromatic, and α, β-unsaturated aldehydes or alicyclic, aliphatic, and aromatic ketones or diketones or keto esters or cyano ketones can undergo the Stobbe condensation (28-31). Dimethyl, diethyl, di-t-butyl succinate and also α-substituted alkyl-, aryl-, aralkyl, and alkylidene-succinates have been widely studied (28).

Sodium ethoxide, potassium-t-butoxide, and sodium hydride are the most commonly used condensing agents (28).

1.5.2. Mechanism of Stobbe Condensation

The mechanism of Stobbe condensation is depicted in Figure 1.2 (28). The condensing agent (a base) catalyzes the loss of a proton from dimethyl succinate. The resulting carbanion (I) facilitates nucleophilic attack on the positively polarized carbon of a ketone molecule (II). The resulting intermediate (III) is stabilized by a lactone ring formation (IV). Deprotonation from the lactone derivative (IV) proceeds via formation of the half ester of substituted itaconic acid (V).

1.5.3. Applications of Stobbe Condensation

The Stobbe condensation is very useful in synthesis of unsaturated and saturated (by hydrogenation) succinic acids, and also has wide applications in preparing some other substances, i.e., substituted lactones, naphthols, indones, tetrahydroindanones, and tetralones. The general applications of the Stobbe condensation are discussed below.

1.5.3.1. Lactonic Acids

Alkylidenesuccinic acids (or half-esters) give bromoparaconic acids (or esters) by treatment with bromine. Bromoparaconic acids on treatment with boiling water give α, β-unsaturated lactonic acids or dilactones. γ-Lactones are formed when the product of Stobbe condensation with a ketone RCOR' is heated with halogen acid, water, and acetic acid (28).

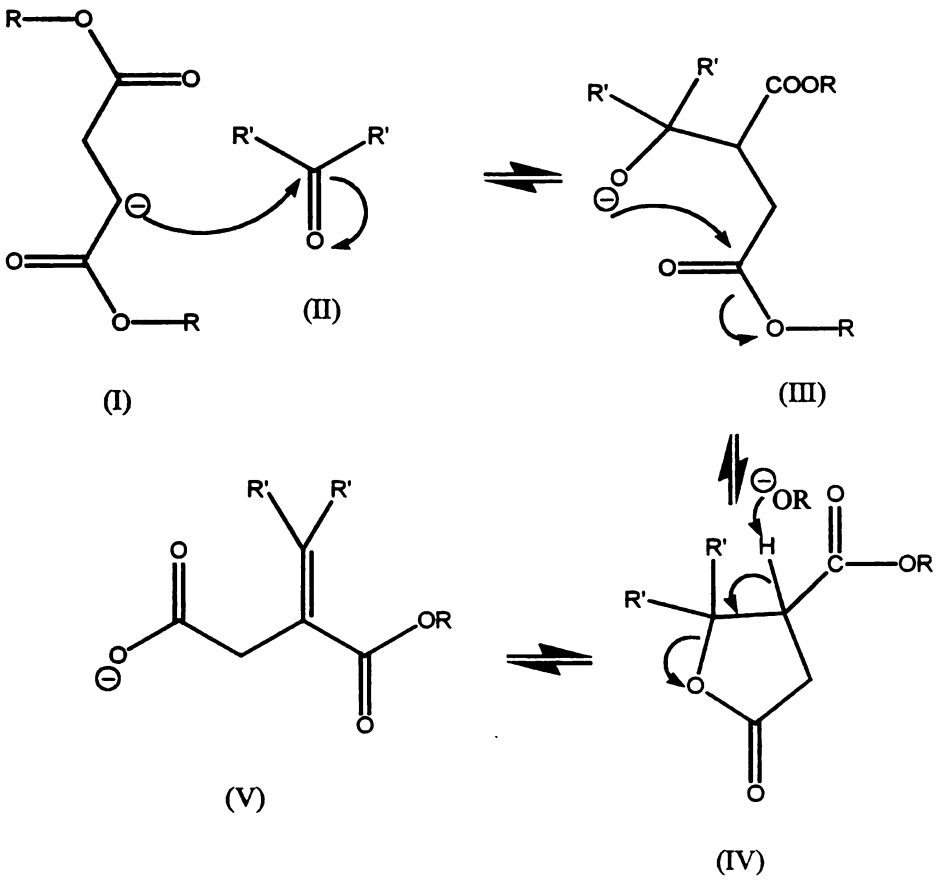


Figure 1.2. Reaction mechanism of stobbe condensation

1.5.3.2. The Naphthol Synthesis

Alkylidenesuccinic acids (or half-esters) may undergo cyclodehydration and enolization to give substituted 1-naphthol-3-carboxylic acid if acids (or esters) have the appropriate stereochemical configuration (an aryl group *cis* to the CH_2COOH group). Sodium acetate and acetic anhydride are commonly used for ring closure (28).

1.5.3.3. The Indone Synthesis

Alkylidenesuccinic acid having an aryl group *cis* to the carboxyl group may undergo cyclodehydration to form a substituted indoneacetic acid and some isomeric lactone. Sulfuric acid, hydrogen fluoride, zinc chloride-acetic acid-acetic anhydride, sodium acetate-acetic acid-acetic anhydride and aluminum chloride have been used for above cyclization (28).

1.5.3.4. The Tetrahydroindanone Synthesis

When the Stobbe condensation product with a cyclic ketone is heated with a mixture of halogen acid, water, and acetic acid, the resulting half-ester is hydrolyzed and the acid loses carbon dioxide to form a γ-lactone (as discussed in Lactonic acid). Either the γ-lactones or the unsaturated dicarboxylic acid thus produced may undergo ring closure with zinc chloride in acetic acid-acetic anhydride to give tetrahydroindanone (28).

1.5.3.5. The Tetralone Synthesis

γ-Arylbutyrolactones produced via the Stobbe condensation according to the lactonic acid synthesis may be reduced to substituted γ-arylbutyric acids, which on

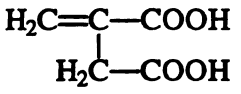
cyclodehydration give substituted 1-tetralones. The reduction and cyclization may be carried out by the conventional methods (28).

1.5.2.6. The Equilenone Synthesis

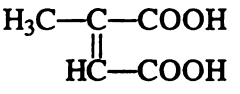
The Stobbe condensation product with 7-methoxy keto nitrile gives an unsaturated ketone upon hydrolysis and decarboxylation, which on catalytic hydrogenation yields an Equilenone (28).

1.6. Itaconic Acid and Its Isomers

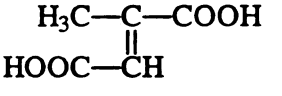
Citraconic acid and mesaconic acid are isomers of itaconic acid. Their structures are as follows:



Itaconic acid



Citraconic acid



Mesaconic acid

Itaconic acid is also known as methylene succinic acid or methylene butanedioic acid. It is a very valuable monomer for polymerization because of conjugation between one of the two carboxylic acid groups and the methylene group. The methylene group is able to take part in addition polymerization, giving polymers with many free carbonyl groups that confer advantageous properties in resulting polymers.

Physical properties of the itaconates and its isomers are given in Table 1.2.

1.6.1. Current Manufacturing Process (Fermentation)

Itaconic acid is currently manufactured by the process of fermentation of sugars. The fermentation is carried out in stainless-steel fermenters utilizing molasses (widely

Table 1.2

Property	
Mol. wt.	
MP °C	
BP °C	
Density	
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Solubility	
g/100 g	
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Appearance

Solubility

Formula

Appearance

Density

Boiling

Relative

Flash

Table 1.2. Physical properties of itaconic acid and its isomers[1]

Properties	Itaconic Acid	Citraconic acid	Citraconic anhydride	Mesaconic acid
Mol. wt.	130	130	112	130
MP (°C)	175	93-4	7-8	204-5
BP (°C)	Dec	Dec	213-4	Sublime
Density (g/ml)	1.632	1.617	1.247	1.466
Solubility in water (g/100 g solvent)	9.5 72.6 @70 °C	360	380	2.7 @18 °C 117.5 @100 °C
Solubility in ethanol (g/100 g solvent)	19.8			30.6 @18°C
Enthalpy (gas) of formation (kJ/mol)	-729.0	-740.0		

[1]Properties at 25 °C, unless otherwise indicated

used because of its cost) or other sugars as the raw material. Initial carbohydrate in the fermenter charge is the order of 15-25%. This mixture is sterilized and incubated with a culture of Aspergillus terreus (32). Sterile air is passed into the broth at 35-40 °C for 3-7 days under a pressure of 10-15 psig. The reaction mixture is kept at constant pH of about 5.0 by adding lime to prevent the formation of any undesired products or contamination. Ammonium sulfates as a nitrogen source and some metals (Mg and Zn) are also added for proper culture growth. Itaconic acid is produced from citric acid present in the broth. Citric acid is dehydrated by the enzyme, aconitate hydratase, to cis-aconitic acid. Decarboxylation of *cis*-acotinic by enzyme, aconitate decarboxylase, gives itaconic acid. Itaconic acid is separated from the broth by acidification, concentration and crystallization when fermentation process is complete. Iwata Kagaku Kogyo Kabushiki Kaisha (Japan) is the largest producer of itaconic acid with 20 million lb per year (32, 37). Cargill is the only US manufacturer of itaconic acid.

1.6.2. Catalytic Route

Tate and Berg in Pfizer first prepared citraconic anhydride and subsequently itaconic acid catalytically (1974) (33). They made these isomers by the vapor phase catalytic condensation of succinic anhydride with trioxane. A 60-80% yield of citraconic anhydride with 90-98% conversion of succinic anhydride was claimed using thorium sulfate, potassium diacid phosphate, lithium carbonate or lithium phosphate on an alumina support, Alundum (Norton, Inc.). The yield of citraconic anhydride was observed to be maximum when the molar ratio was 5 to 1 of formaldehyde to succinic anhydride. The reaction was carried out in a micro reactor at 340-410 °C. Catalyst deactivation was also reported upon prolonged exposure of the catalyst, but details of deactivation were not provided. Citraconic anhydride was hydrolyzed to get citraconic acid and subsequently isomerized at temperatures around 200 °C to form itaconic acid.

The Denki Kagaku Kogyo, Inc. (Japan) also claimed some processes for synthesis methods of itaconic acid, citraconic acid and citraconic anhydride in their patents (1974-75) (34-36). They prepared these compounds from the reaction of succinic acid or its derivatives with formalin (37% solution of formaldehyde in water) using ion exchanged zeolites-13X or silica-alumina containing group IB or IIB metal salts. A maximum 30% yield of citraconic acid, citraconic anhydride, and itaconic anhydride at 92% conversion of formaldehyde and 31% conversion of DMS (molar ratio 2:1 DMS to formaldehyde) is reported with SiO_2–Al_2O_3 catalyst at 370 °C. Contrary to Tate and Berg, the molar ratio of 2:1 ~ 5:1 of succinate to formaldehyde was preferred for better results.

Citraconic acid is also prepared by the pyrolysis of citric acid (37). The pyrolysis of citric acid gives citraconic anhydride along with its isomer itaconic anhydride.

Citraconic acid is obtained by the hydrolysis of citraconic anhydride. Citraconic anhydride can be obtained from pyrolysis of itaconic acid under vacuum at about 170 °C (37).

1.6.3. Uses of Itaconic Acid and Its Isomers

Itaconic acid is a very valuable monomer for polymerization because of the conjunction of its two carboxyl groups and its methylene group. The methylene group is able to take part in addition polymerization giving polymers with many free carboxyl groups that confer advantageous properties on the resulting polymer. Sodium polyitaconate or other alkali salts may be used in detergents to improve clarity and color, used in bleaches as a stabilizer and used in metal cleaner for rust removal (38). The calcium salts of grafts on nylon in itaconic acid exhibit excellent resistance to hole melting (39).

Itaconic acid itself polymerizes very slowly to give low molecular weight products, so it is widely used in copolymerization. Itaconic acid is a specialty monomer that affords performance advantages to certain polymers when the acid is incorporated in small amount as a polymer. Itaconic acid is primarily used in polymerization for improved fiber toughness, improvement of the emulsion stabilization, super absorbing polymers (SAP), and performance characteristics such as adhesion to substrates.

Styrene-butadiene latexes containing low levels of itaconic acid (below 10%) are widely used in carpet backing (40-42) and paper coating (43-44). Emulsion stability, clarity, water resistance of the coatings, and adhesion to substrates are improved by the itaconic acid. Masking tapes impregnated with the copolymer of butadiene, styrene, and

itaconic acid shows higher strength and greater resistance to delamination (45). Resistance to picking of coating from paper in high speed printing with tacky inks is improved in tetrapolymers of butadiene, styrene, acrylonitrile, and itaconic acid (46). The blend of copolymers of styrene, butadiene, and itaconic acid with dispersions of polyethylene and glycerols rosin esters affords excellent heat-sealing and laminating adhesives for paperboards (47).

Acrylic and methylacrylic ester copolymers with itaconic acid exhibit a wide range of applications, such as coating, binders, adhesives, polishes, and textiles finishes. The acrylic-itaconic acid coatings show high hardness, excellent adhesion, and resistance to detergent solutions and staining by foodstuffs (48). Copolymers of butyl methylacrylate, itaconic acid, and higher (hexyl, octyl, decyl) methacrylates may be used in anchor coats for polyester photographic stripping films used in intaglio printing (49-50). Emulsion copolymers of 2-ethylhexyl acrylate, acrylonitrile, and itaconic acid with propyleneimine gives binders for nonwoven rayon webs (51). The resulting fabrics possessed soft hand, good drape, and good resistance to alkaline detergents and cleaning solvents. The aqueous solution of copolymers of acrylamide and itaconic acid is an effective dispersant and adhesive (52). The copolymer of acrylic acid with itaconic acid is a very good etching agent for lithographic plates (53).

Copolymers of vinylidene chloride, acrylic comonomers, and itaconic acid have considerable utility as coating for films, particularly in packaging and photography. The incorporation of itaconic acid provides strongly bonded heat seals that retain their adhesion after immersion in boiling water. Vinylidene chloride coatings containing the monomer exhibit improved adhesion to paper, cellophane, and poly(ethylene

terephthalate) films (54). The copolymers of vinylidene fluoride, tetrafluoroethylene, vinyl butyrate, and itaconic acid give rust-resistant coatings for galvanized steel (55). Copolymers made of vinyl acetate, acrylate, and itaconic acid are also used for coatings (56). Such coatings on chipboard were smooth and receptive to ink and displayed excellent resistance to pick by inks.

Dental cements made of acrylic-itaconic acid copolymers that are cured with polyvalent metal compounds such as aluminosilicates or oxides of zinc and magnesium possess good compressive and adhesive strength and physiological compatibility (57).

The dimethyl, diethyl and di-n-butyl esters of itaconic acid can also be used in copolymers, e.g., for adhesives and esters with long chain alcohol have been proposed as plasticizers.

Itaconic acid produces N-substituted pyrrolidinones with amines that can be used as thickeners for greases (58). Some other pyrrolidinones made from itaconic acid and a wide range of amines have potential uses in detergents, shampoos, pharmaceuticals and herbicides. A condensate of lauric acid and aminoethylethanolamine reacts with itaconic acid to give an imidazoline derivative useful as an active ingredient in shampoos (59). The cyclic adducts of itaconic acid with long-chain alkyl amines, oil soluble adducts, confer antirust properties on gasolines and fuel oils (60).

Citraconates are not as useful as their counterpart itaconates. The α, β-substituted double bond of the citraconates is less reactive in homopolymerization than its isomer itaconates. Copolymers of citraconic anhydride are useful in molding, adhesives, and coating (61).

1.7. Formaldehyde and Its Sources

1.7.1. Formalin

Formaldehyde, CH_2O, is the first in the series of aliphatic aldehydes. Because of its relatively low cost, and high order of chemical reactivity, formaldehyde has become one of the world's most important industrial chemicals (62-64). The carbonyl group of formaldehyde, which carries two hydrogen atoms and no alkyl group, provides it higher chemical reactivity. Annual worldwide production capacity of formaldehyde is 12×10^6 metric ton of equivalent 37 wt% aqueous solution (62). All formaldehyde is produced from methanol and it is usually marketed in the form of aqueous solution about 37 percent by weight dissolved formaldehyde. The standard 37 wt% U.S.P. solution, also known as Formalin, contains sufficient methanol (7 to 15% by weight) to prevent precipitation of polymer under ordinary conditions of transportation and storage. The current selling price of 37 wt% formaldehyde solution, Formalin, is about \$0.09/lb (1), although because of the relatively small volume of merchant material, price assessment is difficult. Mostly, formaldehyde production facilities are located by user facilities; it is not economical to transport the water in the solution for any significant distance.

1.7.2. Properties of Formaldehyde

The properties of monomeric formaldehyde are listed in Table 1.3 (62). Formaldehyde is highly soluble in water. The dissolved formaldehyde is principally in the form of monohydrate, methylene glycol, $CH_2(OH)_2$, which itself tends to polymerize to polyoxymethylene glycols, $HO.(CH_2O)_n.H$ (63-64). A small concentration of monomeric formaldehyde is also present but its concentration is well under 0.1 % even in

Table 1.3. Properties of monomeric formaldehyde (62-63)

Molecular weight	30.026
Boiling point (°C)	-19
Melting point (°C)	-117
Density at –80 C (g/cm^3)	0.9151
Density at –20 C (g/cm^3)	0.8153
Heat of formation at 25 °C (kJ/mol)	-115.9
Free energy of formation (gas phase) at 25 °C (kJ/mol)	-109.9
Heat of combustion (kJ/mol)	561
Heat of vaporization at –19 °C (kJ/mol)	23.3
Heat capacity (J/mol-K)	35.4
Flammability in air (vol%)	7-73
Ignition temperature (°C)	430

concentrated solution at 60 °C. Low formaldehyde concentrations favor methylene glycol and high concentrations favor the polyoxymethylene glycols. The action of methanol in preventing polymer precipitation in formaldehyde solution is due to formation of hemiacetals, which exist in a state of chemical equilibrium with the hydrated formaldehyde (methylene glycols) in solutions to which it has been added (64).

$$HO\text{-}CH_2\text{-}OH + CH_3OH \Leftrightarrow HO\text{-}CH_2\text{-}OCH_3 + H_2O$$

Methylene glycol — Methanol — Formaldehyde hemiformal — Water

The dissolved formaldehyde is completely available for chemical reaction, the solutions do not give up dissolved formaldehyde even on being warmed.

The largest end-use market for formaldehyde is construction (65). Urea-formaldehyde resins, phenol-formaldehyde resins, and polyacetal resins are the largest commercial derivatives of formaldehyde which are widely used in the housing and building industry (63). Dyes, tanning agents, dispersants, vitamins, flavorings, and pharmaceuticals make up its smaller end-use markets. Formaldehyde is also used as a corrosion inhibitor of metals and as a preservative and disinfectant in cosmetics and soap

(65). Borden Packaging and Chemicals (1600 m.t./yr), Georgia-Pacific (1100 m.t./yr), and Celanese (800 m.t./yr) are some of the large US producers of formaldehyde (65).

1.7.3. Manufacturing Processes

Essentially all of the world's formaldehyde production is derived from methanol. There are two existing processes that compete with each other for the manufacture of formaldehyde from methanol (62-63). First, known as the "silver process", is based on the air oxidation of methanol over a silver catalyst and under conditions of excess methanol to avoid the explosive range (62-63). In this process a portion of the methanol is dehydrogenated to formaldehyde. The reactions occur at essentially atmospheric pressure and 600 to 650 °C. Methanol conversion is 65-75% per pass. The other process, known as the "oxide process", is based on air oxidation of methanol under conditions of lean methanol concentration to avoid the explosive range (62-63). The reaction occurs over a mixed oxide catalyst containing iron oxide and molybdenum oxide in a ratio of 1.5 to 3. In contrast to the silver process, all of the formaldehyde is made by the exothermic reaction at atmospheric pressure and at 300-400 °C.

At high temperatures, formaldehyde decomposes almost exclusively to carbon monoxide and hydrogen as indicated by the equation (64):

$$CH_2O\,(g) \quad \Leftrightarrow \quad CO \quad + \quad H_2$$

Catalysts have significant influence on formaldehyde decomposition. In the presence of finely divided platinum, decomposition is stated to occur at 150 °C. Various inorganic materials, such as sodium carbonate, alumina, and chromium oxide etc., also accelerate formaldehyde decomposition at lower temperature.

Formaldehyde is a reducing agent. The Cannizzaro reaction involves the reduction of one molecule of formaldehyde with the oxidation of other (64).

$$2CH_2O\,(aq) + H_2O \rightarrow CH_3OH + HCOOH$$

Although it is normally alkali catalyzed, the Cannizzaro reaction also takes place when formaldehyde is heated in the presence of acids. Formic acid can be decomposed further to carbon monoxide and hydrogen.

1.7.4. Formcel

There are some other formaldehyde solutions available commercially. Formcel (66), a product of Celanese (a member of the Hoechst group), contains 55 wt% formaldehyde, 35 wt% methanol, and 10 wt% water. It is an equilibrium mixture of hemiacetals of the methanol and formaldehyde. Formcel is less subject to side reactions than aqueous formaldehyde solution, is stable at room temperature, and offers readily available formaldehyde and methanol for chemical reactions. The boiling point of Formcel is 102 °C and its specific gravity 1.071.

Georgia-Pacific provides a 60 wt% formaldehyde solution in water, but this formaldehyde solution is not stable, precipitates, below 60 °C.

1.7.5. Trioxane

Trioxane, $(CH_2O)_3$, the cyclic trimer of formaldehyde, is a very good source of water-free pure formaldehyde. It melts at 62 to 64 °C and boils without decomposition at 115 °C. Trioxane forms an azeotrope with water, which distills at 91.3 °C and contains

70 wt% trioxane. Trioxane is soluble in water, dimethyl succinate, diethyl succinate, alcohol, ketones, organic acids, ethers, phenols etc.

Trioxane preparation primarily involves distilling a 60 to 65 wt% formaldehyde solution in the presence of 2 wt% sulfuric acid and extracting trioxane from the distillate by means of a water-immiscible solvent such as methylene chloride (64). A crystallization process is used to isolate trioxane from the mixture.

The thermal decomposition of trioxane in the gaseous state occurs at 270 to 345 °C and it is a homogeneous reaction of first order (64). Decomposition of trioxane vapors to formaldehyde gas can be achieved at 200 to 240 °C in fixed bed reactor using a suitable catalyst like potassium acid sulfate on activated carbon or silicon carbide, phosphoric acid on silicon carbide or "Amberlite" IR-120 ion exchange resins. Trioxane readily depolymerizes to monomeric formaldehyde at comparatively low temperature in the presence of strong acids, such as sulfuric acid, hydrochloric acid, and phosphoric acid, or acidic material such as ferric chloride and zinc chloride (64). The monomeric formaldehyde produced by this method is very reactive and polymerizes to a high molecular weight polyoxymethylene in the absence of a formaldehyde acceptor (64). By use of this depolymerization reaction, trioxane may be employed as a special form of anhydrous formaldehyde.

1.7.6. Paraformaldehyde

Paraformaldehyde, $HO.(CH_2O)_n.H$ (n = 8 to 100), is a polymer of formaldehyde. It is a mixture of polyoxymethylene glycols containing about 95 wt% formaldehyde and a balance of free and combined water. The melting point of paraformaldehyde ranges from

120 to 170° C and it depends on degree of polymerization. Paraformaldehyde gradually vaporizes to formaldehyde at ambient conditions upon prolonged exposure (64). The depolymerization is very fast at elevated temperature. Paraformaldehyde completely depolymerizes to monomeric formaldehyde and some water.

Paraformaldehyde dissolves slowly in cold water, but it dissolves rapidly in hot water, hydrolyzing and depolymerization as it dissolves. Formaldehyde solutions are obtained by dissolving paraformaldehyde in hot water. Dilute acids or alkalies considerably accelerate the rate of depolymerization of paraformaldehyde in hot water. Paraformaldehyde is not soluble in other common solvents.

Dissolving gaseous formaldehyde excessively in water produces paraformaldehyde (64). When the concentration of formaldehyde in aqueous solution is increased by evaporation or distillation, the concentration and average molecular weight of dissolved polyoxymethylene glycols increases and precipitation takes place. The lower polyoxymethylene glycols primarily formed undergo further reaction upon standing and paraformaldehyde is formed.

1.7.7. Methylal

Methylal, $CH_2(OCH_3)_2$, also known as formaldehyde dimethyl acetal, formal, and dimethoxymethane, is the dimethyl ether of methylene glycol. It is a colorless, flammable, ether-like liquid that boils at 42.3 °C and freezes at –105 °C (64). It dissolves in approximately three times its volume of water and is infinitely miscible with alcohol, ether, and other organic solvents. It is converted to formaldehyde by vapor phase oxidation in the presence of a methanol oxidation catalyst. Methylal is prepared by

distillation from the equilibrium mixture obtained by addition of an acid catalyst to an aqueous solution of formaldehyde and methanol (64).

1.7.8. Safety Factors

Formaldehyde is poisonous by inhalation and by swallowing (62). The vapors of formaldehyde are irritating to the eyes, nose, and throat. The formaldehyde solutions are irritating to the skin and can cause severe eye burns. Ingestion of the solution irritates and inflames the mouth, throat, and stomach, causing nausea and vomiting. The carcinogenic potential of formaldehyde has not been determined. Results from various studies differ.

1.8. Catalyst

Most of the largest-scale catalytic processes take place with gaseous reactants in the presence of solid catalysts, which are mostly porous inorganic materials. Catalysis takes place as one or more of the reactants is chemisorbed on the surface and reacts there. The activity and selectivity of the catalyst depends strongly on the surface composition, texture, and structure. The surface area, porosity, pore shape, pore size distribution, mean pore size, particle size distribution, and the shapes and sizes of particle are some of important parameters which describe the catalyst texture of porous solid.

1.8.1. Surface Area

The surface area of a solid catalyst involves the internal surface area associated with pores and of the external surface area developed by the outer boundary of the

particles. The BET method, developed in 1938 by Brunauer, Emmett, and Teller, is widely used for surface area determination of a solid catalyst (67). The basis of BET procedure is physisorption. Physical adsorption is equilibrium coverage similar to surface liquefaction. Produced by van der Waals forces originating in surface atoms, it is approximately the same for all materials. Coverage proceeds first with adsorption on surface atoms but is quickly followed by the generation of additional layers even before complete monolayer forms. Since the process is exothermic and at equilibrium, the amount decreases as temperature increases. Easily measurable quantities are found close to the normal boiling point of the adsorbate. At low pressures ($p/p_0 = 0.1$), monolayer formation follows the Langmuir equation

$$\frac{V_{ads}}{V_m} = \frac{(Kp / p_0)}{(1 + Kp / p_0)} \qquad \text{(I)}$$

with V_m the monolayer volume, p the pressure, p_0 the saturation pressure at measurement temperature, V_{ads} the volume of gas adsorbed at pressure p, and K a constant. The BET equation is given by

$$\frac{p}{V_{ads}(p_0 - p)} = \frac{1}{V_m C} + \frac{(c-1)}{V_m C}(p / p_0) \qquad \text{(II)}$$

The parameter c is the BET constant that is related to the heat of adsorption. By plotting $p/V_{ads}\ (p_0\text{-}p)$ against p/p_0 a straight line results in which

$$Slope = S = \frac{(c-1)}{V_m C} \qquad \text{(III)}$$

$$Intercept = I = \frac{1}{V_m C} \qquad \text{(IV)}$$

$$V_m = \frac{1}{(S + I)} \qquad \text{(V)}$$

$$Surface\ Area = V_m * N * A_m \qquad \text{(VI)}$$

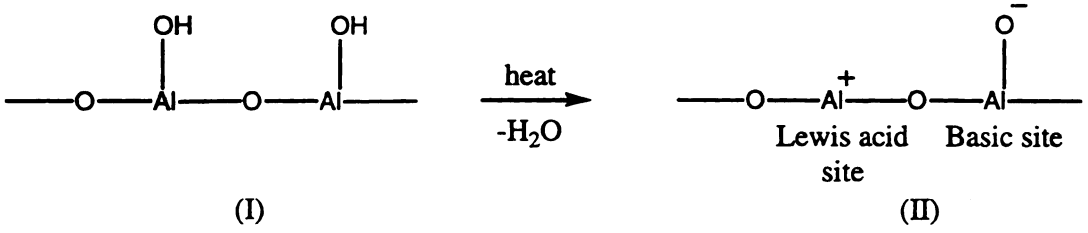
Where N is Avogadro's number and A_m is the cross sectional area of adsorbate molecule, which, for nitrogen, is 16.2 A^2. The BET surface area of the sample is expressed in m^2/g.

In this technique a weighed sample of the catalyst material to be analyzed is placed in a tube and heated under vacuum to be degassed. The sample tube is then cooled in liquid nitrogen in a flowing stream of nitrogen in helium at a fixed nitrogen partial pressure. After equilibrium, the sample is heated and the amount of nitrogen desorbed is measured. The sequence is then repeated with successively higher partial pressures.

1.8.2. Acidic and Basic Properties on Solid Surfaces

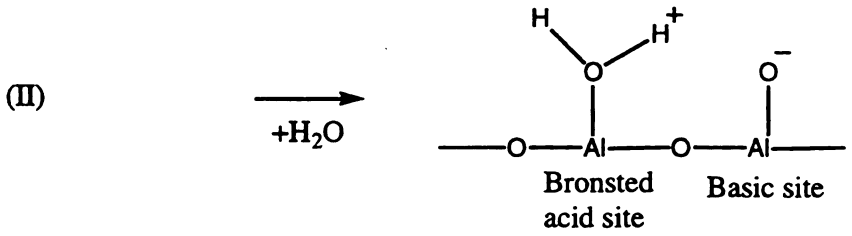
Solid acids have been widely used as catalysts or catalyst supports in the industry for many years. Use of solid acid catalysts provides several advantages over liquid acid catalysts, e.g., high catalytic activity and selectivity are observed, repeated use of solid acid catalysts is possible, separation of a solid acid catalyst from a reaction mixture is easy, solid acid catalysts do not corrode reactors, and there is no disposal problem.

A solid acid shows a tendency to donate a proton or to accept an electron pair, whereas a solid base tends to accept a proton or to donate an electron pair. Acidic and basic sites on the surface of γ-alumina can be visualized according to the scheme shown below. Alumina dehydrates at high temperature:



(I) (II)

However, there is always sufficient water present on the catalyst surface to give



(III)

The Lewis acid site is visualized as an incompletely coordinated aluminum atom formed by dehydration, and the weak Bronsted site as a Lewis site which has adsorbed moisture, while the basic site is considered to be negatively charged oxygen atom. The electronegativity of the Lewis site is weakened by adsorption of water, since an electron pair from the oxygen atom of the water molecule is donated to the Lewis site. Thus, the negative charge of oxygen at a basic site becomes higher when water is adsorbed on a Lewis site due to a weaker inductive effect of the aluminum atom.

1.8.2.1. Acid Strength and Hammett Acidity Function

The acid strength of a solid is defined as the ability of the surface to convert an adsorbed neutral base into its conjugate acid. If the reaction proceeds by means of proton transfer from the surface to the adsorbate, the acid strength is given by the Hammett acidity function H_0,

$$H_0 = pK_a + \log[B]/[BH+], \qquad \text{(VII)}$$

Where [B] and [BH^+] are respectively the concentrations of the neutral base (basic indicator) and its conjugate acid and pK_a is pK_{BH}^+. If the reaction takes place by means of electron pair transfer from the adsorbate to the surface, then the Hammett function, H_0, is given by

$$H_0 = pK_a + \log[B]/[AB], \qquad \text{(VIII)}$$

Where [AB] is the concentration of the neutral base which reacted with the Lewis acid or electron pair acceptor, A.

The acidity of a solid is expressed as the number or mmol of acid sites per unit weight or per unit surface area.

For the determination of strength of a solid acid, the amine titration method using Hammett indicators is used (68-69). In the amine titration method, pretreated catalyst samples in a nonpolar solvent like dry benzene are titrated using a base, n-butyl amine, in presence of suitable Hammett indicators. Hammett indicators, a series of arylalcohols, which react with acid to form carbonium ion, have a known pK_a value for the acid-base color change. Catalyst samples are distributed to several sample glasses, and two drops of one of the Hammett indicator solutions are added into it. The end point of titration is determined visually from the resultant color changes and quantity of added titrant gives the number of acid sites with strength less than pK_a's of the Hammett indicator used. Using a range of Hammett indicators with different pK_a, the distribution of acid strength is determined. Similarly, benzoic acid titration is used to determine the basicity of the support.

1.8.2.2. Temperature Programmed Desorption (TPD) method

The gas chemisorption method using Temperature Programmed Desorption (TPD) is used to determine the acid-base properties of the catalyst (68-69). In TPD, the solid sample is kept in quartz spring balance, evacuated, and a base is introduced for adsorption. Now, evacuation is carried out at high temperature for desorption of adsorbed base on acid sites. No further decrease in sample weight on evacuation indicates the base is chemically adsorbed on the surface and gives the acid strength. Strong gaseous bases such as ammonia, pyridine, and triethyl amine adsorb on acid sites with a strength proportional to the acid strength and are difficult to desorb on elevated temperature evacuation of the adsorbed bases from acid sites. The acid strength distribution of the catalyst surface is studied by temperature-programmed desorption of ammonia or pyridine or triethyl amine, whereas surface basicity of the catalyst is measured by stepwise thermal desorption of CO_2, phenol or nitric oxide. In our work, gases (NH_3, CO_2, etc.) are adsorbed onto the catalyst surface in controlled quantities and then desorbed by programmed heating in a Micromeritics Pulse-Chemisorb 2700.

The amine titration method and TPD method give the sum of the amount of both Bronsted and Lewis acid sites. So, another method is needed to distinguish the Lewis and Bronsted acidities on the surface.

1.8.2.3. DRIFTS Study

The infrared spectra of bases (ammonia or pyridine) adsorbed onto the catalyst surface show different IR peaks for Lewis and Bronsted acidities. A Perkin Elmer 2000 FTIR spectrophotometer is used for DRIFTS studies in our work. The peaks at 1,450,

1,490, and 1,610 cm^{-1} which are observed on all the mixed oxides are characteristic peaks of pyridine coordinately bonded to Lewis acid sites (68). The peak at 1,540 cm^{-1} is due to pyridinium ion formed by the adsorption on Bronsted acid sites (68).

1.8.3. Different Catalyst Supports

1.8.3.1.Alumina

Alumina has been extensively used as a catalyst or catalyst support since it has all of the interesting features of a satisfactory support and also represents many of the problems encountered in the selection of a support. Alumina is amphoteric in nature, which means that can act as an acid in a basic medium or as a base in acidic medium. Alumina has a high melting point, ~2000 °C, which is also a desirable characteristic for a support. Alumina in the hydroxide form can also be a voluminous gel. This makes possible the production of alumina in the form of high surface area, highly porous, comparatively low-density support material.

The most important properties of alumina are its transition phases that exist over a very large temperature range (70). Aluminas are the trihydroxides, $Al(OH)_3$, of which the two crystalline forms, Gibbsite and Bayerite, are the most common. Loss of a water molecule leads to the oxyhydroxide, AlO(OH), Boehmite. Further dehydration leads to the transition aluminas that have the generic formula, $Al_2O_3.xH_2O$ with $0<x<1$. These phases distinguish themselves by the existence of crystalline defects in their structure. There are six principal phases designated by the Greek letters *chi, kappa, eta, theta, delta, and gamma*. The nature of the product obtained by calcination depends on the starting

hydroxide (Gibbsite, Boehmite, Bayerite, and diaspore) and on the calcination conditions. The ultimate product of dehydration is corundum or α-alumina.

γ-Alumina is the most common catalyst support among the transitional aluminas which is best prepared by heating Boehmite (70). This process gives a γ-alumina having surface area between 150-300 m^2/g, a pore volume between 0.5-1 cm^3/g and a large numbers of pores in the 3-12 nm range. In contrast, α-alumina, the most dehydrated form of alumina, is essentially non-porous with surface areas between 0.1 and 5 m^2/g.

1.8.3.2. Zirconia and Titania

Zirconia has both weakly acidic and basic properties (68). The acid is mainly Lewis acid and partly Bronsted acid. Titania is classified as a weakly acidic metal oxide, but becomes basic on reduction. The acid sites of TiO_2 are of the Bronsted type when calcined at higher temperatures and of the Lewis type when calcined at higher temperatures (68).

1.8.3.3. Silica

Silica is produced from an alkaline metasilicate and an acid (70). This is commonly done by bubbling carbon dioxide through a dilute solution of sodium metasilicate or by the addition of dilute acid to a pH of about 7. Typically the solution will gel and the resulting material is washed free of the sodium ions and then dried. The surface of silica gel consists of a layer of silanol group (SiOH) and physically adsorbed water. Heating the gel to about 100 °C removes only the physically adsorbed water giving the material commonly referred to as silica gel. Further heating to 200 °C results

in some dehydration of the surface hydroxide groups. The newly formed siloxane bonds are very reactive since dehydration leaves the surface in a strained condition. The rehydration is completely reversible up to 400 °C. On heating to higher temperatures, reorientation of the SiO_4 tetrahedra occurs to relieve strain. Thus the sites become nonsusceptible to rehydration. Heating to 500 °C decreases the surface hydroxide concentration to about 20-30% of that present on the 200 °C heated material.

Silica is very weakly acidic in nature (68). The acidity in silica is due to hydroxide groups present on the surface and hence silica exhibits only Bronsted acidity, but does not show any Lewis acidity like alumina.

1.8.3.4. Zeolites

Zeolites are crystalline aluminosilicates with uniform pore structure having minimum channel diameter of 0.3 to 1.0 nm (70). The presence of molecular sized cavities and pores make the zeolites effective as shape selective catalysts for a wide range of reactions. The size depends primarily upon the type of zeolite. The X and Y zeolites are structurally similar, but differ chemically by their Si/Al ratios, which are 1 – 1.5 and 1.5 – 3.0 for X and Y zeolites, respectively. The structure of zeolites consists of a three dimensional polymeric framework of tetrahedral of SiO_4 and AlO_4 units joined through shared oxygens. The framework thus obtained contains pores, channels, and cages, or interconnected voids. Zeolites may be represented by the general formula,

$$M_{x/n}[(AlO_2)_x(SiO_2)_y].mH_2O$$

where the term in brackets is the crystallographic unit cell. During catalysis, the mH_2O molecules are removed, leaving a large cavity in which reaction takes place. The metal

cation of valence n, usually H^+, Na^+, or NH_4^+, is present in framework to maintain electrical neutrality with the AlO_4^- species. These extra framework cations can be replaced by other cations using ion-exchange techniques.

Zeolites are considered as acidic materials (70). The acid strength of a zeolite increases with increasing Si:Al ratios. On the other hand, the basic character of these materials increases with increasing numbers of AlO_4^- species. Adsorption of pyridine on Bronsted sites and Lewis sites gives characteristics infrared peaks at 1540 and 1450 cm^{-1}, respectively. The Bronsted acidic sites dominate at lower temperature range (< 500 °C), whereas Lewis acid sites develop at higher temperatures.

1.8.3.5. Aluminum Phosphate

Aluminum phosphate ($AlPO_4$) is a mixed oxide of Al and P, isostructural with SiO_2 because both are built with tetrahedral MO_4 units. Strong OH bands at 3680 and 3800 cm^{-1} which were assigned to P-OH and Al-OH respectively, decreased in intensity with temperature, but nevertheless remained quite strong even after heating of the sample (71). The adsorption of pyridine on $AlPO_4$ suggests the presence of both Lewis and Bronsted sites on $AlPO_4$ with the former apparently predominating. The acid sites on the $AlPO_4$ surface increases with P/Al ratio before decreasing considerably at P/Al = 1.5.

1.8.3.6. Hydrotalcites/Magnesium-Aluminum Mixed Oxides

Hydrotalcite compounds consist of layers containing octahedrally coordinated bivalent cations (e.g., Mg^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}) and trivalent cations (e.g., Al^{3+}, Fe^{3+}, Cr^{3+}), as well as interlayer anions (e.g., CO_3^{2-}, SO_4^{2-}, NO_3^-, Cl^-, OH^-) and water (73).

After calcination, these compounds lose interlayer anions and water to form mixed oxides that can be used as solid base catalysts (e.g., Mg-Al-O). The structure, acidity and basicity of Mg-Al-O mixed oxides have been investigated by several research groups (74-76). The hydrotalcites show a spinel phase ($MgAl_2O_4$) in addition to γ-Al_2O_3 phase and MgO phase. The number and strength of the base sites for calcined hydrotalcites were considerably lower than for γ-alumina but higher than for magnesia (73). In contrast, the number and strength of the base sites for calcined hydrotalcites were lower than for MgO but higher than for γ-alumina. Accordingly, calcined hydrotalcites exhibit moderate acidity and basicity. The acid sites in hydrotalcites are mainly Lewis acid sites, whereas the base sites are surface oxygen anions.

1.9. Research Objectives

As mentioned above, the overall goal of this work is to develop a continuous process for production of value-added chemicals from succinates. Specific objectives were also defined to achieve the goal. Those specific objectives are as follows:

1. A continuous fixed-bed reactor operable at a wide range of temperatures, pressures, and flow rates is designed. The setup also includes the design of the liquid and gas feed flow and product collection, controlling, and monitoring the flow rates as well as pressure and temperature in the reactor, method of catalyst loading. Appropriate analytical methods to analyze reaction products are developed.
2. Several different catalyst and support materials are screened to identify and optimize the active catalyst materials for the continuous process. A series of catalyst is

prepared and characterized for the surface properties and then these catalyst characteristics are related to results.

3. Following identification of promising catalysts for citraconic anhydride production, the reaction parameters over an optimal catalyst are optimized for maximizing yield and selectivity of citraconic anhydride. These studies involves changing feed compositions, pressure, catalyst loading, residence time, flow rate, and temperature to determine the region where both desired product yields are high and the catalyst is stable over time.
4. The prior art noted a substantial decline in citraconic anhydride yields upon prolonged exposure to reaction conditions. This deactivation poses a potential barrier to commercial development. Using promising catalysts, the activity of the catalyst for prolonged operation is investigated to gain a broader profile of catalyst performance with time. We also identified those species or conditions responsible for the deactivation.
5. A process for separation of citraconic anhydride from unreacted succinates and other byproducts is designed. A continuous process for isomerization of citraconic anhydride to itaconic acid and for recovery of itaconic acid is developed.
6. Kinetics and thermochemistry of the reaction are also studied.

This project is interdisciplinary. The mechanistic studies are done by Dr. J. E. Jackson and his group in the Department of Chemistry. Dr. D. J. Miller and his group are responsible for engineering aspect of this project. Dr. N. Kirthivasan, postdoctoral fellow in the Department of Chemistry, did the catalyst preparation and catalyst characterization for this work. Mr. Bryan Hogle, an undergraduate student in the Department of Chemical

Engineering, did the isomerization and separation studies. Dr. Kirthivasan also contributed to the isomerization studies.

CHAPTER 2

EXPERIMENTATION AND ANALYSIS

The fixed bed reactor system was designed to produce desired products continuously at a temperature range of 300-500 °C and moderate pressure range of 50 to 400 psi. The complete design of the reaction system is discussed in the following sections.

2.1. Reactor Vessel

An Autoclave Engineers cone closure tubing reactor (Part No. CC.985SS20), made of 316 stainless steel, was used as the reactor vessel. The above model is capable of handling a maximum pressure of 16,800 psi at 800 °F. The length, outer diameter, and internal diameter of reactor vessel (Part No. 103A-2454) are 102, 19.1, and 11.1 mm, respectively. The nominal capacity of the reactor is 9.85 ml. The length of the whole reactor was chosen to 16.7 cm because of the available standard heating element length from Mellen Furnace discussed later in this chapter. The two open ends of the reactor tube are connected to nipples (Part No. CN6608-316) by a coupling and a cover assembly made of 316 stainless steel with standard connections (Part No. F375C) also supplied by

Autoclave Engineers. The reactor is opened and closed from the top for catalyst loading and unloading. A medium quartz frit fitted in a 5 mm long and 10 mm OD glass tube is used to hold the catalyst in the reactor. A steel screen was wrapped over it to fit at the bottom of the reactor. This holds the solid catalyst yet allows the liquid and vapor phase to flow through and also enables the catalyst to be loaded and unloaded easily. A schematic of the cross-section of the reactor part of the experimental setup is shown in Figure 2.1.

A longer reactor (Part No. 104A-2454 from Autoclave Engineers), double in length and the same in cross-sectional area as the regular reactor, was also used in some experiments. The nominal capacity of longer reactor is 19.6 ml. The longer Mellen furnace was used for this longer reactor.

A schematic of the experimental reactor setup is depicted in Figure 2.2

2.2. Reactor Furnace

Mellen split type tubular heaters are used to obtain high temperatures needed to vaporize the feed. The furnace is made up of two 317 mm ID and 228 mm long split type-heating elements (Part No. 12-155). The maximum hex size of the reactor is 254 mm and hence it fits the furnace correctly. The Mellen heating element utilizes a high quality ceramic holder and helical coiled iron - chromium - alumina wire embedded in high purity alumina cement. The furnace elements can reach up to a maximum of 1200 ^{0}C and are wired in parallel so that they can be powered by a 120 Volt source. The furnace elements are enclosed by two 23 x 11.5 x 12.5 mm K20 type fire bricks. The bricks were cut and grooved to accommodate the furnace elements and the wiring

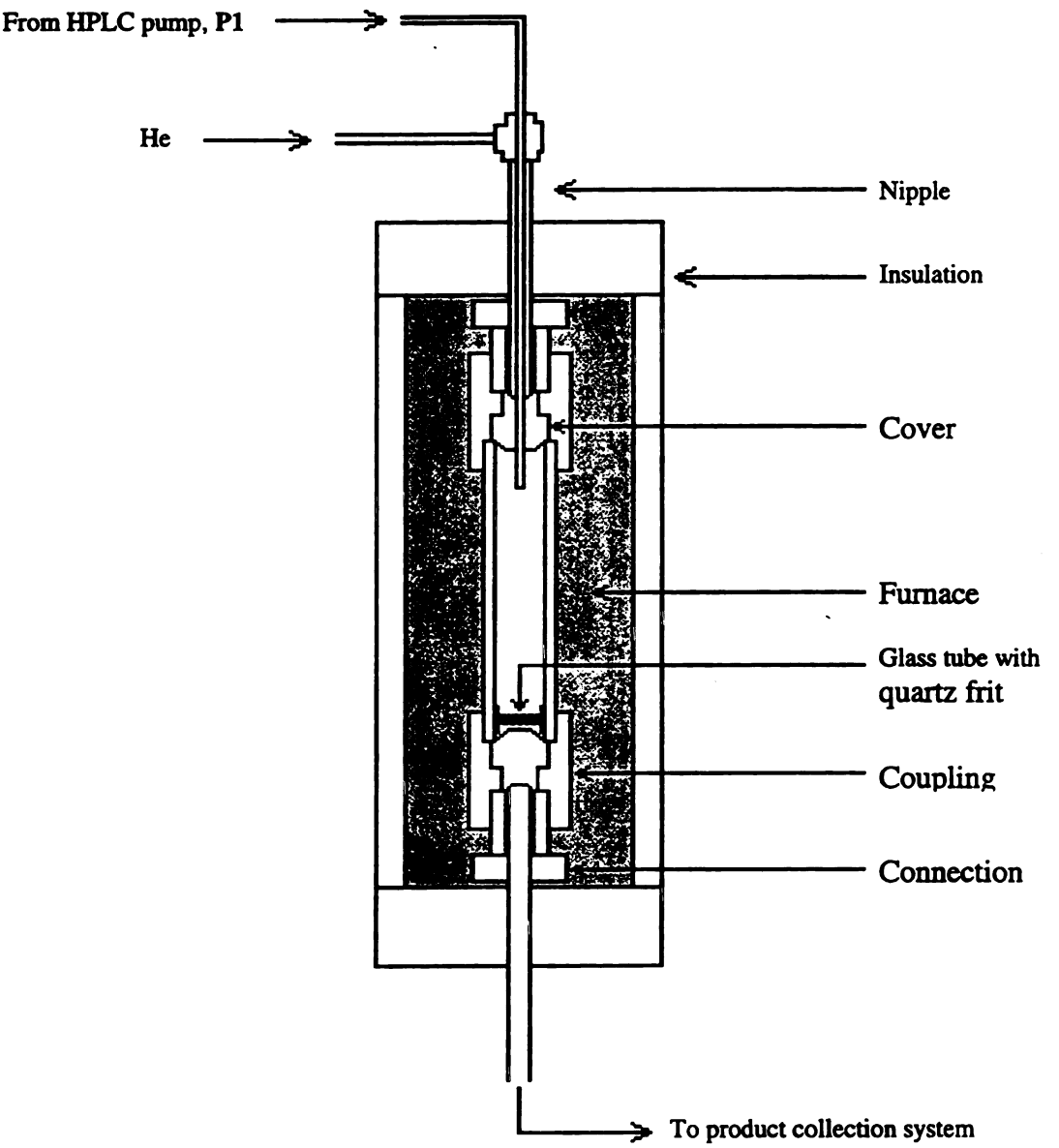


Figure 2.1. Cross-section of Vapor Phase Reactor

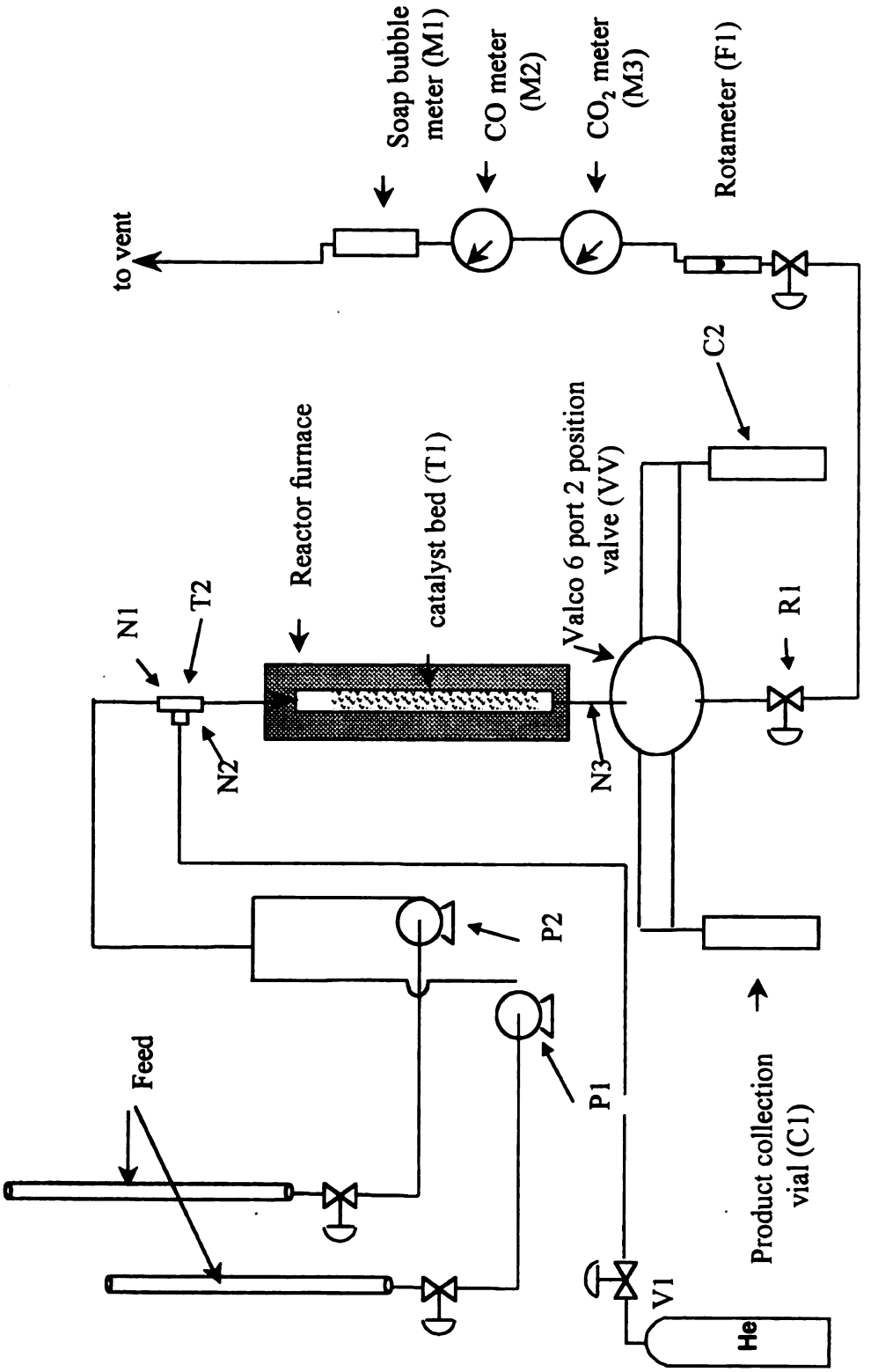


Figure 2.2. Schematic Flow Diagram of Reactor System

without any gaps to give good insulation. Two more 6 x 11.5 x 12.5 mm brick pieces were added at the top and bottom for insulation of the connecting assembly and a part of the nipple on either side. The whole assembly, including the bricks enclosing the furnace which encloses the reactor, is mounted on an aluminum stand for stability and access.

The furnace is controlled by an Omega series CN-2010 programmable temperature controller with the temperature of the surface of the reactor being read with a thermocouple. The set point is then adjusted to achieve the desired catalyst bed reaction temperature and the difference is always accounted by keeping a higher set point.

2.3. Feed System

The feed was fed into the reactor using Bio-Rad Soft-Start Pumps (Model No. 125-1250), a dual piston and positive displacement pump. The pump is capable of pumping fluids up to 6000 psi and has a flow rate range of 0.02 ml/min to 9.9 ml/min in increments of 0.01 ml/min and also measures the pressure it is pumping against. The pump sounds an alarm if pressure of the reactor system exceeds the defined pressure limit. A 1/8 inch Teflon tubing was used from the burette to the pump and 1/16 inch stainless steel tubing was used from pump outlet to the reactor inlet. The feed was kept in a burette well above the pump heads.

The choice of feed dictates the feed configuration of the system used and so, the liquid feed system was designed accordingly.

2.3.1. Succinic Acid Esters and 1,3,5-Trioxane Feed

If trioxane is used as a formaldehyde source, then the feeds are combined and only a single pump is used. The solubility of 1,3,5-trioxane in diethyl succinate and dimethyl succinate is 1 mol/mol of ester. The feed line from the burette to 60 cm before the reactor inlet, including pumps, is heated at a temperature of 70 °C using heating tapes and variable autotransformer if the feed ratio is above 1 mol of trioxane to 1 mol of succinate. In all cases, the 60 cm of feed tubing just before the reactor inlet is heated at 250 °C using 0.5 inch wide heating tape.

2.3.2. Succinic Acid Esters and Formalin Feed

Dimethyl succinate is not miscible with Formalin when the molar ratio of formaldehyde to DMS is less than one. Diethyl succinate is immiscible with Formalin at any molar ratio. In these cases, the two reactants are pumped by separate Bio-Rad pumps; otherwise one pump is enough.

2.3.3. Succinic Anhydride and 1,3,5-Trioxane Feed

Succinic anhydride (mp 118 °C) and trioxane (mp 64 °C) both are solids at room temperature. The Bio-Rad pumps are not advised to be used at temperature above 50 °C. A Simplex syringe pump (Model No. MSP-5 Series 1) from PDC Machines was therefore used to feed succinic anhydride and trioxane in molten phase. The syringe barrel, 500 ml capacity, is made of stainless steel and has packing of Graphite Filled Teflon (GRTEF), which allows its use at temperature up to 200 °C. The syringe of the syringe pump was wrapped with 1 inch wide heating tapes. The barrel outlet on the top was connected to a

three-way Autoclave Engineers Valve that can be also used at high temperature. One port of valve was connected to the top of the reactor through 1/16 inch stainless steel tubing. The 1/16 inch was kept inside 1/4 inch copper tubing and steam was flowed through the copper tubing to keep the 1/16 inch feed line above 100 °C. The whole copper tubing was insulated with glass wool and polyethylene pipe insulation. The valve and copper tubing between the pump and reactor were also wrapped with 0.5 inch wide heating tape to superheat the steam around to 115 °C. The mixture of feed melts completely around 105 °C and trioxane vaporizes at 118 °C, so it was desired to keep everything between those temperature limits. Four different surface thermocouples were used for better temperature control of feed. The first thermocouple was cemented on the body of the barrel, the second was on the top of the barrel, the third was installed on the body of the valve, and the fourth one was on the outer surface of the copper tubing. The third port of the valve was used for refilling the pump.

The pump is huge, but very capable of pumping the liquid accurately from flow rates of 2.5 ml/hr to 66.63 ml/hr at a wide range of pressures. But the dead volume inside the barrel after the plunger reaches the top caused a lot of problems for us. The syringe barrel has to be disassembled to clean inside the barrel.

An Eldex pump (Model No. A-30-S) was also tried to feed trioxane and succinic anhydride in the molten state. The feed line including the pump head and burette was kept at 120 °C and the feed line length was also minimized to avoid any clogging, but the Eldex pump was not efficient for feeding in molten phase.

It was very tedious and cumbersome to feed succinic anhydride and trioxane in the molten state, as the feed lines and reactor inlet often plugged and the reactor had to be disassembled and cleaned before it could be used.

2.3.4. Monomethyl Succinate and 1,3,5-Trioxane

It was decided to feed succinic anhydride and trioxane in methanol. Succinic anhydride and trioxane were dissolved in methanol at 60 °C. Succinic anhydride was converted completely into monomethyl succinate (MMS); it was confirmed by GC and HPLC that the conversion of succinic anhydride was complete and that no dimethyl succinate was formed. The mixture of monomethyl succinate, trioxane, and methanol was pumped into the reactor using a Bio-Rad pump at desired flow rates.

2.4. Gas Flow System

Helium was used as a carrier gas in most experiments to aid in vaporization of feeds and to sweep the vaporized feed into the reactor. A 1/8 inch tubing connects the helium cylinder to the top of the reactor. The helium line was also heated at 200 °C using 0.5 inch wide heating tape. The pressure delivered to the reactor is controlled by the regulator on the cylinder, and the reactor pressure is monitored using the digital readings from the pump as well as the analog readings from the regulator. No carrier gas was used in some experiments when monomethyl succinate and trioxane were taken in methanol, because an excess amount of methanol acted as a carrier gas in the reactor system. Carbon dioxide was also used as a carrier gas in one experiment.

A backpressure regulator was used downstream to control any pressure drop around the fixed-bed reactor and for better pressure control in the reactor system. The exiting gas flow rate is controlled by using Omega Rotameter (Part No. FL-3445-C) and outlet gas flow rate is calculated using simple soap bubble meter. Two Riken Infrared Gas Analyzers (Model No. RI-550A) were used to analyze carbon dioxide and carbon monoxide directly from the exiting gas.

2.5. Product Collection System

The product collection system also evolved over time. In earlier studies, a three-way switching valve (Part No. SS-41XS2) from Whitey was used to switch the product collection after each 30 minutes. The three-way valve was not operable at higher temperature, because the system used to plug all the time and the valve started leaking because of its high temperature incompatibility. The three-way valve was replaced by two two-way high temperature compatible valves (Part No. SS-2H) from Nupro. The whole reactor outlet system from reactor outlet to the product trap was kept at 200 °C using 0.5 wide heating system. Now, the problem arose from the dead volume between the tee and the closed two-way valve. The performance of these two-way valves was not satisfactory either, as they started leaking after some time. Next, a 6-port two position Valco valve (Part No. 26UWTY) with small internal port size (0.030 inch) was used to switch the product collection. The carbonaceous material resulting from cracking in the reactor plugged the small diameter internal ports, and it was very difficult to clear those ports. Finally, a large internal port (0.067 inch) Valco valve (Part No. 2L6UWTY) was used for the latter part of these studies. The Valco valve is kept in a heating chamber at

200 °C, also supplied by Valco (Part No. HVEB). Tubing from the reactor outlet to the valve and tubing from the valve to the sample cylinders is heated at 200 °C using 0.5 inch wide heating tape to keep the products in the vapor phase as long as possible.

Products are trapped in 25 ml stainless steel Whitey sample cylinders (Part No. SS-4CS-TW-25). The outlet from the 25 ml cylinders was connected to a 10 ml Whitey sample cylinders (Part No. SS-4CS-TW-10) to collect the remainder of liquid which went with the gas stream. The schematics of the product collection system and whole reactor system are shown in Figure 2.3 and Figure 2.2, respectively.

The temperature of product traps was varied with the feed used for the reaction. The traps were kept in cold or icy water if the feed was dimethyl succinate and formalin, in order to collect the highly volatile methanol and formaldehyde in the stream. Boiling water was used to surround to the product trap if succinic anhydride and trioxane were fed in molten phase, because they solidify at temperature below 100 °C.

In some experiments, the product collection traps contained dimethyl sulfoxide (DMSO) and were immersed in boiling water to avert solidification of the unreacted succinic anhydride and paraformaldehyde resulting from polymerization of formaldehyde in the collection trap

2.6. ANALYSIS

Products like succinic acid and succinic anhydride are not volatile enough to elute in the gas chromatography (GC) column used for analysis. It is also not possible to detect quantitatively formaldehyde dissolved in the product mixture in the GC. Some of our product mixtures from each run were hydrolyzed to obtain the total yield of

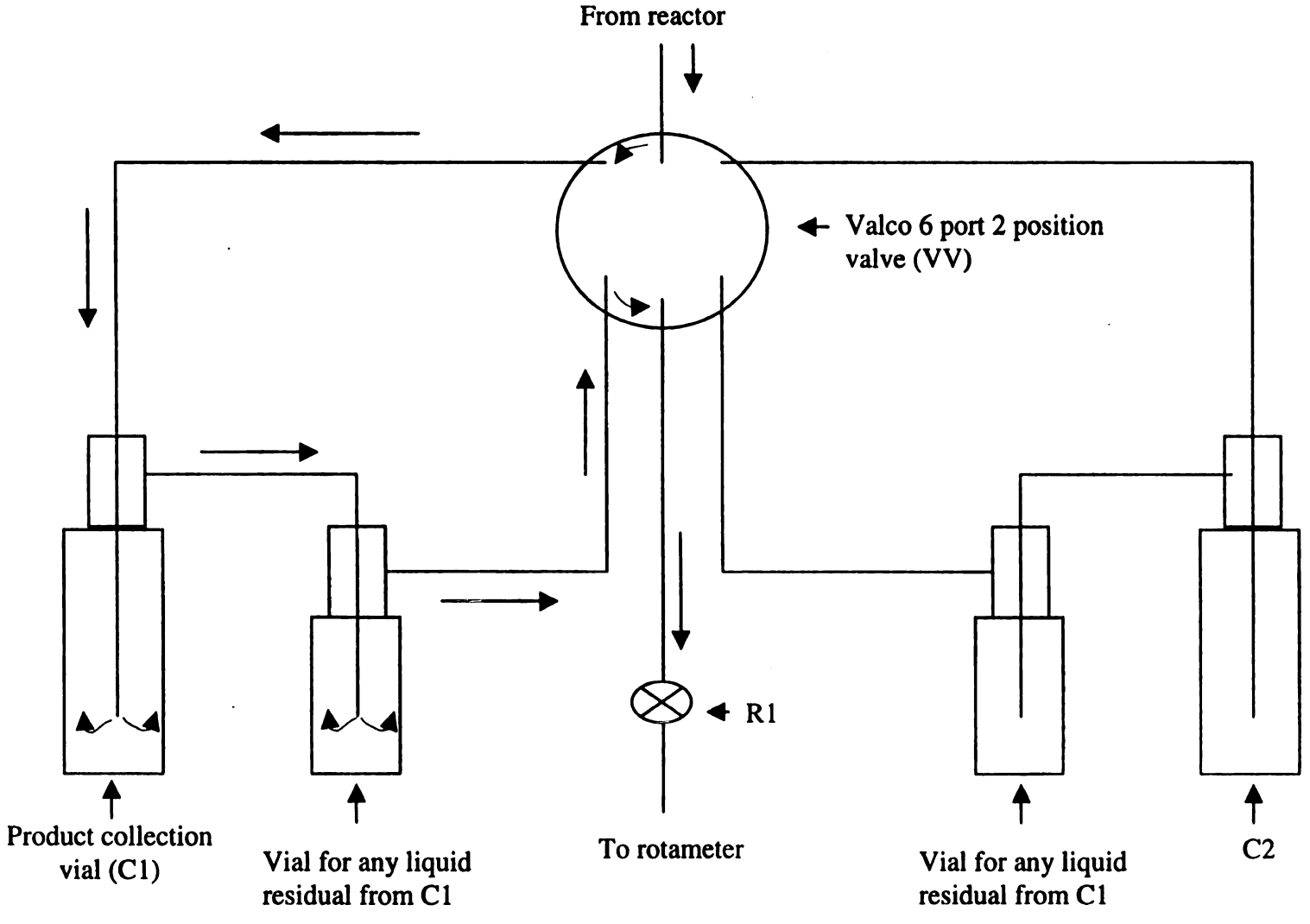


Figure 2.3. Product Collection System

citraconates. Hydrolyzed products cannot be injected in GC, because of the nonvolatile sulfuric acid added for hydrolysis. Because the response of dimethyl succinate in high-performance liquid chromatography (HPLC) was very poor and methanol does not appear in the column used for HPLC analysis, both HPLC and GC were used to identify and separate the reaction products.

2.6.1 High-Performance Liquid Chromatography

An Isco Model 2350 dual piston HPLC pump was used for flow of the mobile phase. A Bio-Rad HPX-87H organic acid column is used for the product identification. This 300 x 7.8 mm ID Aminex HPLC column uses crosslinked styrene divinylbenzene resin as a packing material. The HPX-87H column separates organic acids using ion exclusion and reverse phase mechanisms. Organic acids elute from the column in order of increasing pK_a. Anions are eluted near the void volume, and acids which have been ionized in the acidic eluent elute according to the fraction of the acid ionized. The column separates neutral species, such as esters and alcohols, by reverse phase partitioning. The eluant is polar while the resin matrix is nonpolar, so the nonpolar compounds are adsorbed by the resin and are eluted after charged molecules.

A guard column, 30 x 3.6 mm, (Part No. 125-0129) from Bio-Rad was also employed just before the column to remove anything that interferes with the separation or shortens the lifetime of the primary column. A cartridge holder (Part No. 125-0131) from Bio-Rad was used to hold the guard column. The guard column and cation H refill cartridge are specifically prepared of divinyl benzene matrix for the acidic mobile phase used in HPLC analysis.

In earlier studies, only a UV detector was used in HPLC analysis at a λ_{max} of 225 nm. A UV detector gives a very large peak for small amounts of a highly conjugated compound like citraconic acid, whereas it does not respond much for dimethyl succinate even at high concentrations. To overcome this problem, an RI detector (Waters 410 Differential Refractometer) was also used with the UV detector. The maximum wavelength in the UV detector was increased to 270 nm to avoid offscale peaks from highly UV sensitive citraconic acid and its isomers, because concentrated samples were injected in the HPLC for good response in the RI detector.

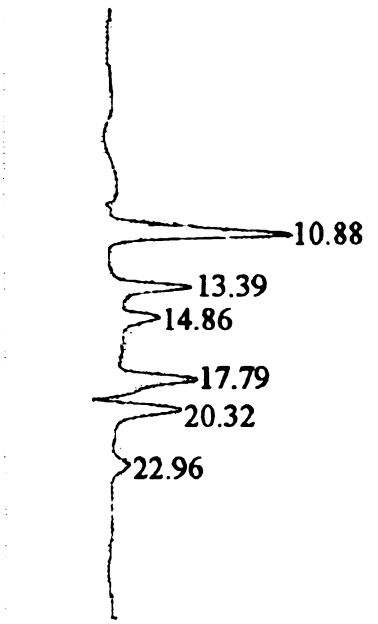
Chromatograms were recorded using a Waters 745 Data Module. A typical chromatogram from the HPLC is shown in Figure 2.4. Values of retention times and response factors of products and reactants in HPLC (RI detector) are given in Table 2.1. The HPLC calibration was conducted several times during this work, so the most recent values of retention times and response factors are listed here. The method for calculation of response factors, the actual product concentrations, Data Module parameters, and RI detector parameters are given in Appendices.

Table 2.1. Retention time and response factors of different compounds in HPLC

Compound name	Retention Time (min)	Response Factor
Oxalic acid	11.0	1.00
Citraconic anhydride/acid	13.6	0.52
Succinic anhydride/acid	15.2	0.52
Monomethyl succinate	18.0	0.44
Formaldehyde	20.5	0.80
Dimethyl succinate	22.7	3.00

CHANNEL A INJECT 08/27/99 15:56:08

A140.2
50% of Run 140.2 + 3.9 ml of CH_3CN
50% 15.86 g/l oxalic acid



INPUT OVERRANGE AR RT= 19.84

DSS		8/27/99		15:56:68
FILE 1	METHOD	2	RUN 162	
NAME	CONC	RT	AREA	RF
1	0	10.08	309736	
OXALIC	INT STD	10.38	15704640	1
CITRACONIC	0.226	13.88	6019402	0.52
SUCCINIC	0.114	14.86	3443745	0.52
MMS	0.25	17.79	10305180	0.38
FORMAL	0.243	20.32	7645473	0.8
DMS	0.27	22.96	1572312	2.7

Figure 2.4. A typical chromatogram from HPLC

An acidic solvent is required as a mobile phase for HPX-87H columns. But, our products and reactants are not soluble in water. So organic modifiers like acetonitrile are needed not only to improve the column resolution but also to solublize compounds to be separated in the mobile phase. Adding acetonitrile to the eluent reduces resin/compound interactions and subsequently the strongly bound compounds elute more rapidly. Acetonitrile is the most suitable organic modifier because it has intermediate polarity, low viscosity, and low UV adsorption. 40% acetonitrile is an upper limit for the HPX-87H column used in analysis. The high volatility of acetonitrile introduces analytical complication. The composition of the mobile phase in the sample loop of the RI detector, the mobile phase reservoir, and the sample injected cannot be the same, because highly volatile acetonitrile tends to escape during handling. This difference in the mobile phase composition results in an additional signal in the HPLC chromatogram. A UV detector is not affected by small changes in the mobile phase compositions, because the mobile phase solvent does not absorb at low UV wavelengths. In earlier studies, 32% acetonitrile in 0.005 M sulfuric acid solution was taken as a mobile phase. But, the solvent peak from the mobile phase of 32% acetonitrile solution interferes with the monomethyl succinate peak. So 20% acetonitrile in 0.005 M sulfuric acid was used as a mobile phase in the analysis after Run 91.

Oxalic acid was used as an internal standard. All samples and oxalic acid solutions were prepared in the mobile phase. The HPLC column temperature was kept at 40 °C using a column heater for a better resolution. A six port Valco valve with a manual standard electric actuator (Part No. EHC6W) was used for the sample injection. With the valve in "load" position, sample was injected into a twenty microliter sample loop

through the injection port. The valve was switched to "inject" position to carry the sample contained in the sample loop into the column. The sample loop was being flushed several times just before the injection by the mobile phase.

2.6.2 Gas Chromatography

Products were also analyzed in a Varian 3300 Gas Chromatograph (GC) with a Flame Ionization Detector (FID) and helium as a carrier gas. The column used for analysis was a Supelco fused silica intermediate capillary column, SPB1, of 0.53 mm ID and 30 m long. The output signal generated from the GC was collected using a Perkin Elmer Single Channel Interface and the data were analyzed using Omega-2 software from Perkin Elmer. The separation in this intermediate column depends on the volatility of injected compounds; the higher volatile compounds elute earlier in the column and the low volatile compound elutes later. The temperature program for the column was developed using trial and error method to obtain maximum separation of the peaks in the product distribution. A typical chromatogram from the GC is shown in Figure 2.5.

The GC was initially run with a series of known concentrations to determine response factors. Methyl lactate was used as an internal standard since its retention time does not interfere with that of expected products and reactants. The response factor of methyl lactate was taken as one and response factors of the various compounds in the mixture sample were calculated relative to methyl lactate. Sample injection size was 0.2 micro liter. Values of retention times and response factors (only the most recent values) of products and reactants are given in Table 2.2. The method for calculation of response

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Dushyant

Collection: 15:45:34 Aug 27 1999 Method: KIRTHI

pk#	RT	Area	
1	1.157	50494304	
2	6.019	108268536	
3	10.139	21401244	
4	10.237	25995980	
5	10.416	9511146	0.2189 g of Run 140.2
6	10.515	5872434	+ 0.0436 g methyl lactate
7	10.553	11080857	
8	11.960	16711015	
9	12.320	31338521	
10	14.128	20906634	

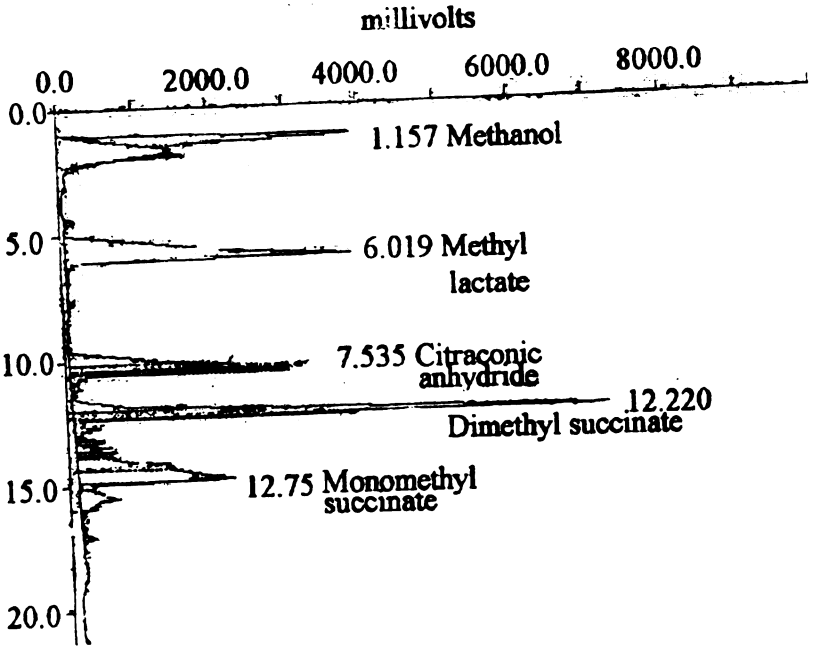


Figure 2.5. A typical chromatogram from GC

factors, the actual product concentrations and GC conditions and parameters are given in Appendices. Outlet gases from reactor were analyzed directly using CO and CO_2 meter.

Table 2.2. Retention time and response factors of different compounds in GC

Compound name	Retention Time (min)	Response Factor
Methanol	1.1	0.65
Formaldehyde	1.8	-
Methyl lactate	5.9	1.00
Citraconic anhydride	9.6 – 11.0	0.59
Dimethyl succinate	11.9 – 12.3	0.65
Monomethyl succinate	13.5 – 15.0	0.92

2.6.3. Formaldehyde Analysis

The HPLC was used for quantifying formaldehyde in the liquid products, but the sodium sulfite method was used to quantify the formaldehyde present in the gaseous products. In some experiments, outlet gases from the reactor were flowed through a test tube containing sodium sulfite solution to trap the unreacted formaldehyde gas. The quantitative liberation of sodium hydroxide occurs when formaldehyde reacts with sodium sulfate to form the formaldehyde-bisulfate addition product:

$$CH_2O + Na_2SO_3 + H_2O \Longrightarrow NaOH + CH_2(NaSO_3)OH$$

In the sodium sulfite method, fifty ml of a 1.0 M solution of pure sodium sulfite (prepared by dissolving 126 g of the anhydrous salt in sufficient distilled water to make one liter of solution) and three drops of thymolphthalein indicator solution (0.1% in

alcohol) are placed in a 500 ml flask and carefully neutralized by titration with acid solution until the blue color of the indicator has disappeared. An accurately measured formaldehyde sample is then added to the sodium sulfite and the resulting mixture titrated slowly with the hydrochloric acid solution to complete discoloration. One millimole of normal acid is equivalent to 0.03003 g formaldehyde and the per cent formaldehyde in the sample is determined by the following equation:

$$\%\text{Formaldehyde} = \frac{\text{Acid titer x Normality of acid x } 3.003}{\text{Weight of sample}} \qquad \text{(I)}$$

The sodium sulfite method was also used to analyze the formaldehyde in control runs of formaldehyde.

2.7 Product Identification

A majority of the reaction products were identified using gas chromatography by comparing their relative retention times with those of the mixtures of neat samples. Gas Chromatography coupled with Mass Spectrometry (GC-MS) was also used to verify the identification of the reaction products. The various compounds in the sample collected were identified by matching the mass spectra and retention time of each compound with reference spectra collected by analyzing a standard sample. The database in the GC-MS facility enables easy comparison, and a near-perfect match was made for almost all compounds. Other analytical methods like Thin Layer Chromatography and NMR Spectroscopy were also tried to determine unknowns.

2.8. Hydrolysis of Products

The raw product exiting the reactor was a mixture of citraconates and succinates as discussed in detail in Chapter 4.1. Analysis of all of these products was difficult in HPLC or GC, as several of the citraconates co-elute with their analog succinates. To clearly evaluate product yield and selectivity, it was necessary to hydrolyze the product mixture in aqueous sulfuric acid solution to recover all species as the free acid. Usually, 20% of the citraconate was in the form of monomethyl or dimethyl ester, so reported yields for unhydrolyzed mixtures were lower than the actual values.

The hydrolysis of product mixture was carried out by refluxing the sample in the mobile phase used in HPLC analysis plus 5-7 drops of concentrate sulfuric acid for 24 hours.

2.9 Product Yield and Selectivity Calculations

GC and HPLC results were placed in an Excel spreadsheet to facilitate ready calculation of product yield, conversion, selectivity and an overall carbon balance on the system was performed. The percentage yield of a product based on feed was calculated by the relation,

$$\text{Yield of product A (\%)} = \frac{\text{Moles of A in product}}{\text{Moles of succinate in feed}} \times 100 \qquad \text{(I)}$$

The carbon dioxide yields are also based on succinate in feed, but divided by two to account for fact that each mole of succinate ester gives two mole of carbon dioxide upon cracking. The percentage conversion of dimethyl succinate (DMS) is given by

$$\text{Conversion (\%)} = \frac{\text{Moles of DMS in feed - Moles of DMS in product}}{\text{Moles of DMS in feed}} \times 100 \qquad \text{(II)}$$

The conversion of dimethyl succinate to the monomethyl ester of succinic acid and succinic acid is not considered part of "succinate conversion", because these species can be recycled along with unreacted dimethyl succinate in the process. Conversion of succinates is calculated by the relation

$$\text{Conversion of succinates (\%)} = (\text{Conversion of DMS - Yield of MMS - Yield of SA}) \qquad \text{(III)}$$

The percentage selectivity of citraconic acid is defined by,

$$\text{Selectivity} = \frac{\text{Yields of citraconic anhydride}}{\text{Conversion of succinates}} \times 100 \qquad \text{(IV)}$$

Finally, a balance on total succinate carbon is done for the experiment as a measure of the quality of the experiment. Results are reported as the percentage of initial succinate carbon recovered in the product mixture. Carbon of succinate recovered is given by

$$\text{Carbon recovered (\%)} = \left(100 - \left(\begin{array}{l}\text{Conversion of DMS - Yield of CA -} \\ \text{Yield of MMS - Yield of SA - Yield of } CO_2\end{array}\right)\right) \qquad \text{(V)}$$

For some experiments, an overall carbon balance was also performed. Overall carbon recovery is given by

$$\text{Overall carbon recovery}\,(\%) = \left(100 - \left(\frac{\text{moles of carbon in - moles of carbon out}}{\text{moles of carbon in}} \times 100\right)\right) \quad \text{(VI)}$$

CHAPTER 3

EXPERIMENTAL METHODS

3.1. Catalyst Materials

Several types of commercial aluminum oxide (Al_2O_3) were obtained from Norton Chemical Process Product Corporation for use as catalysts. These include the Norton materials specified as SA3132, SA3177, SA6173, and SA6175. These alumina materials were ground to the 30/60 mesh size particles using sieve plates and calcined for six hours at 500 °C before loading into the reactor. Zirconia supports manufactured by MEI, Inc. were also evaluated; this zirconia has about 15% alumina as a binder. Magnesium oxide and iron oxide (Aldrich Chemical Co.) were also tested. A number of metal oxides were prepared in the laboratory and evaluated for the condensation reaction. These include alumina, titania, iron oxide, aluminum phosphates ($AlPO_4$), and hydrotalcites (MgO/Al_2O_3 compounds). The catalyst preparation and characterization were done by Dr. N. Kirthivasan. Typical preparation procedures for these materials are given in the following sections.

3.1.1. Aluminum Phosphates ($AlPO_x$)

Aluminum phosphates were prepared from aluminum chloride ($AlCl_3.6H_2O$, FW = 241.43) or aluminum nitrate ($Al(NO_3)_3.9H_2O$, F. W. = 375.13) and ammonium hydrogen phosphate ($(NH_4)_2HPO_4$, FW = 132.06) by the method given in the literature (71). Samples with P/Al molar ratios of 0.5, 1, and 1.5 were prepared. Aluminum chloride or aluminum nitrate and ammonium hydrogen phosphate were dissolved in water, acidified with nitric acid and the hydrogel was formed by adding 30% ammonia solution to achieve a pH of 5. The resultant residue was filtered and washed with deionized water. The sample was dried at 120 °C overnight and then calcined at 400 °C for three hours. As an example, an $AlPO_x$ with P/Al ratio of 0.5 was prepared by dissolving 75 g of aluminum nitrate nonahydrate and 11.5 g of ammonium hydrogen phosphate in 800 ml of water. Acidifying the solution with nitric acid dissolved any insoluble white residue that was formed during the process. About 22 ml nitric acid was required for dissolving the precipitate. The pH of this solution was 0.5. This solution was precipitated with 49 ml ammonia (25%) to a pH of 5. The final residue was washed with 4 liters of water, dried in an oven at 110 °C overnight, and calcined at 400 °C for three hours.

3.1.2. Hydrotalcites

Hydrotalcite catalyst samples with Mg/[Al + Mg] molar ratios of 0.005, 0.01, 0.02, 0.04, 0.06, 0.12, 0.25, and 0.33 were prepared from gels produced by mixing two solutions to the procedure described by Corma et al (74). In each batch, $MgCl_2$ (FW 95.22) and $AlCl_3.6H_2O$ (FW 241.43) were mixed to obtain the desired Mg/[Al + Mg]

ratio, and then the mixture was dissolved in deionized water to prepare an aqueous solution with a concentration of 1.5 M. A second aqueous solution was prepared by dissolving NH_4OH and $(NH_4)_2CO_3$ in deionized water with appropriate amounts calculated according to the relations $NH_4OH = 2.2\ Mg^{2+} + 3.2\ Al^{3+}$ and $CO_3^{2-} = 0.5\ Al^{3+}$ (73). Na_2CO_3 and NaOH salts were also used instead of ammonium salts for coprecipitation. To prepare hydrotalcite, the second solution was added slowly into the first solution over a period of 2-3 hours to maintain the pH of the slurry at 13 and stirred, during which time a white precipitate formed. The precipitate was then filtered and washed with deionized water at room temperature. The catalyst sample was dried at 100 °C overnight and then calcined at 450 °C.

For example, a catalyst preparation with Mg/(Al + Mg) = 0.25 involved dissolution of 1.78 g of $MgCl_2$ and 14.30 g of $AlCl_3$ in 60 ml water. In solution B, 5.6 g of Na_2CO_3 and 3.5 g of NaOH were dissolved in 50 ml water to make a solution that was 0.1 M in Na_2CO_3 at pH 13. The latter solution was mixed into the former over a period of two hours, wherein a gel was obtained and the final pH was 10. The gel was aged overnight and washed with deionized water until the residual filtrate was free of Cl^- ions. The residue was dried overnight and calcined at 450 °C for six hours. The weight of the final catalyst was 3.6 g. A similar procedure was followed for preparing catalysts with Mg/(Al + Mg) atomic ratios of 0.5 and 0.75.

A different approach was followed for the preparation of magnesia-alumina co-catalysts with low quantities of magnesia. Mg-Al mixed oxides with Mg/(Mg + Al) ratios of 0.005, 0.01, 0.02, 0.04, 0.06, 0.1, and 0.12 were prepared using aqueous solutions of aluminum nitrate and magnesium chloride and coprecipitated with ammonia

solution. The residue was filtrated and washed free from chloride and later calcined in the air at 350 °C. As an example, a magnesia-alumina co-catalyst with a Mg/(Mg + Al) ratio of 0.02 was prepared by dissolving 110.3 g of aluminum nitrate and 0.63 g of magnesium chloride in 800 ml water. The initial pH of the solution was 1.8. The solution was precipitated wit 25% ammonia solution over a period of 2 hours until a pH of 9.0 was attained. This required about 85 ml of ammonia. The gel was aged overnight, washed free from chloride, dried at 100 °C overnight, and calcined at 350 °C for three hours. The weight of the final catalyst after calcination was 15.50 g. A similar procedure was followed while preparing catalysts with Mg/(Mg + Al) ratios of 0.005, 0.01, 0.04, 0.06, 0.1, and 0.12. The molarity of the precipitating solution was maintained constant when catalysts with varying Mg content were prepared.

3.1.3. Aluminum Oxide

A sample of pure alumina (also known as Alumina-In-House) was also prepared by using method described above starting with $AlCl_3.6H_2O$ or $Al(NO_3)_3.9H_2O$. As an example, alumina was prepared by dissolving 60 g of aluminum chloride in 800 ml of water. The pH of initial solution was about 2.2. The solution was filtered to remove any suspended impurities and then precipitated with 100 ml of 25% ammonia solution to a pH of 9.0. The precipitate was aged overnight, filtered, and washed free of chloride ions. The residue was dried overnight in an oven at 110 °C and then calcined at 400 °C for three hours. The weight of calcined catalyst was 16.75 g.

3.1.4. Zirconia

Zirconium hydroxide or zirconia (ZrO_2, F. W. = 132.22) was obtained by hydrolysis of zirconium oxychloride ($ZrOCl_2.8H_2O$, F. W. = 322.25) with 28% aqueous ammonia solution at a pH of 8, followed by washing with deionized water until no chloride ion was detected in the filtrate. Resulting $Zr(OH)_2$ was dried at 110 °C for twenty four hours and then calcined at 500 °C for six hours. Alumina – zirconia (80 : 20) was also prepared starting from $ZrOCl_2.8H_2O$ and $Al(NO_3)_3.9H_2O$.

3.1.5. Iron Oxide

Fifty grams of ferric chloride ($FeCl_3.6H_2O$, F. W. = 270.3) was dissolved in 350 ml of water to get 15 g of ferric oxide (Fe_2O_3, F. W. = 159.69). A 30 % ammonia solution was added into ferric chloride solution to attain pH of solution to 8.0. The residue was washed with deionized water, dried at 100 °C overnight, and calcined at 500 °C for six hours.

3.1.6. Titania

Titania (TiO_2, F. W. = 79.86) catalyst was prepared from titanium (IV) butoxide ($Ti[O(CH_2)_3CH_3]_4$, F. W. = 340.36) by dissolving it in water and acidifying it with nitric acid until a clear solution was obtained. Thus, 63 g of titanium butoxide was dissolved in 500 ml water and acidified with 60 ml nitric acid. The initial pH of the solution was 0.7. This solution was precipitated with aqueous ammonia followed by washing the precipitates with deionized water, drying at 110 °C overnight, and calcining at 400 °C for three hours. The final weight of the catalyst after calcination was 15.95 g.

3.2. Supported Salt Catalysts

The incipient wetness method was used to load catalyst salt on support. A solution with the desired quantity of salt, in an amount just sufficient to fill the pores and wet the outside of the particle, was introduced into the support in incipient wetness method. The wetted support oxide was dried slowly to properly crystallize the salt on the pore surface. The dry mixture was then calcined in a furnace at 500 °C for 4-5 hours. The supported salts include KH_2PO_4, $Ce_2(SO_4)_3$, $Ce(SO_4)_2$, $ZnCl_2$, $LaCl_3$, Li_2CO_3, K_2CO_3, and KOH. The quantities of these salts on the support oxides varied; specific loadings are given in the Results.

3.3. Catalyst Characterization

In this Section, methods for measuring the catalyst properties are discussed. The catalyst properties studied are: BET surface area, acidic strength, surface acidity and basicity, and type of acidic sites (Lewis or Bronsted).

3.3.1. BET Surface Area

The Pulse-Chemisorb 2700 from Micromeritics was used to determine the BET surface area of solid material used in experiments. The Pulse-Chemisorb and the N_2/He flow controller was turned on for 20-30 minutes before testing begins. A Dewar flask filled with liquid nitrogen was placed around the glass loop located on the right hand side of the Pulse-Chemisorb 2700 apparatus to trap any impurities in the test gases. A known amount of a sample was taken into a sample tube. The mass of the sample was ideally taken such that the total area of the sample being tested was near 25 m^2.

The sample tube containing solid catalyst was attached to the Pulse-Chemisorb 2900. The nitrogen and helium tanks valves were opened and the pressure was kept at least 15 psig. The set points on the flow controller were adjusted to 15.2 (ml/min) for the helium and 0.8 (ml/min) for the nitrogen (95% He, 5% N_2). The two valve on the flow controllers and the He/N_2 valve on the Pulse Chemisorb 2700 were opened.

The sample was outgassed by placing a heating mantel around the sample tube and heating to 250 °C for about an hour. Then, the sample was cooled to room temperature.

Once the detector output was stable, the signal was adjusted to zero and the area counter was cleared. The chart recorder was turned on at 0.5 cm/min and 50 mV span. The relative conductivity was kept negative. One ml of pure nitrogen gas was injected into the Pulse-Chemisorb 2700 via the septum located at the center of the apparatus. A peak appearing a few seconds after injection represents the excess nitrogen in the stream. When the detector had re-stabilized, the calibration knob was adjusted such that the area displayed on the LED display was 0.93. This represents the volume of nitrogen (in ml) injected at STP.

The relative conductivity was changed to positive, and the area counter was cleared. A Dewar flask filled with liquid nitrogen was placed around the sample tube. A peak appeared due to nitrogen adsorption on the sample. The peak area was recorded and the area counter was cleared when the detector returned to almost zero. The area of this peak was not used in the final analysis.

The relative conductivity was changed back to negative and the Dewar flask around the sample tube was removed. A beaker of water was placed around the sample

tube in order to bring the sample back to room temperature quickly. A peak evolved as the nitrogen desorbed from the material's surface. This peak area is the volume of nitrogen desorbed from the sample and was used to determine the total surface area.

The set points on the flow controller were now adjusted to 14.4 (ml/min) for the helium and 1.6 (ml/min) for the nitrogen (90% He, 10% N_2). The desorption peak area was measured using method discussed above. The above method was again repeated for the flow rates of 13 (ml/min) for the helium and 3 (ml/min) for the nitrogen (81.25% He, 18.75% N_2). The sample was removed form the Pulse-Chemisorb 2700. The total surface area can be obtained using the BET program found on the computer in the laboratory.

3.3.2. Acid Strength by Hammett Indicators

The determination is made by placing the catalyst sample in powder form into a test tube, adding dry benzene (a non-polar solvent), and shaking briefly. The indicators used for the acid strength determination are described in several publications (74). Catalyst samples are distributed to several sample glasses, and two drops of one of the Hammett indicator solutions are added to each. Now, catalyst samples are titrated with n-butyl amine. The end point of titration is determined visually from the resultant color changes and quantity of added titrant gives the number of acid sites with strength less than pK_a's of the Hammett indicator used. Using a range of Hammett indicators with different pK_a, the distribution of acid strength is determined. Similarly, benzoic acid titration is used to determine the basicity of the support.

3.3.3. Temperature Programmed Desorption (TPD) Using Probe Molecules

The Pulse-Chemisorb 2700 machine was also used in acid-base characterization of the catalyst using temperature programmed desorption method. The machine was turned on for 20-30 minutes before testing began. The known amount of catalyst was placed into a sample tube. The argon was passed through the catalyst sample at 500 °C for two hours. The catalyst was then saturated with the probe molecule (ammonia for acidic sites and carbon dioxide for basic sites) at room temperature for one hour at a flow rate of 10 ml/min. The catalyst was then flushed with helium for one hour at room temperature to remove loosely adsorbed probe molecules, then was heated at a steady rate of 20 °C/min in helium up to 500 °C. The profile was recorded as chemisorbed probe molecules left the surface of the catalyst with increasing temperature. The flow diagram of a TPD setup is shown in Figure 3.1.

The titration and TPD methods do not distinguish between Lewis sites and Bronsted sites. The acid amount, which is measured, is the sum of the amounts of Bronsted and Lewis sites at a certain acid strength. It order to elucidate the catalytic action of solid catalysts, it is necessary to distinguish between Bronsted and Lewis sites.

3.3.4. DRIFTS Study of Pyridine Adsorption

DRIFTS spectra were collected in a Perkin Elmer 2000 FTIR equipped with a DRIFTS cell (Harrick Scientific, HVC-DR2) in conjunction with a praying mantis mirror assembly (Harrick Scientific, DRA-2C0). The DRIFTS cell had a provision for heating the catalyst with the aid of a heating tape that was fixed inside the reactor. A thermocouple underneath the cup measured the temperature of the catalyst. The cell also

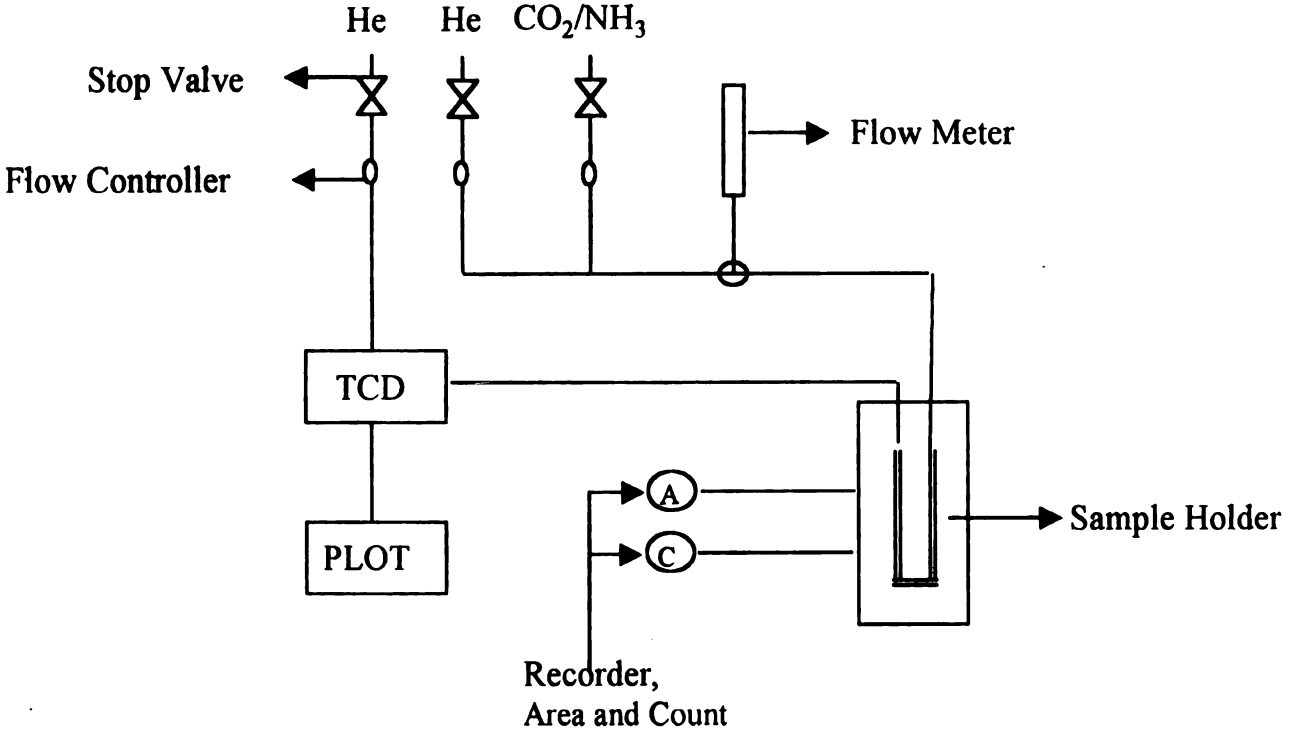


Figure 3.1. Flow Diagram of the TPD Setup

had a provision for gas flow and cooling. For DRIFTS studies, the catalysts were crushed and mixed with KBr to give a 33 wt % mixture. The KBr-catalyst mixtures were calcined at 400 °C for three hours and cooled back to room temperature prior to contact with pyridine. The vapors of pyridine were passed over the catalyst in a steady stream of helium (BOC, 99.995 %) at a rate of 50 ml/min. The reactor was heated to the desired temperature and the spectra were recorded by taking 10 scans at that particular temperature. A subtraction of spectra before and after pyridine adsorption was done to minimize background peaks.

3.4. Feed Preparation

There were two reactants, succinates and formaldehyde, in our reaction. Three different forms of succinates were evaluated: dimethyl succinate, diethyl succinate, and succinic anhydride. Diethyl succinate was used in earlier experiments, but the transesterification reaction of methanol from formaldehyde with diethyl succinate led to formation of dimethyl succinate and ethyl methyl succinate. The other byproducts (monomethyl succinate, monoethyl succinate, and succinic anhydride) were also observed, complicating analysis of the product mixture. Diethyl succinate was thus replaced by dimethyl succinate to avoid the transesterification and to minimize undesired byproducts.

Three sources of formaldehyde were evaluated: 1,3,5-trioxane (a cyclic trimer of formaldehyde), Formalin (a mix of 37 wt% formaldehyde, 12 wt% methanol, and 51 wt% water), and Formcel (blends of 55 wt% formaldehyde, 10 wt% water, and 35 wt% methanol). Trioxane decomposes to gaseous formaldehyde on heating above 350 °C.

1,3,5-Trioxane's solubility in diethyl succinate and dimethyl succinate is 1 mol/mol of ester. If the desired molar ratio was above this value, then the whole feed line from burette to 60 cm before to inlet of reactor including pumps was heated at temperature of around 70 °C using heating tapes and variable autotransformer; otherwise only 60 cm of tubing just before the reactor inlet was heated at 250 °C using 0.5 inch wide heating tape. Succinic acid esters and Formalin were pumped separately using two separate Bio-Rad pumps.

3.5. Reactor Operation

The following sections describe the procedure for conducting a reaction. The symbols referred to are shown in Figure 2.2 in Chapter 2.

3.5.1. Catalyst Loading and Unloading in Reactor

The reactor tube was accessed by opening three Swagelok nuts N1, N2, and N3 and moving the reactor up and clamping it at the top. The connection at the top of the reactor was then opened and the reactor was pulled down and removed. This procedure was followed to avoid the removal of the furnace element and the insulating firebricks in each experiment. The known amount of catalyst material was then added through the top of the reactor and was held in place at the bottom by a glass tube fitted with a quartz frit as shown in Figure 2.1. A similar procedure was followed for catalyst unloading after completion of an experiment. The catalyst after completion of the run was weighed for possible weight gain and stored.

In selected experiments, the reactor system was tested for any leakage. The helium inlet valve (V1) was turned on to allow helium to be fed into the reactor and the reactor was pressurized to 60 psi. Now, the backpressure regulator (R1) and the helium gas cylinder regulator were closed all the way to hold the helium in the reactor system. If there were no leakage in the reactor system then the reading on helium gas cylinder downstream pressure gauge would not change over time, otherwise the leak was traced by using soap and then fixed it.

3.5.2. Operation of Reactor

After loading the calcined catalyst into the reactor tube, the thermocouple (T1) was inserted (from the bottom) in the gap between the furnace and the reactor tube and the tip of the thermocouple was placed against the outer surface of the reactor body. The set point was then adjusted to achieve the desired catalyst bed reaction temperature and the difference was always accounted by keeping a higher set point. The glass wool and duct-tape were used to close the gaps between the insulation bricks and the reactor tubing at the top and bottom, respectively. Now, heating tapes were wrapped at the top and bottom of the reactor. The thermocouple (T2) was used to measure the temperature at the reactor top (feed preheat). The helium inlet valve (V1) was then turned on to allow helium to be fed into the reactor and the reactor was pressurized to the desired value using the helium gas cylinder regulator. Helium flow rate was set using the flow controller (F1), and the actual flow rate was measured with the soap bubble meter (M1). The CO (M2) and CO_2 (M3) meters were also turned on. The reactor tubing was heated to the desired temperature using the furnace; the temperature was measured by the

thermocouple touching the outer wall of the surface and allowed to stabilize for 50-60 minutes.

With the reactor heated up and pressurized to the desired conditions, the feed was pumped into the reactor using the Bio-Rad pump(s) (P1 (and P2) at the flow rate of 0.10 ml/min to 0.45 ml/min. Liquid flow rate was set with the digital meter in the pump, but actual flow rate was calculated by measuring the differential volume of liquid fed from the burette over time. Outlet helium flow rate was set using the rotameter and the actual flow rate was measured with the bubble soap meter (M1). The product was collected in the 25 ml collection vessel (C1) for 30 minutes and after 30 minutes the product line was switched to the other collection vessel (C2) using the Valco valve (VV). Most experiments were carried out for three to five hours and samples were taken every 30 minutes. The product was weighed and also the reading from the burette, CO, and CO_2 meters was taken.

3.5.3. Reactor Shutdown

For experiment shutdown, first the feed pump was stopped. Heaters, CO, and CO_2 meters were turned off one hour after stopping the pump. Helium flow was also stopped by closing the regulator on the gas cylinder and by turned off the valve (V1). The reactor system was cleaned thoroughly. The catalyst after completion of the experiment was weighed for possible weight gain and stored.

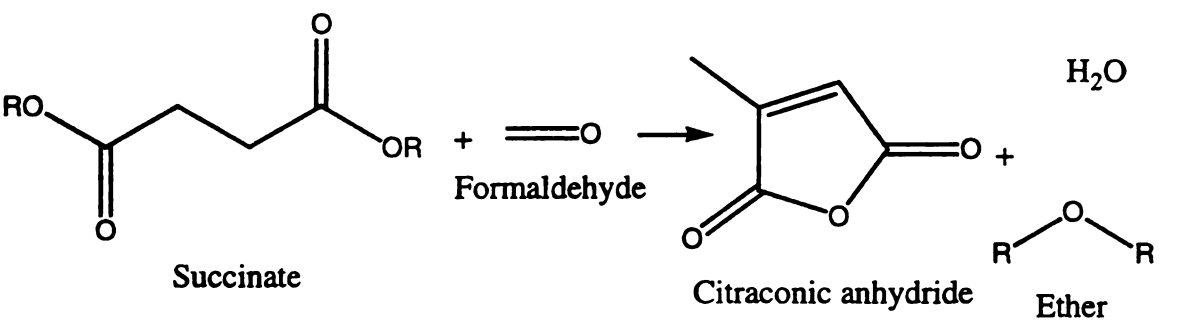
CHAPTER 4

CATALYST SCREENING FOR THE REACTION OF DIMETHYL SUCCINATE AND TRIOXANE

4.1. Introduction

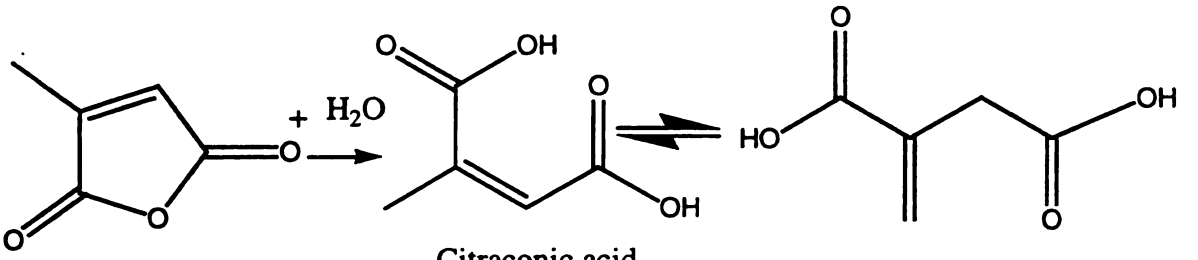
A series of catalyst and supporting materials were tested to achieve an optimal yield of citraconic anhydride from succinates and formaldehyde. The state of feed and catalyst evolved along the course of time. Several different forms of succinates and formaldehyde were used as feedstocks for the reaction. Pros and cons of each source of formaldehyde and succinate were evaluated.

The condensation of succinates with formaldehyde leads to the formation of citraconic anhydride:



Where R = CH_3, C_2H_5.

Citraconic anhydride easily hydrolyzes to citraconic acid and subsequent isomerization of citraconic acid gives itaconic acid:



Citraconic anhydride Citraconic acid Itaconic acid

4.2. Products from Succinates and Formaldehyde

Diethyl succinate (DES) was the first succinate employed in the reaction with 1,3,5-trioxane, a source of formaldehyde. The basic idea behind this work was to utilize a cheap fermentation-derived product, succinic acid. Diethyl succinate is an ideal green chemistry product because it can be produced from fermentation-derived succinic acid and ethanol. But the use of diethyl succinate as a reactant led to difficulty in product analysis and was thus discontinued. Formaldehyde in the presence of a basic catalyst gives methanol via the Cannizzaro reaction:

Formaldehyde Methanol Formic acid

The resulting methanol forms a series of transesterification products with diethyl succinate, as shown in Figure 4.1 (R = C_2H_5). The desired product, citraconic anhydride, also gives a series of esters in presence of methanol and ethanol as depicted in Figure 4.2 (R = C_2H_5). To avoid this, diethyl succinate was replaced by dimethyl succinate to avoid transesterification and thus minimize undesired byproducts.

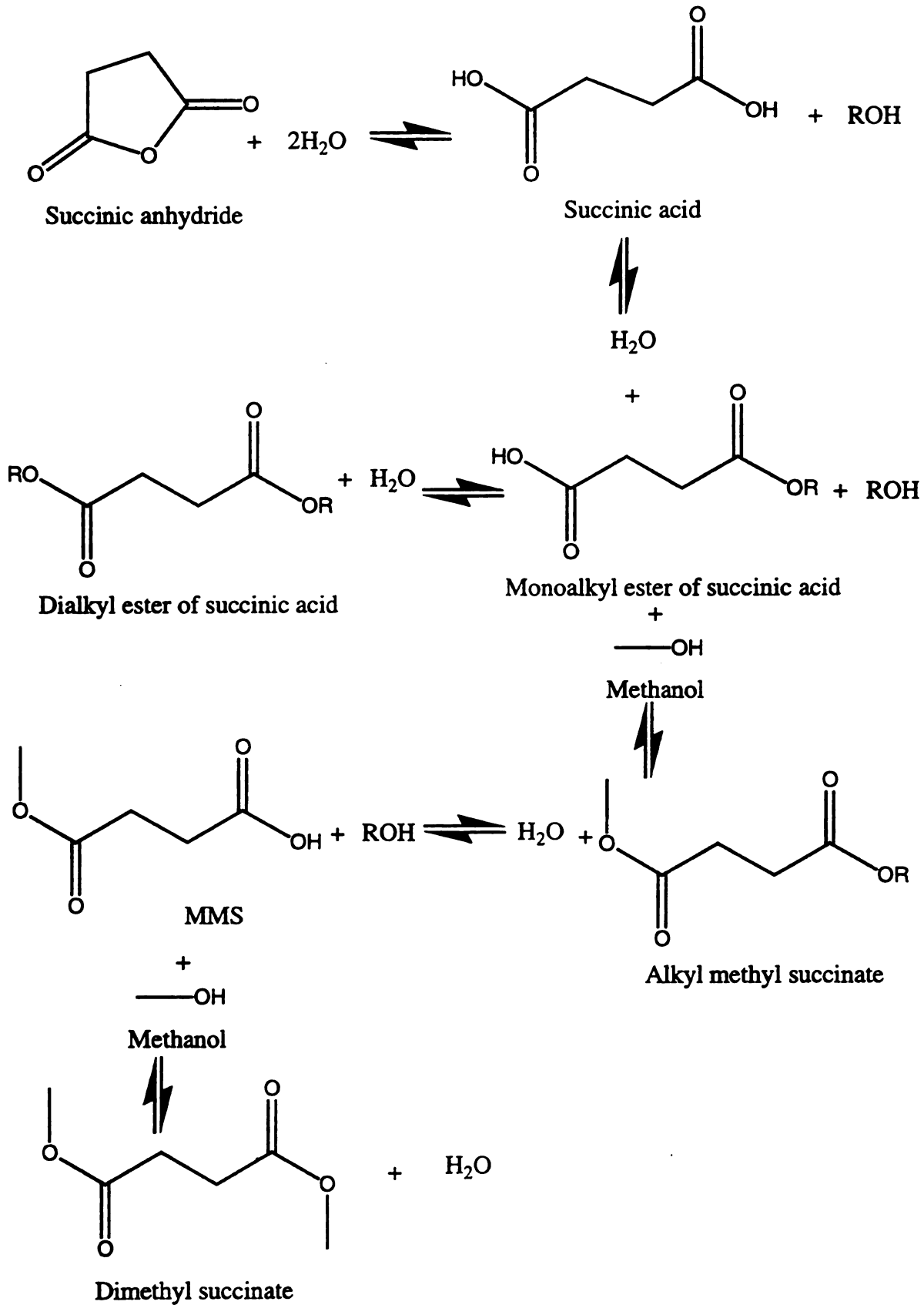


Figure 4.1. Transesterification products from succinates

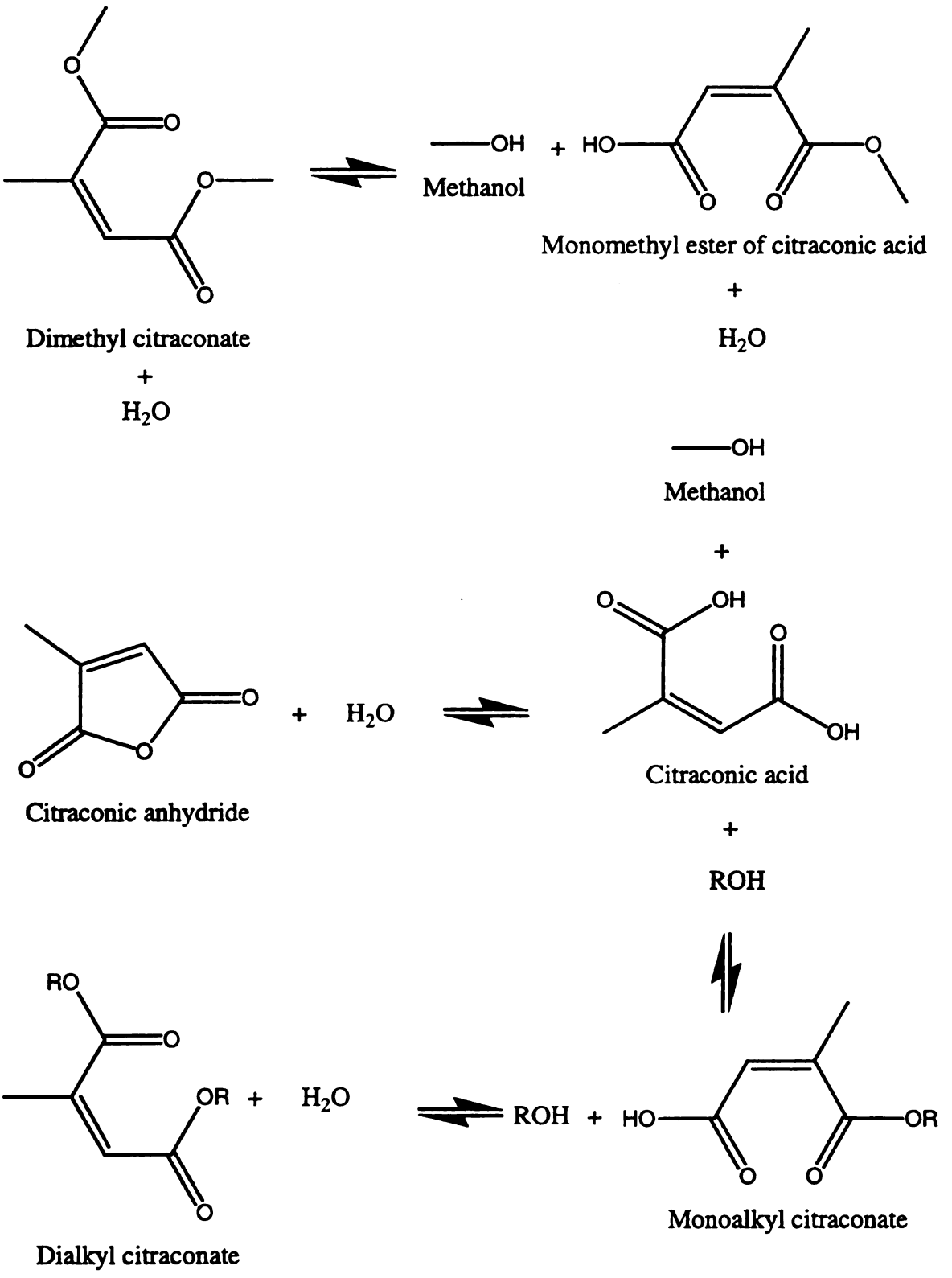
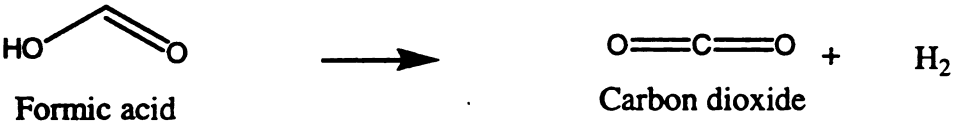


Figure 4.2. Transestrification reactions of citraconic acid

Carbon dioxide, carbon monoxide, and lower alkanes were also noticed in the products, in addition to citraconic anhydride and hydrolyzed products of succinates and citraconates. The source of carbon dioxide and lower alkanes was the cracking of succinates and citraconates. Formic acid, a Cannizzaro product, also contributes in the formation of carbon dioxide at high temperature:



Formic acid — Carbon dioxide

Carbon monoxide mainly comes from the decomposition of formaldehyde:

Formaldehyde — Carbon monoxide

4.3. Reaction Conditions

The reaction studies involve primarily succinic acid esters and trioxane as the feed with helium as the carrier gas. The reaction conditions that were used included temperatures from 320 to 450 °C with a preferred range of 350-380 °C, pressure from 40 to 400 psi, with a preferred value of 60 psig, liquid flow rate of 0.1 to 0.5 ml/min, and a succinate to formaldehyde ratio of 1:0.5 to 1:5. The amount of catalyst material used in each experiment depended upon the support used. The weight of the catalyst taken, and hence the height of the catalyst bed, along with the reactor dimensions, reaction conditions, and reactant flow rates were used to calculate the residence times. The residence time and the Weight Hourly Space Velocity (WHSV) calculations are presented in the Section 7.3.

The "base case" conditions for the experiments conducted are 60 psig (0.5 Mpa absolute), a total liquid flow rate of 0.12 ml/min, helium flow rate of 25 ml(STP)/min, a catalyst quantity of 5.0 g, a succinate to formaldehyde ratio of 1:2, and a temperature of 380 °C. Most experiments were carried out for five hours at steady state, with samples taken in 30 minute intervals.

4.4. Catalyst Characterization

The properties of the catalysts obtained from commercial sources or prepared by the methods described in Section 3.3 have been characterized for their surface area and acid/base properties. Results of these characterization measurements are given in Table 4.1 for the catalysts used in this study.

4.4.1. Surface Area

Total surface area measurements were conducted by nitrogen adsorption according to the standard BET method. Table 4.1 gives the surface area of different catalyst material used in this study. Surface area was also measured for some used and regenerated catalysts.

The loading of salts on catalyst supports did not make any difference on surface area of catalyst supports.

4.4.2. Acid-Base Measurements

Acid site concentration and strength on the catalyst surface was measured by temperature programmed desorption (TPD) of ammonia using a Micromeritics

Table 4.1. Properties of Different Catalyst Material Used in This Study

S.N.	Catalyst	S. A. (m^2/g)	Acid Strength (k)	Acid site density(mmol/g)	Basic site density(mmol/g)
1	AlPO, P/Al ratio				
A	0.5	150	-0.2 to –3.2	0.582	-
B	0.8	137	-0.2 to –3.2	1.220	-
C	1.0	156	-0.2 to –3.2	2.345	-
D	1.5	76	-0.2 to –3.2	1.810	-
2	Alumina, MSU	173	+1.1 to –0.2	0.671	0.150
3	Alumina, Norton				
A	SA3132	32	-	-	-
B	SA3177	107	+1.1 to –0.2	0.250	0.050
C	SA6173	220	-	-	-
D	SA6175	236	-0.2 to –3.2	-	0.091
4	Hydrotalcites, % Mg				
A	0.5	163	+2.4 to –1.2	0.608	0.157
B	1	178	+2.4 to –1.2	0.646	0.161
C	2	150	+2.4 to –1.2	0.782	0.220
D	4	174	+2.4 to –1.2	1.020	0.195
E	6	176	+2.4 to –1.2	0.676	0.141
F	10	-	-	-	-
G	12	171	+2.4 to –1.2	0.704	0.260
H	25		-	-	-
I	75	143	+2.4 to –1.2	-	-
5	Iron oxide	-	-	-	-
6	Magnesia	0.77	>+4.8	0	0.196
7	Titania	45	+2.4	0.122	0.007
8	Zirconia, MEI Inc	62	+2.4	0.066	0.068
9	Zirconia, MSU	-	-	-	-

Chemisorb 2700. Base site concentration was determined by TPD of carbon dioxide in the same instrument. Acid site strength and base site strength were further characterized by adsorption of Hammett indicators in dry benzene. DRIFTS study with pyridine and CO_2 gave the nature of the sites, e.g. whether they were Bronsted or Lewis in character.

4.4.2.1. Temperature Programmed Desorption (TPD) Studies

The ammonia TPD profiles of the catalysts used in this study are given in Figure 4.3. The acid site density of $AlPO_4$ was much greater than the other catalysts and had a peak maximum at 240 °C. Table 4.1 shows acid site densities of the catalysts calculated by calibrating the peak areas obtained with known volumes of ammonia. When a quantity of NaOH amounting to 0.7 mmol/g of catalyst was loaded on $AlPO_4$, the total number of acid sites reduced considerably, as can been seen in the TPD profile. The peak maxima shifted to 210 °C, indicating that the base neutralized the stronger acid sites. The TPD profile of $NaOH/AlPO_4$ was very close to that of SA 3177 and CPG-75. CPG-3000 did not adsorb ammonia, indicating it did not have any acid sites. Alumina magnesia co-catalyst with Mg/[Mg + Al] = 0.36 (AM-36) had an acid site density similar to SA3177 but the peak maxima was at 290 °C. TPD experiments showed no presence of acid and base sites on magnesia. Although magnesia is known to have a strong basic character, the low surface area did not provide enough sites to show any acid-base characteristics. Any contribution towards the acid or base character for such low surface area supports is only due to the surface sites. CPG-3000 did not adsorb any NH_3 or CO_2 because it also has a low surface area. CPG-75, alumina-magnesia co-catalyst (36% Mg) and $NaOH/AlPO_4$ had surface areas from 150-170 m^2/g and had comparable values of acid sites. Even though $AlPO_4$ had a surface area of 171 m^2/g, its acid site density was the largest of any material studied.

Figure 4.4 shows the carbon dioxide TPD profiles of the catalysts used in the study. $AlPO_4$ did not adsorb any carbon dioxide, while $NaOH/AlPO_4$ had enough basic sites to adsorb carbon dioxide. Table 4.1 shows basic site densities of the catalyst used in

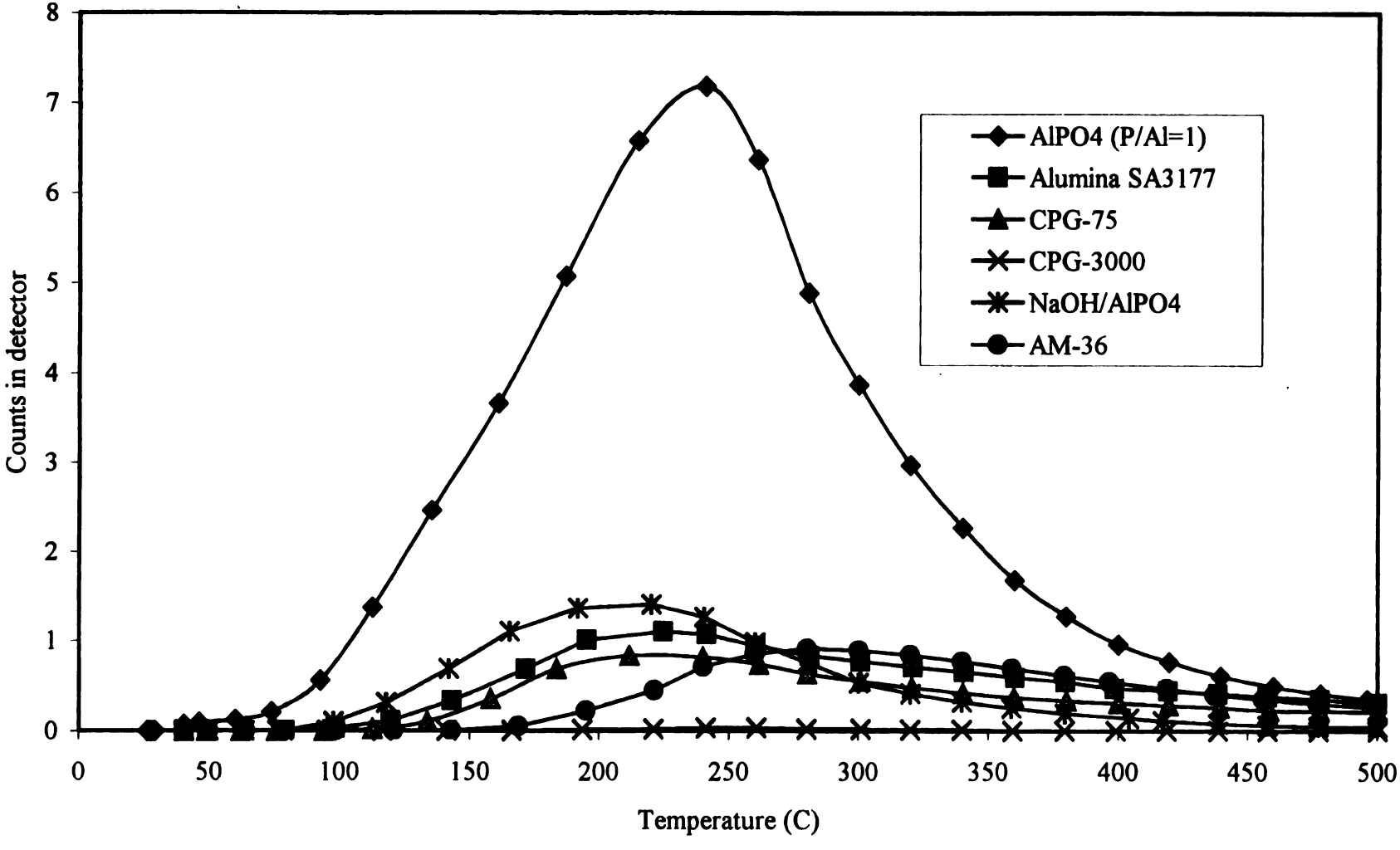


Figure 4.3. Ammonia TPD profiles of the catalysts used

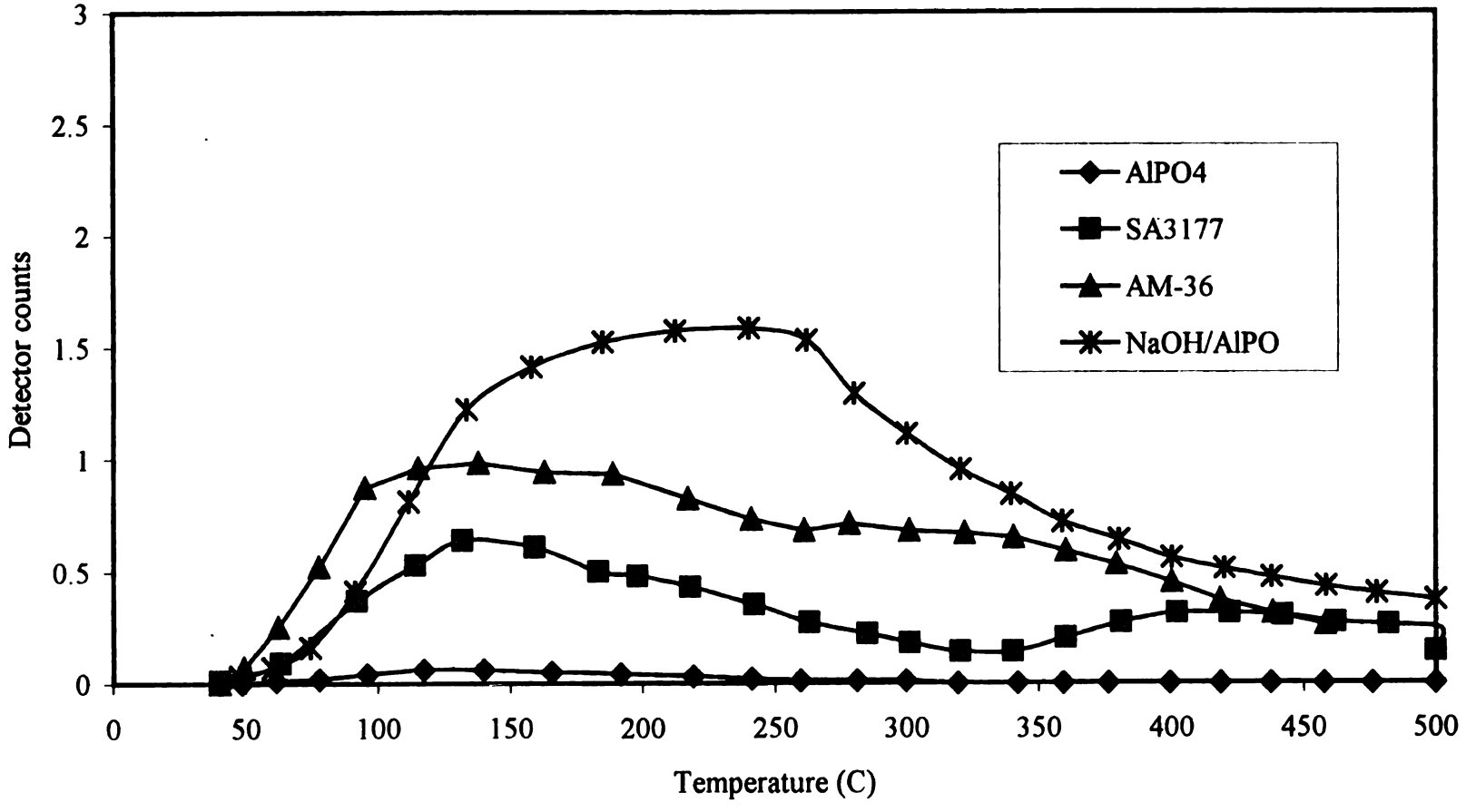


Figure 4.4. CO_2 TPD Profiles of the catalyst used

this work. The catalysts employed in the study therefore encompass a range of acid and base character.

Aluminum phosphate is completely acidic in character. The NaOH/SA3177 is completely basic in character; it had no acidic character because of the neutralization of all acidic sites by NaOH. The aluminum phosphate did not possess any basic sites strong enough to adsorb carbon dioxide. Alumina SA-3177 and AM-36 had both acidic and basic sites and the ratio of the acidic to basic sites varied in each of them. While the strength of the acid sites was more pronounced in SA 3177, AM-36 had stronger basic sites compared to acidic sites.

4.4.2.2. Acid Strength by Hammett Indicators

The catalysts were titrated with Hammett indicators to determine the strength of acid sites. $AlPO_4$ was the most acidic catalyst, and the least acidic was magnesia followed by NaOH/SA 3177. Acid strengths of all the other catalysts were intermediate between $AlPO_4$ and magnesia. The acid strengths of the catalysts as determined by Hammett titration are shown in Table 4.1.

4.4.2.3. DRIFTS Studies

The nature of the acid sites was investigated by pyridine adsorption. Catalysts were exposed to a stream of helium saturated with pyridine vapors and DRIFT spectra were taken to study the nature of the adsorbed species. Figure 4.5 shows the DRIFT spectra of pyridine adsorbed on SA3177, $AlPO_4$, NaOH/SA3177, NaOH/$AlPO_4$, and CPG-75. SA3177 did not have any Bronsted sites, as evidenced by the absence of an

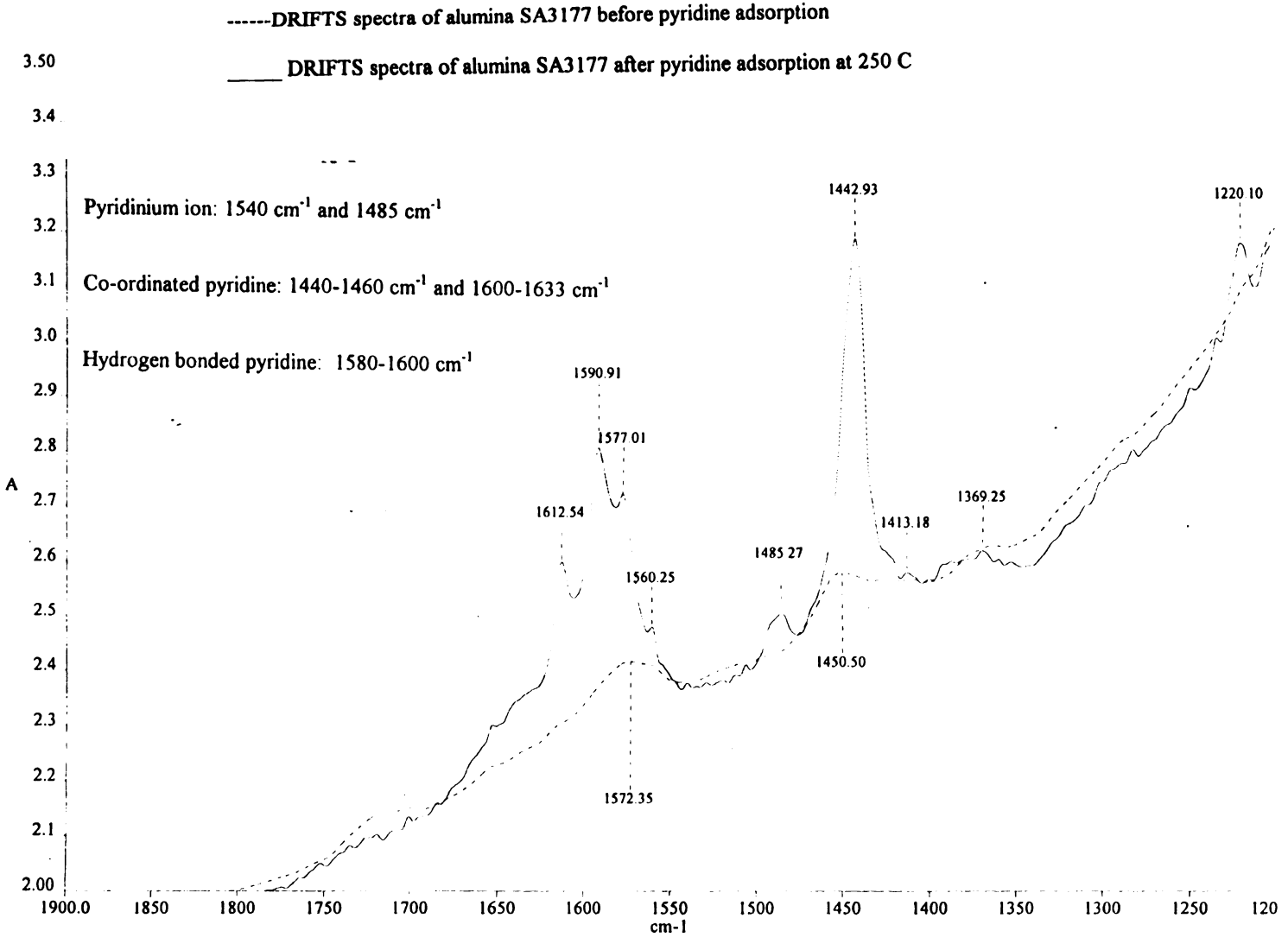


Figure 4.5. DRIFTS spectra from pyridine adsorption

absorption band at 1540 cm^{-1}. The absorption band at 1444 cm^{-1} corresponds to the Lewis site. This band shifts to higher frequencies when pyridine was adsorbed at higher temperatures. This indicates that pyridine adsorbs to stronger acid sites at higher temperatures. When NaOH was loaded on SA-3177 this shift at higher temperatures was not observed, indicating that the base neutralized stronger acid sites. CPG-75 had some amount of Lewis sites that were linked to the surface hydroxyl groups. $AlPO_4$ had a less intense band at 1540 cm^{-1} indicating fewer Bronsted sites but had a greater number of Lewis sites (1440 cm^{-1}).

4.5. Control Experiments

A set of control runs testing the catalyst supports for possible side reactions from reactants or products were conducted. Control runs of formaldehyde using Formalin as a source of formaldehyde are discussed in detail in Section 6.3. The following sections discuss control runs of some reactants and products used in this work.

4.5.1. Dimethyl Succinate

Control runs of dimethyl succinate with γ-alumina (SA3177), silica (CPG-3000), 85% zirconia + 15% alumina, and glass beads were performed at 380 °C. Table 4.2 gives conversion of dimethyl succinate and yields of carbon dioxide and monomethyl ester of succinic acid with different catalyst materials when feed was dimethyl succinate only. No conversion of dimethyl succinate with glass beads suggests that dimethyl succinate can not be de-esterified thermally and dimethyl succinate is thermally stable at the reaction conditions. Cracking and de-esterification of dimethyl succinate depend upon

the activity of catalyst material utilized in the reaction. Coking was observed with all catalyst materials used for control runs of dimethyl succinate except glass beads.

Table 4.2. Results from control runs with dimethyl succinate[1]

S.N.	Catalyst material	Conv of DMS (%)	Yield of MMS (%)	Yield of CO_2 (%)	Mass recovered (%)
1	CPG-3000 (silica)	25	*	**	94
2	SA3177 (alumina)	51	20	7	80
3	85% zirconia + 15% alumina	30	6	5	90
4	Glass beads	0	0	0	100

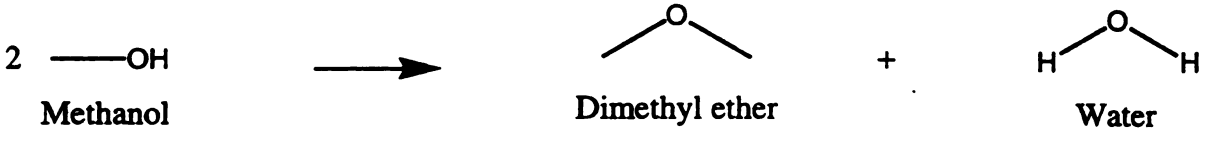
[1]Reaction temperature = 380 °C; pressure = 60 psi (300 psi with CPG-3000); feed = dimethyl succinate; liquid feed flow rate = 0.10 ml/min
* The amount of MMS was not quantified, but GC shows no significant amount of MMS in product.
** Carbon dioxide meter was not used for this experiment.

4.5.2. Diethyl Succinate

Zeolite-13X was found to be very active for diethyl succinate conversion even at low temperature (350 °C), where 100% conversion of diethyl succinate was observed. The Riken meter for carbon dioxide quantification was over range and only water was found in the product collection trap because cracking of diethyl succinate was predominant with the zeolite. Low surface area silica, CPG-3000, gave 25% conversion of diethyl succinate, whereas low surface area alumina, SA3132, yielded 30% conversion of diethyl succinate.

4.5.3. Trioxane

1,3,5-Trioxane, a source of formaldehyde, is a solid at room temperature, so its solution in methanol (17 wt% trioxane + 83 wt% methanol) was fed into the reactor to observe the side reactions from formaldehyde at the base case conditions. Carbon monoxide, a decomposition product of formaldehyde, and carbon dioxide, resulting from the Cannizzaro product formic acid, were detected in the gaseous products. Water was the only liquid product trapped in the collection vessel. Trioxane decomposition to gaseous formaldehyde was complete at the base case conditions. Methanol yielded dimethyl ether and water.



One mole of water is expected to form from two moles of methanol fed into the reactor. The Cannizzaro reaction utilized resulting water and, hence, left less water in the trap than stoichiometrically possible from the above reaction. In one other run, only methanol was fed into the reactor at the base case conditions. The stoichiometrically expected amount of water was collected in the product trap and dimethyl ether was observed as a gas-phase product.

4.5.4. Citraconic Anhydride

Conversion of citraconic anhydride over alumina, SA3177, was studied at 350 °C and 80 psi. Carbon dioxide was the only product formed from citraconic anhydride. A significant amount of coking (1.8 g of catalyst weight gain after 2.5 hours of the reaction)

was observed on the surface of the catalyst. Citraconic anhydride recovery was 78% after the reaction. Decomposition of anhydrides is anticipated at elevated temperatures (11-12). Detailed results from one of the control runs of citraconic anhydride are given in Table 4.3.

Table 4.3. Results from the control run of citraconic anhydride

Total time of the reaction	2.5 hr
Total citraconic anhydride fed	28.43 g
Total citraconic anhydride recovered	21.96 g
Total carbon dioxide out	1.82 g
Expected carbon dioxide from 6.33 g lost citraconic anhydride[1]	2.50 g
Total catalyst weight gain	1.84 g
Expected catalyst weight gain from 6.33 g lost citraconic anhydride[2]	2.10 g

[1]Assume 1 mole of carbon dioxide per mole citraconic anhydride lost
[2]3 moles of coke (mol wt. ~ 13) are expected from each mole of citraconic anhydride lost

4.5.5. Citraconic Anhydride and Diethyl Succinate

Citraconic anhydride and diethyl succinate were fed together into the reactor to check any reactivity of reactant, diethyl succinate, towards the desired product, citraconic anhydride. This reaction was carried out with SA3132 alumina at the temperature range of 350 to 410 °C (single experiment) and the reactor pressure of 350 psig. The molar ratio of 4:1 of diethyl succinate to citraconic anhydride was taken in the feed because this molar ratio was anticipated in the product. Conversion of citraconic anhydride was not significant (2%) at low temperatures (350 to 380 °C), but 27% conversion of citraconic

anhydride was observed at 410 °C. Similarly, diethyl succinate conversion was very low (11 - 18%) at low temperatures (350 - 380 °C) and higher (21%) at 410 °C. In this experiment, the temperature was ramped without changing the catalyst or stopping the run.

4.5.6. Itaconic Acid

Itaconic acid is a solid at room temperature and its solubility in water is also very low, so very dilute solution of itaconic acid in water (70 g/l) was fed into the reactor. Complete conversion of itaconic acid was achieved with alumina, SA3177, at the base case conditions. The products of itaconic acid conversion included citraconic anhydride, carbon dioxide, and carbon monoxide. Yields of citraconic anhydride, carbon dioxide, and carbon monoxide from itaconic acid were 45%, 20%, and 5%, respectively. This indicates, at reaction conditions, citraconic anhydride is the preferred product and itaconic acid is not expected to be present.

4.6. Catalyst Screening Studies

4.6.1. Silica

In early studies, three different surface area CPGs (Controlled Pore Glass) containing KH_2PO_4 and KOH were tested for the reaction of dimethyl/diethyl succinate and trioxane at the temperature range of 350-470 °C, but were not found to be promising. The reactor pressure was kept higher, ~300-400 psi, to obtain higher residence time and to push the products through the reactor. The yield of citraconic anhydride never exceeded one percent based on the diethyl succinate feed. The conversion of diethyl

succinate was highest with the higher surface area CPG-75 (surface area = 240 m^2/g). The conversion of diethyl succinate over CPGs increased with increasing temperature. Catalyst deactivation was also observed along with the catalyst coking. The other two CPGs employed for this reaction were CPG-3000 (surface area = 7 m^2/g) and CPG-500 (35 m^2/g). This work was started with the loading of KH_2PO_4 on CPG because the Stobbe condensation reaction is base-catalyzed and requires strong bases like alkali alkoxides or hydrides.

Most runs with CPGs could not be completed because of reactor plugging. 1,3,5-Trioxane was used in an excess molar quantity (5:1) with succinates, and conversion of trioxane into formaldehyde was limited by the low activity of silica supports. The unconverted trioxane always caused plugging of the reactor outlet and forced the run to be stopped before completion several times. These preliminary experiments were not successful as far as product formation was concerned, but gave a valuable insight into designing and operating the reactor system to handle all possible reactants, products, and operating conditions.

4.6.2. Zeolites

The zeolite-13X, zeolite-13X with $Ce_2(SO_4)_3$, and ion-exchanged zeolite-13X with $NdCl_3$ and $LaCl_3$ were found to be very active for the cracking the reactants into carbon dioxide and carbon monoxide. As discussed earlier, zeolites have strong Bronsted and Lewis acid sites which were responsible for coking formation on zeolite; subsequently deactivation of zeolites was quite a bit faster than other catalysts utilized. Carbon dioxide, carbon monoxide, and water were the only products in the first sixty

minutes of the reaction of dimethyl succinate and trioxane when zeolite was used as a catalyst. After 60 minutes of cracking, catalyst activity was not sufficient for the desired reaction. At low temperature (300 °C), 100% conversion of dimethyl succinate via cracking was observed without forming any citraconic anhydride. A maximum citraconic acid of 7% yield at 80% conversion of diethyl succinate was obtained with zeolites at 380 °C.

4.6.3. Other Supports

A series of other metal oxide supports like iron oxide, zirconia, titania, and hydrotalcites have been also screened as catalysts to obtain citraconic anhydride from dimethyl/diethyl succinate and trioxane. Runs were carried out with both commercial metal oxides, if available, and in-house prepared metal oxides to confirm results. Results from different metal oxides are given in Table 4.4 and are discussed in the following sections in detail.

4.6.3.1. Iron Oxide

Iron oxide was screened for the formation of citraconic anhydride from dimethyl succinate and trioxane at the base case conditions. Iron oxide was completely inactive for the desired reaction. Formaldehyde was entirely converted into methanol and carbon dioxide via the Cannizzaro reaction. This suggests that formaldehyde was not available for the desired reaction. Conversion of dimethyl succinate was not significant (30%) over iron oxide catalyst. The products of dimethyl succinate conversion included monomethyl ester of succinic acid, succinic anhydride, and carbon dioxide.

Table 4.4. Results from different metal oxides

Support	Surface area (m^2/g)	DMS conv (%)	CA yield (%)	MMS yield (%)	CO_2 yield (%)	CH_2O conv (%)
Iron oxide[2]	-	33	0	0	52[4,5]	100
Iron oxide[3]	-	72	0	14	40[4,5]	100
Titania[2]	-	30	0	20	2	21
Titania[3]	45	80	0	20	28	90
Zirconia[2]	-	31	3	9	10	93
Zirconia[3]	62	33	7	9	8	86
Hydrotalcite[2,6]	170	38	4	12	11	93

[1]Reaction conditions: Temperature = 380° C; pressure = 60 psi; feed = DMS + Trioxane; liquid feed flow rate = 0.10 ml/min; molar ratio = 2 to 1 (formaldehyde to DMS)
[2]In-house metal oxide
[3]Commercial metal oxide
[4]Yield of CO_2 is based on DMS fed, but here the main source of CO_2 is the Cannizzaro reaction
[5]CO_2 meter was out of range all the time, so the maximum range of the meter was used in the calculation
[6]85% Zirconia + 15% Alumina
[7]90% Magnesia + 10% Alumina

4.6.3.2. Titania

Reactions of dimethyl succinate with trioxane were also performed over titania prepared in laboratory from titanium (IV) butoxide and titania obtained from Degussa. No citraconic anhydride was obtained from either of the titanias used for dimethyl succinate conversion. Conversions of dimethyl succinate and formaldehyde were different over each titania. Detailed results are shown in Table 4.4. In-house titania was prepared from titanium (IV) butoxide, so it might be possible that the organic ligand was

not removed from titania crystals completely. Residue of the organic substance could cause blocking of pores and hence curtail activity of the catalyst.

4.6.3.3. Zirconia

A maximum of 3% yield of citraconic anhydride at 20% conversion of dimethyl succinate was obtained at the base case conditions using zirconia as a catalyst material. Zirconia support was prepared in laboratory from zirconium oxychloride using the sol-gel method described in Section 3.1.4. Monomethyl ester of succinic acid and carbon dioxide were other products obtained from the reaction over zirconia. A formaldehyde conversion of 80% was obtained with zirconia. Commercial zirconia, which contains 15% alumina, was supplied by MEI Corporation and was also employed for succinate conversion to citraconates. This MEI zirconia (15% alumina + 85% zirconia) yielded 6% citraconic anhydride at 32% conversion of dimethyl succinate. The product distribution from MEI zirconia was similar to zirconia prepared in the laboratory.

4.6.3.4. Hydrotalcites

Results from hydrotalcite support are also summarized in Table 4.4. Contrary to strongly acidic zeolites, basic catalysts facilitate the Cannizzaro reaction of formaldehyde. Hydrotalcite catalysts (90:10 :: Al:Mg) gave little citraconic anhydride but catalyzed the Cannizzaro reaction of formaldehyde to form methanol and formic acid. Hydrotalcites supports were studied extensively in the later part of work with Formalin and dimethyl succinate as a feed.

4.7. Alumina Supports

Several different γ-aluminas were evaluated with surface area ranging from 32 m^2/g to 225 m^2/g. Most of the aluminas used in this work were supplied by Norton, Inc with the trade name Alundum. Intermediate surface area alumina and aluminum phosphate were also prepared in the laboratory by methods described in Section 3.3. Commercial aluminas are described in this work by the stock number used by Norton, e.g., SA3132 for low surface area alumina, SA3177 for intermediate surface area alumina, and SA6173 and SA6175 for high surface area alumina. Intermediate surface area alumina and aluminum phosphate prepared by Dr. N. Kirthivasan in lab are known here by Alumina-In-House and $AlPO_4$, respectively. Figure 4.6 summarizes the citraconic anhydride yields obtained over time from various alumina catalyst supports for the conversion of dimethyl succinate. Conversion of dimethyl succinate, yield of the cracking product carbon dioxide, and selectivity over time from different alumina catalyst supports are depicted in Figure 4.7, Figure 4.8, and Figure 4.9, respectively. Results from different types of aluminas are discussed in the following sections in detail.

4.7.1. Low Surface Area Aluminas

The low surface area Alundum, SA3132, was found to be less active than other aluminas used. Several different salts supported on SA3132 were surveyed for the formation of citraconic anhydride from diethyl succinate and trioxane. Results from different salts surveyed are listed in Table 4.5.

A series of experiments were carried out with SA3132 impregnated with ceric sulfate. There were two reasons behind the selection of ceric sulfate as a catalyst for the

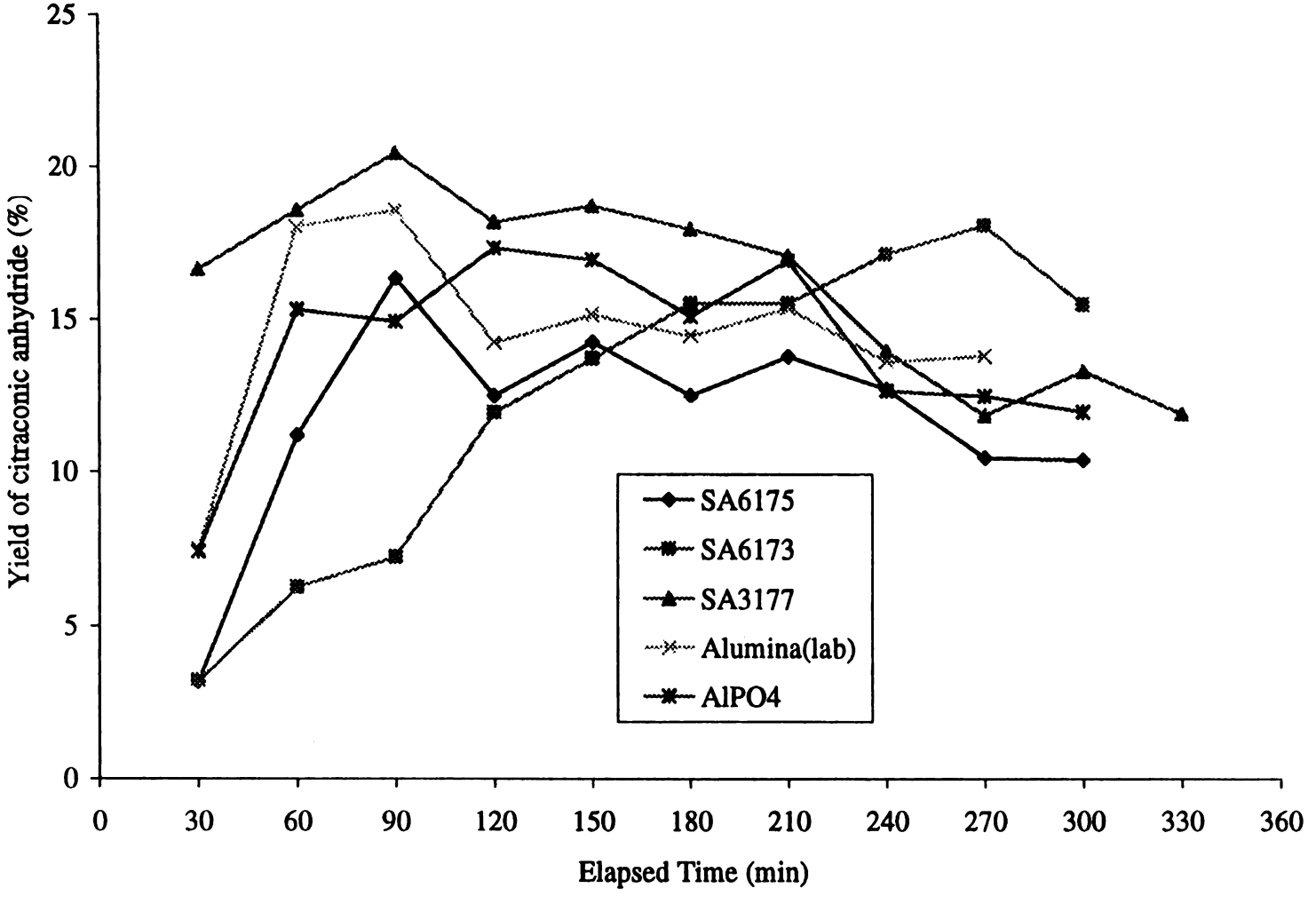


Figure 4.6. Yield of citraconic anhydride from different alumina catalyst supports

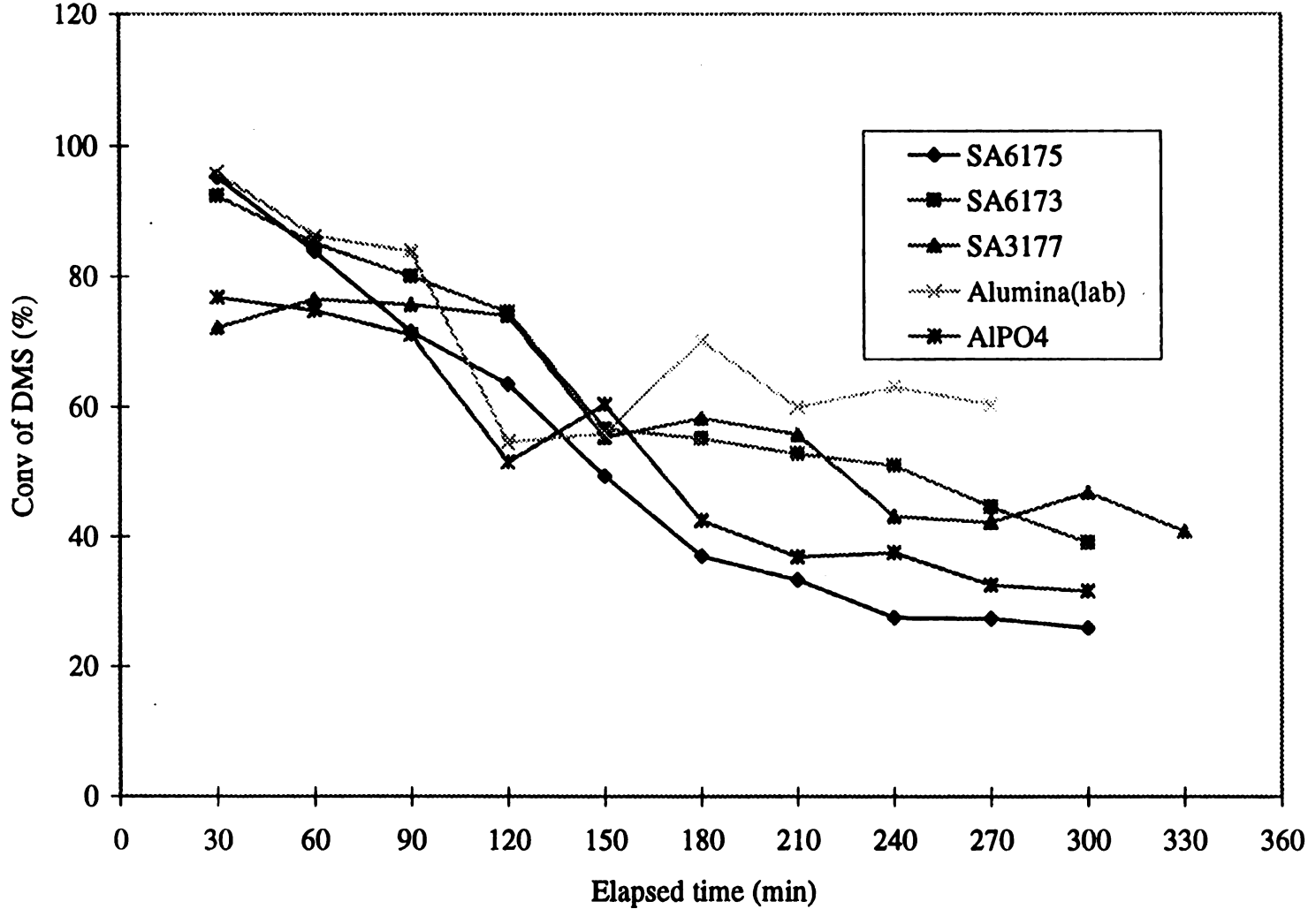


Figure 4.7. Conversion of DMS from different alumina catalyst supports

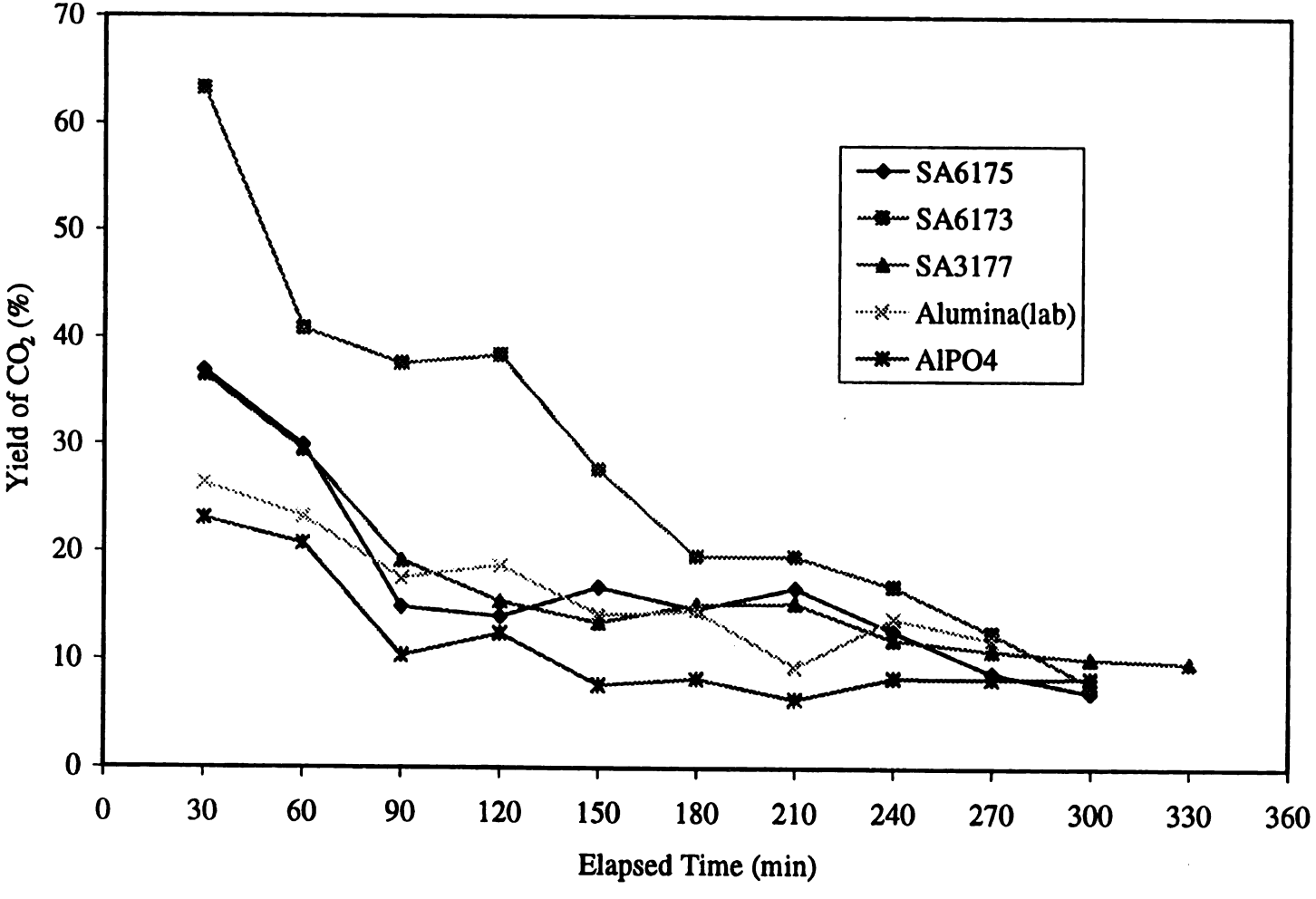


Figure 4.8. Yield of CO_2 evolved from different alumina catalyst supports

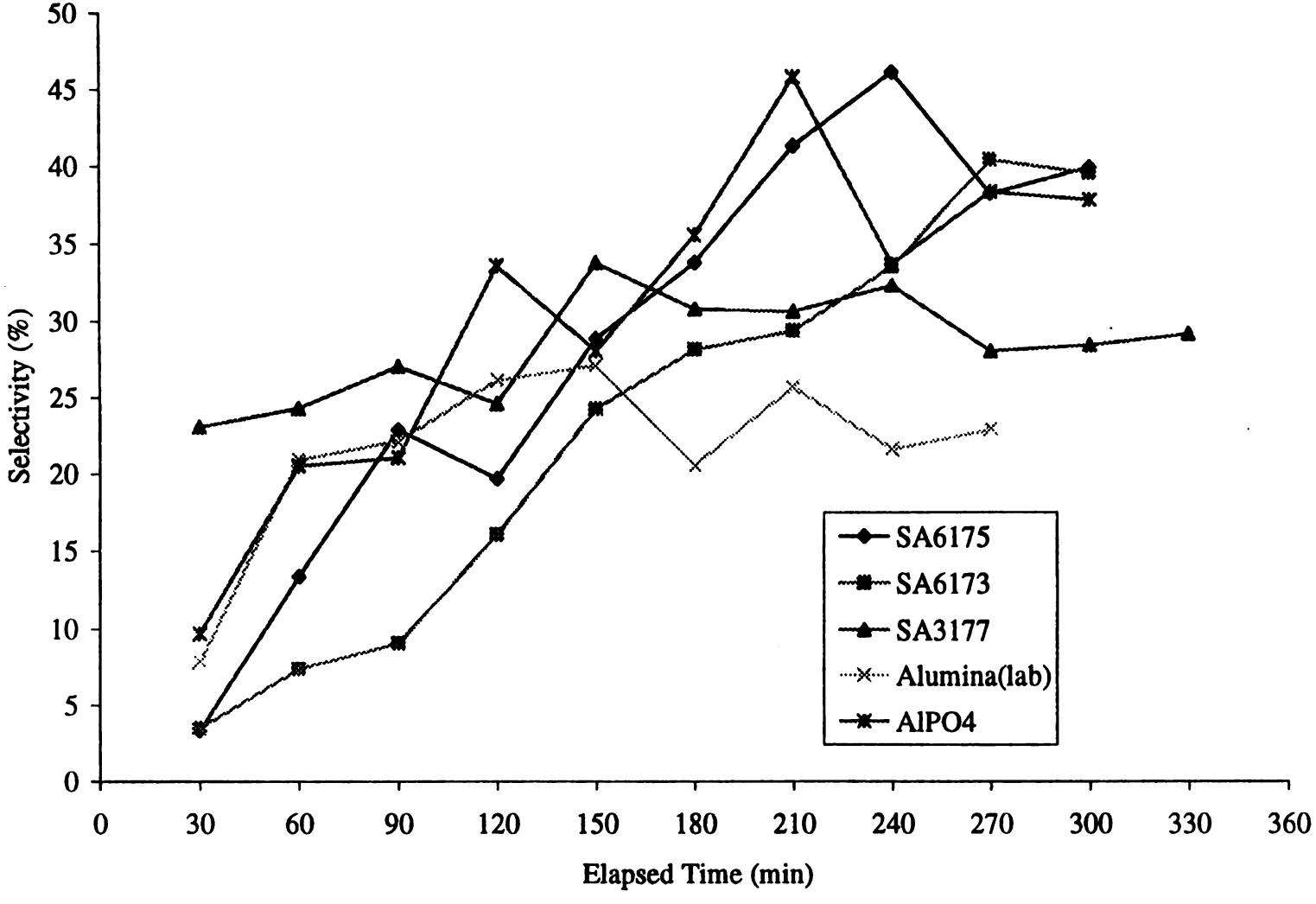


Figure 4.9. Selectivity of citraconic anhydride from different alumina catalyst supports

Table 4.5. Results from salts supported on SA3132[1]

S. N.	Salt	Loading (mmol/g)	Molar ratio[2]	Temp (°C)	Pressure (psi)	Conv of DES (%)	Yield of CA (%)
1	-	-	1:2	410[3]	300	31	3.2
2	Li_2CO_3	1.00	1:4	380	280	0	0.0
3	$Ce_2(SO_4)_3$	0.25	1:4.6	380	300	25	5.4
4	$Ce_2(SO_4)_3$	0.25	1:1.5	380	300	42	4.5
5	$Ce(SO_4)_2$	0.53	1:2	410[4]	350	62	3.8
6	$Ce(SO_4)_2$	0.53	2:1	410[4]	350	58	3.6
7	$Ce(SO_4)_2$	0.53	1:4	410[4]	350	55	4.8
8	$Ce(SO_4)_2$	0.39	1:2	380	60	50	6.9
9	$LaCl_3$	0.50	1:2	380	60	26	1.0
10	$Ce(SO_4)_2$	0.50	1:2	410	60	50	7.0
11	$Ce(SO_4)_2$	0.50	2:1	410	60	52	7.8
12	KH_2PO_4	2.00	1:2	380	60	10	0.4

[1]Feed consists of diethyl succinate and trioxane.
[2]Molar ratio of diethyl succinate to trioxane
[3]Temperature was 350 °C in beginning of the run and then ramped 30° C/hour.
[4]Temperature was 380 °C in beginning of the run and then ramped 30° C/hour.

formation of citraconic anhydride. One, initially, thorium sulfate was selected as a salt additive because thorium sulfate supported alumina was successfully used, in a prior art, for this reaction (33). But, the radioactive nature of thorium sulfate made its intended use difficult, so ceric sulfate, a similar compound to thorium sulfate, became our choice. Two, cerium salts are widely used as coking reducers in industry. With ceric sulfate coking over the catalyst was observed, but at the same time catalyst weight loss after completion of the reaction was observed in ceric sulfate-supported on SA3132. The catalyst weight loss occurred because ceric sulfate releases hydrated water at high temperatures used for reactions. Impregnation of salt on SA3132 did not make any difference on citraconic anhydride yields.

The highest citraconic anhydride yield of 8% was obtained over ceric sulfate-supported on SA3132 with a diethyl conversion of 52% at 410 °C. No conversion of diethyl succinate was observed with lithium carbonate-supported on SA3132. Similarly, 2 mmol/g loading of monobasic potassium phosphate on SA3132 was also not active for conversion of diethyl succinate. Bases like lithium carbonate and monobasic potassium phosphate are supposed to block highly acidic coking sites, but they killed the activity of the catalyst for the desired reaction, too. Lanthanum chloride on Alundum SA3132 gave only 1% yield whereas cerous sulfate on SA3177 gave 4.5% yield of citraconic anhydride. In earlier studies, runs were not carried out at constant temperature. Instead, temperature was increased by 30 °C after each hour and then samples were collected, so catalyst was not fresh at the next temperature level. So, results at higher temperatures do not predict actual activity of catalyst if the runs were not started from that temperature.

Nevertheless, the catalyst screening provided an early, meaningful result of relative catalyst activity.

4.7.2. Intermediate Surface Area Aluminas

4.7.2.1. SA3177 Alumina

The best activity was obtained using intermediate surface area (100 to 150 m^2/g) aluminum supports (alumina and AlPOs) without adding any salt. SA3177 gave 21% yield of citraconic anhydride and 35% yield of all citraconates at 48% conversion of dimethyl succinate, and thus a selectivity of 70% at the base case conditions. Yield of citraconic anhydride was low in the first sample before reaching a maximum and then somewhat stabilizing after 120 minutes (Figure 4.6). Alumina-in-house, having a surface area of 137 m^2/g, gave 19% yield of citraconic anhydride at 56% conversion of dimethyl succinate.

Yields of citraconic anhydride, conversions of dimethyl succinate, selectivities of citraconic anhydride from dimethyl succinate, and yields of carbon dioxide evolved from the reaction over SA3177 and alumina-in-house are given and compared with other aluminas in Figure 4.6, Figure 4.7, Figure 4.8, and Figure 4.9, respectively.

Since SA3177 was found to be an optimal catalyst for the formation of citraconic anhydride from the condensation reaction of dimethyl succinate and formaldehyde, further parametric studies were carried out with SA3177.

4.7.2.2. Bases Supported on SA3177

Conversion of dimethyl succinate and formaldehyde was also performed over KOH and K_2CO_3 supported on SA3177. It is well known fact that coking occurs on strong acidic support sites. The strong acidic sites may be poisoned to selectively deactivate coking sites. This is usually accomplished by loading potassium oxide on the acidic support. Potassium oxide can be loaded on support by loading KOH or K_2CO_3 and then calcining it at 500 °C. Loading of 0.15 mmol K_2CO_3/g SA3177 was taken for the reaction because it corresponds to the density of strong acidic sites on SA3177. But, loading of KOH was taken 0.30 mmol/g SA3177, because one mole of K_2O is formed from two moles of KOH.

The effects of salt addition to the catalyst are seen in Table 4.6. No citraconic anhydride was obtained for K_2CO_3 supported on SA3177, whereas 2% yield of citraconic anhydride was achieved for KOH supported on SA3177. Conversion of dimethyl succinate was lower with base supported compared to SA3177 without any salt added. Significantly lower conversion of dimethyl succinate was observed over KOH supported on SA3177, compared to K_2CO_3 supported on SA3177. Conversions over KOH supported on SA3177 were nearly half of those observed K_2CO_3 supported on SA3177, although this difference was less pronounced in the first sample collected after thirty minutes of starting the reaction. Yields of methanol and carbon dioxide were significantly higher with base supported on SA3177 compared to SA3177 alone. Yields of monomethyl succinate (MMS) over base supported on SA3177 were less than half of those observed with SA3177 alone.

Table 4.6. Effects of Loading on SA3177[1]

Elapsed time (min)	Conversion of DMS (%)			Yield of MMS (%)			Yield of CO_2 (%)[2]			Yield of methanol (%)[3]		
	K_2CO_3/ SA3177	KOH/ SA3177	SA3177	K_2CO_3/ SA3177	KOH/ SA3177	SA3177	K_2CO_3/ SA3177	KOH/ SA3177	SA3177	K_2CO_3/ SA3177	KOH/ SA3177	SA3177
30	89	65	92	10	9	19	55	48	37	63	111	36
60	64	33	76	11	10	23	50	24	30	75	67	39
90	48	25	75	12	6	21	51	24	20	111	60	40
120	27	17	73	7	4	19	26	9	15	56	46	45
150	27	14	67	6	5	23	28	7	13	52	64	45

[1]Reaction temperature = 380° C; pressure = 60 psi; feed = DMS + 1,3,5-Trioxane; liquid feed flow rate = 0.10 ml/min; molar ratio = 2 to 1 (formaldehyde to DMS)
[2]If CO_2 meter was out of range then maximum range of CO_2 meter is taken
[3]Methanol yields are based on fed dimethyl succinate

As discussed above, the objective behind using base supported on SA3177 was to enhance the activity of SA3177 by selectively poisoning the coking sites on it. However, no citraconate formation was observed, and lower conversions of dimethyl succinate from base supported on SA3177 suggest that the base also killed the weakly acidic sites which are active for the desired reaction. However, the presence of a base on SA3177 facilitated the Cannizzaro reaction and, hence, the formation of methanol and formic acid. Formic acid results in carbon dioxide at elevated temperatures employed for the reaction.

4.7.3. High Surface Area Aluminas

Yields of citraconic anhydride from the reaction of dimethyl succinate and trioxane over high surface area alumina SA6173 (surface area = 220 m^2/g), SA6175 (surface area = 236 m^2/g), alumina-in-house (prepared in lab from $AlCl_3$), and $AlPO_4$ (prepared in lab) were 16 to 19%; these values were close to alumina SA3177 (surface area = 100 m^2/g). Yield of citraconic anhydride was low in the first sample before reaching a maximum and then stabilizing after 120 minutes with trioxane and dimethyl succinate (Figure 4.6). High surface area aluminas were very active in the beginning of the reaction but deactivated by coking upon prolonged exposure to reactants. For high surface area aluminas, high conversion of succinates (Figure 4.7) was accompanied by lower yield of citraconic acid in the beginning of the reaction due to heavy cracking of succinates into carbon monoxide and carbon dioxide (Figure 4.8). The selectivity for citraconic anhydride of these higher surface area materials started low and increased over time, finally approaching that of the SA3177. The production of carbon monoxide and

carbon dioxide was very high in the reaction, and then declined to a small value after about 240 minutes (Figure 4.8).

4.7.4. Aluminum Phosphates

Aluminum phosphate ($AlPO_4$) employed in this study were prepared from two different set of precursors as described in Section 3.1.1 to determine the effect of precursor on surface characteristics and, hence, the effect on citraconic anhydride yields. A maximum citraconic anhydride yield of 18% at 60% conversion of dimethyl succinate was observed over $AlPO_4$ as a support at the base case conditions. Yield of citraconic anhydride, conversion of dimethyl succinate, yield of carbon dioxide, and selectivities are given and also compared with alumina supports in Figure 4.6, Figure 4.7, Figure 4.8, and Figure 4.9, respectively. $AlPO_4$ results also follow alumina trends. A higher activity in the beginning of the run resulted in high conversion of dimethyl succinate; later the citraconic anhydride yield (Figure 4.6) and dimethyl succinate conversion (Figure 4.7) stabilize. Significantly lower yield of carbon dioxide was observed over $AlPO_4$ compared to SA3177 (Figure 4.8). Yields of monomethyl succinate and methanol over $AlPO_4$ were 25% and 31%, respectively.

4.8. Parametric Studies

4.8.1. Effect of Pressure

Most experiments were run at a reactor pressure of 60 psi and temperature of 350 to 410 °C. Experiments in the beginning of this work using CPGs were carried out at high pressure of 400 psi. The reason behind selecting high pressure was to avoid

clogging by pushing products through reactor using high pressures. In the latter part of this study, it was confirmed that high reactor pressure did not make any difference on the total yield of citraconates. The comparison of results (unhydrolyzed) at low and high pressures is presented in Figure 4.10. The yield of citraconic anhydride before hydrolysis at high pressure was slightly lower than the yield at low pressure. But, overall yields of citraconates after hydrolysis at both pressures were the same at high and low pressures. Yield of citraconates before and after hydrolysis at high (400 psi) and low (60 psi) pressures are shown in Figure 4.11. At high pressures, the equilibrium favors the esterification reaction and, thus, more mono ester and diethyl esters of citraconic acid are formed. The conversion of dimethyl succinate was higher at 400 psi than at 60 psi and so selectivity was lower at high pressure. Surprisingly, the amount of carbon dioxide evolved was significantly lower at high pressure. But the catalyst deactivation rate and catalyst weight gain after the completion of the reaction were the same at low and high pressures. One other run was duplicated to confirm the results at 400 psi.

4.8.2. Effect of Temperature

The effect of temperature on citraconic anhydride yield (unhydrolyzed results) and dimethyl succinate conversion is given in Figure 4.12 and Figure 4.13, respectively. The conversion of dimethyl succinate or diethyl succinate increased with increase in temperature, but selectivity decreased with temperature. The yield of citraconic anhydride went through a maximum at 380 °C with the reactor temperature (Figure 4.12). At higher temperature, succinates cracked into carbon monoxide and carbon dioxide

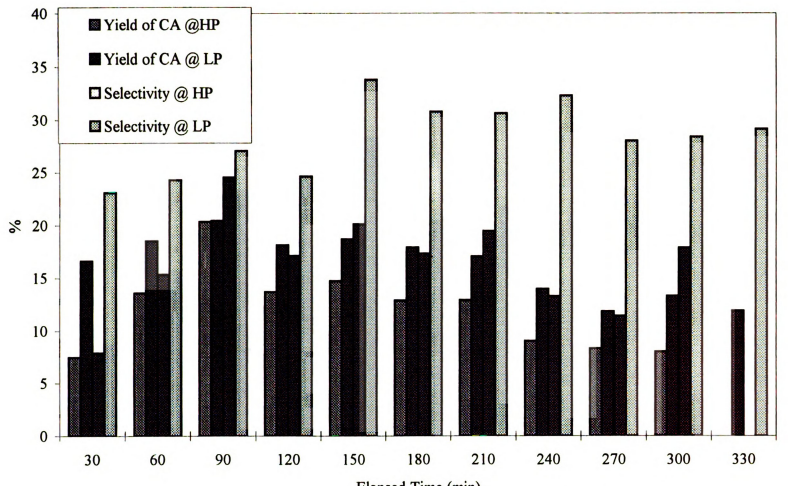


Figure 4.10. Comparison of results at low pressure vs high pressures (at same WHSV)

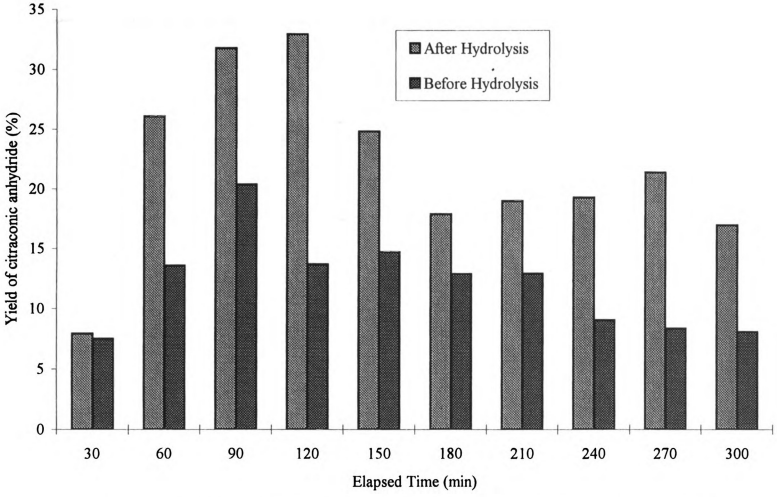


Figure 4.11. Effect of hydrolysis on the yield of citraconic acid at high pressures (at same WHSV)

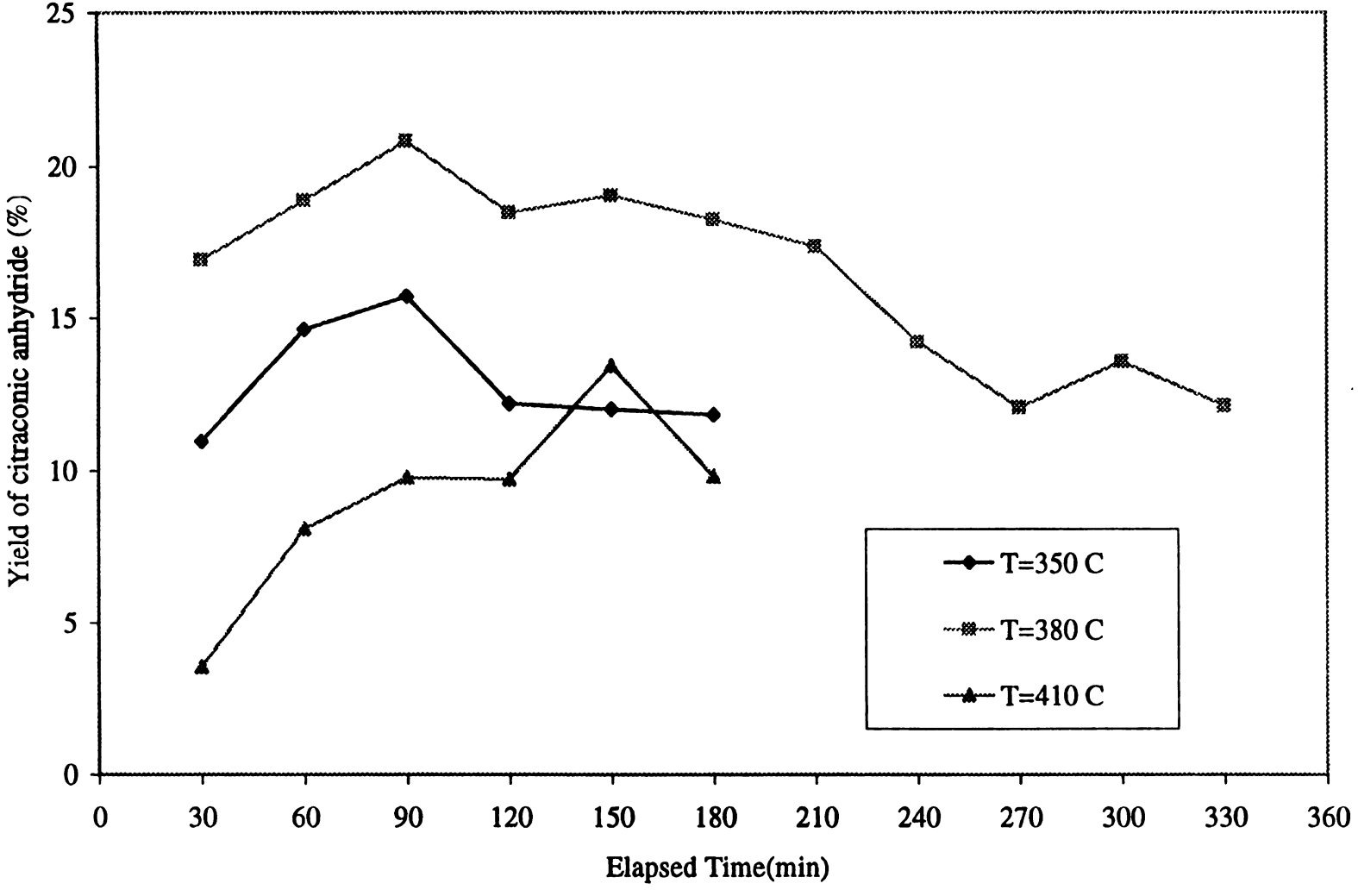


Figure 4.12. Yield of citraconic anhydride at various temperatures (at same WHSV)

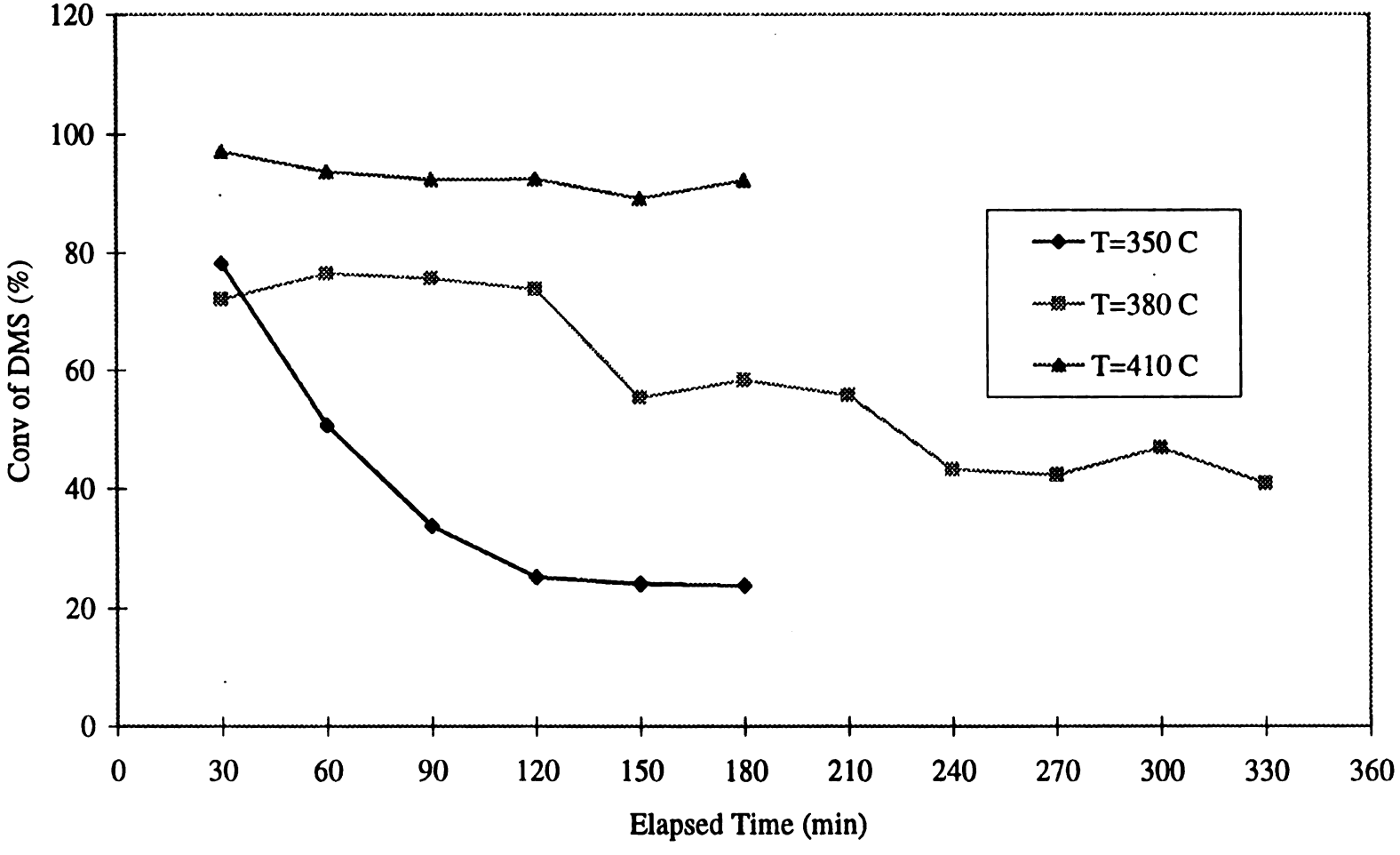


Figure 4.13. Conversion of DMS at various temperatures (at same WHSV)

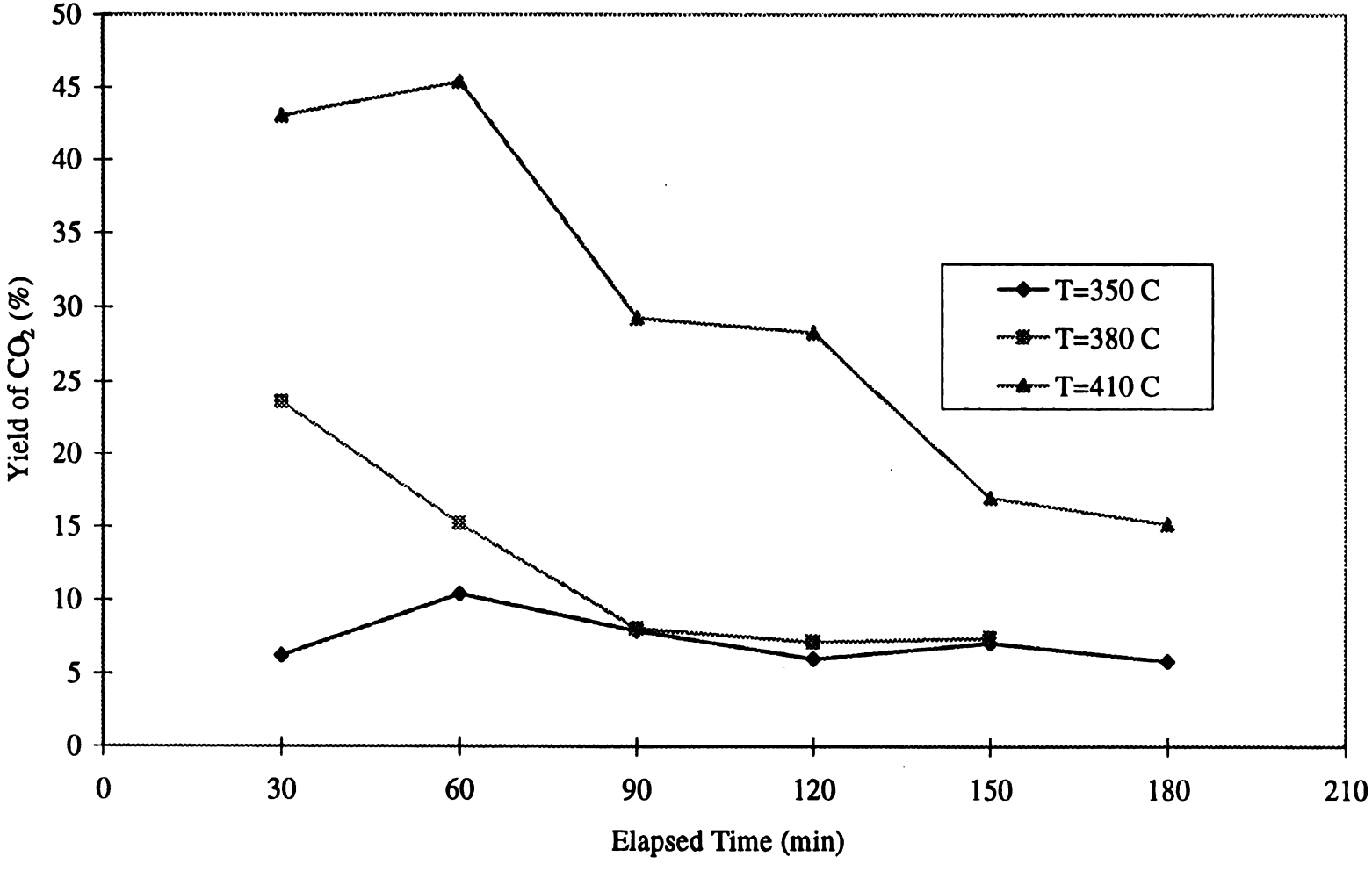


Figure 4.14. Yield of CO_2 evolved at various temperatures

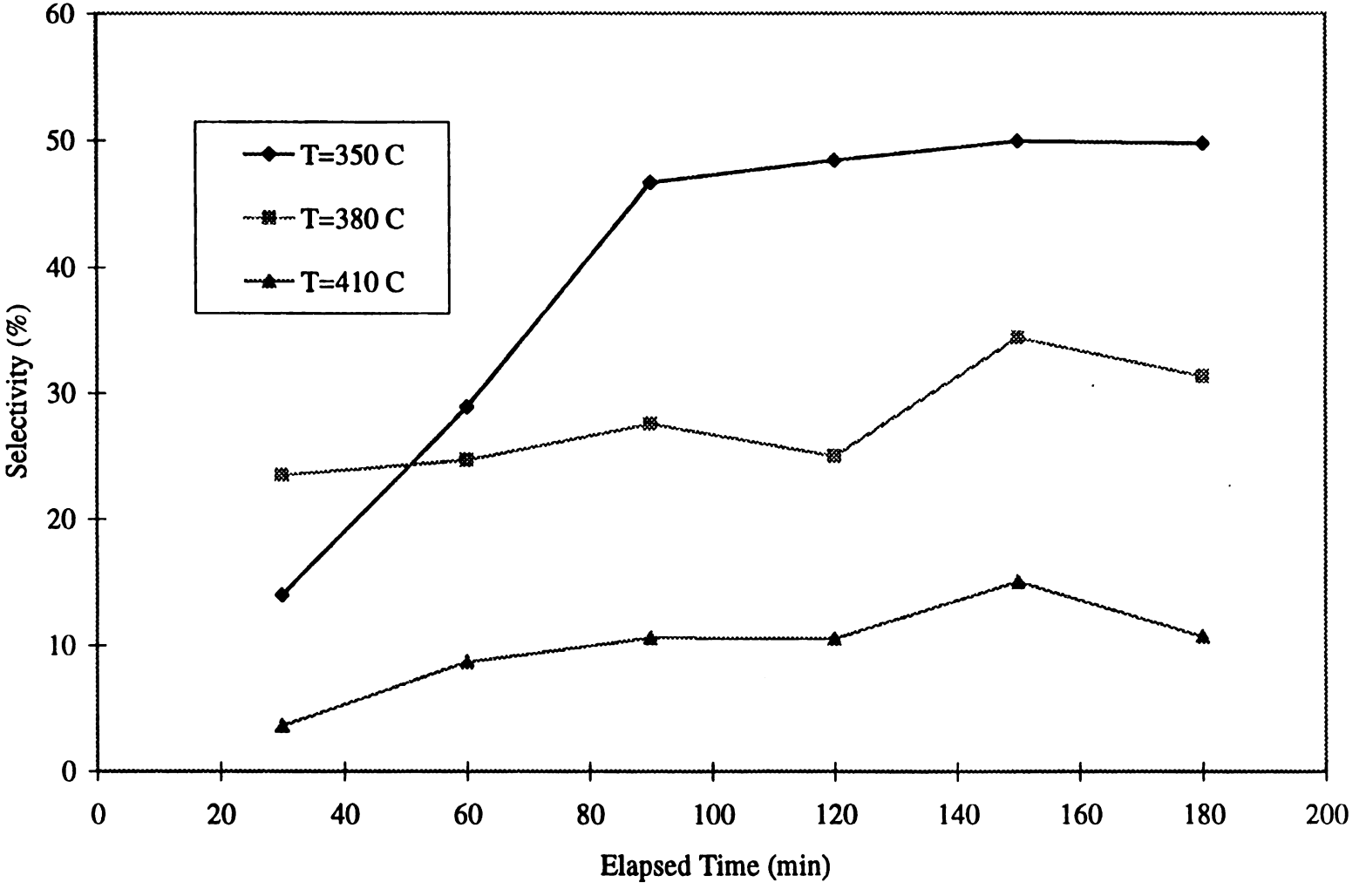


Figure 4.15. Selectivity of citraconic anhydride from DMS at various temperatures

(Figure 4.14) resulting in high conversion of succinates (Figure 4.13) and lower selectivity (Figure 4.15).

4.8.3. Feed Molar Ratio

Formaldehyde was used in molar excess over the alkyl ester of succinic acid. Several different molar ratios of formaldehyde to succinate (1 : 2, 2 : 1, and 4 : 1) were examined for our reaction. The effect of molar ratio of formaldehyde to dimethyl succinate in feed was studied in detail in the later part of this work and discussed in Section 6.6.5.

The effect of feed molar ratio on the yield of citraconic anhydride, conversion of dimethyl succinate, yield of carbon dioxide, and selectivity to citraconic anhydride using SA3177 are shown in Figure 4.16, Figure 4.17, Figure 4.18, and Figure 4.19, respectively. Yield of citraconic anhydride is based on the dimethyl succinate fed into the reactor. Yields of citraconic anhydride from the 2 to 1 molar ratio (dimethyl succinate to formaldehyde) feed were almost half of those observed from the feed molar ratio of 1 to 2 molar ratio of dimethyl succinate to formaldehyde. Increasing the feed molar ratio (DMS to formaldehyde) produced a decrease in the conversion of dimethyl succinate. Selectivity of citraconic anhydride formation from dimethyl succinate increased with increasing the feed molar ratio of dimethyl succinate to formaldehyde. Yield of carbon dioxide decreased with increasing dimethyl succinate to formaldehyde molar ratio because the most of carbon dioxide was produced from formaldehyde via the Cannizzaro reaction.

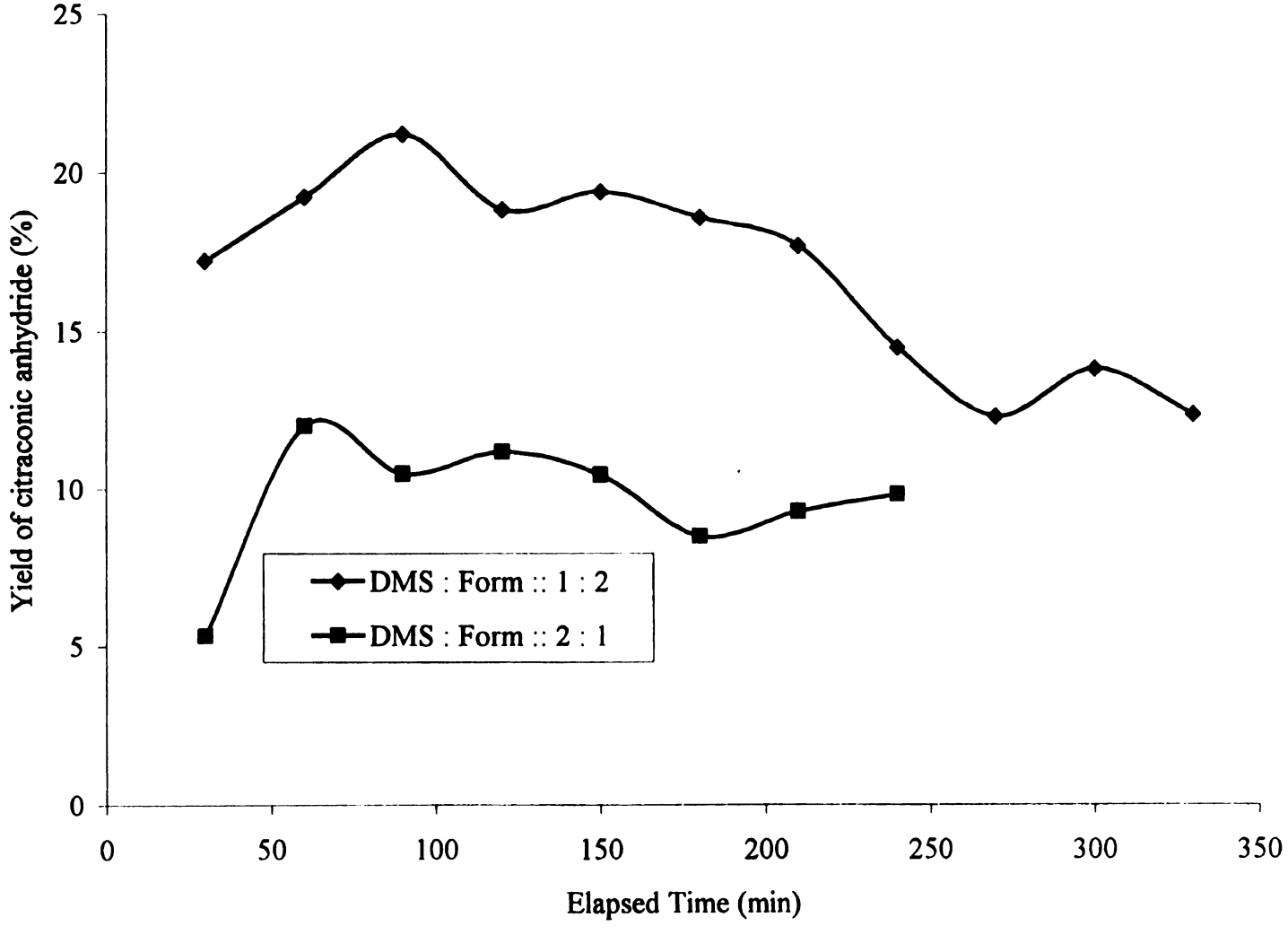


Figure 4.16. Effect of feed molar ratio on yield of citraconic anhydride

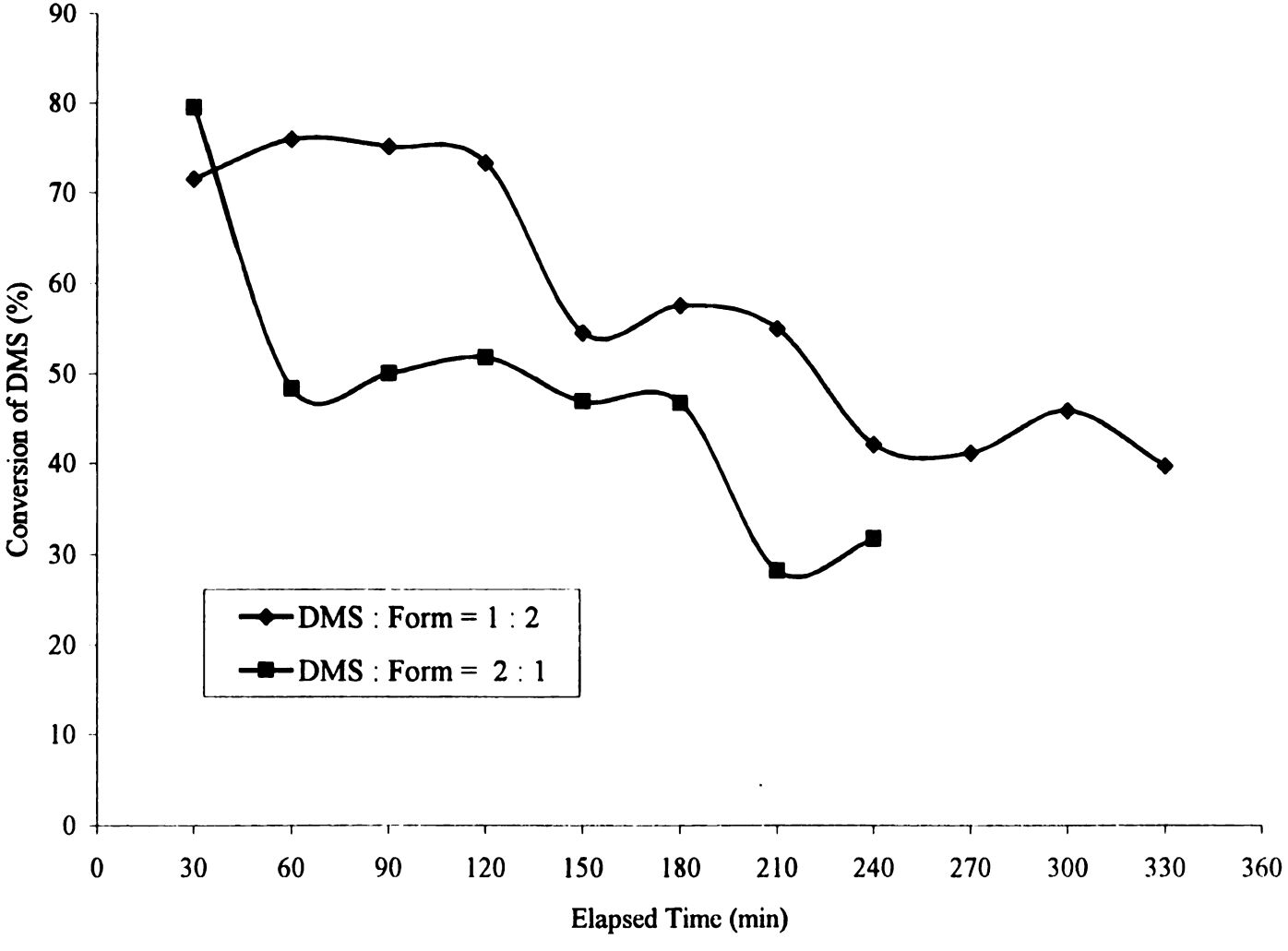


Figure 4.17. Effect of feed molar ratio on conversion of dimethyl succinate

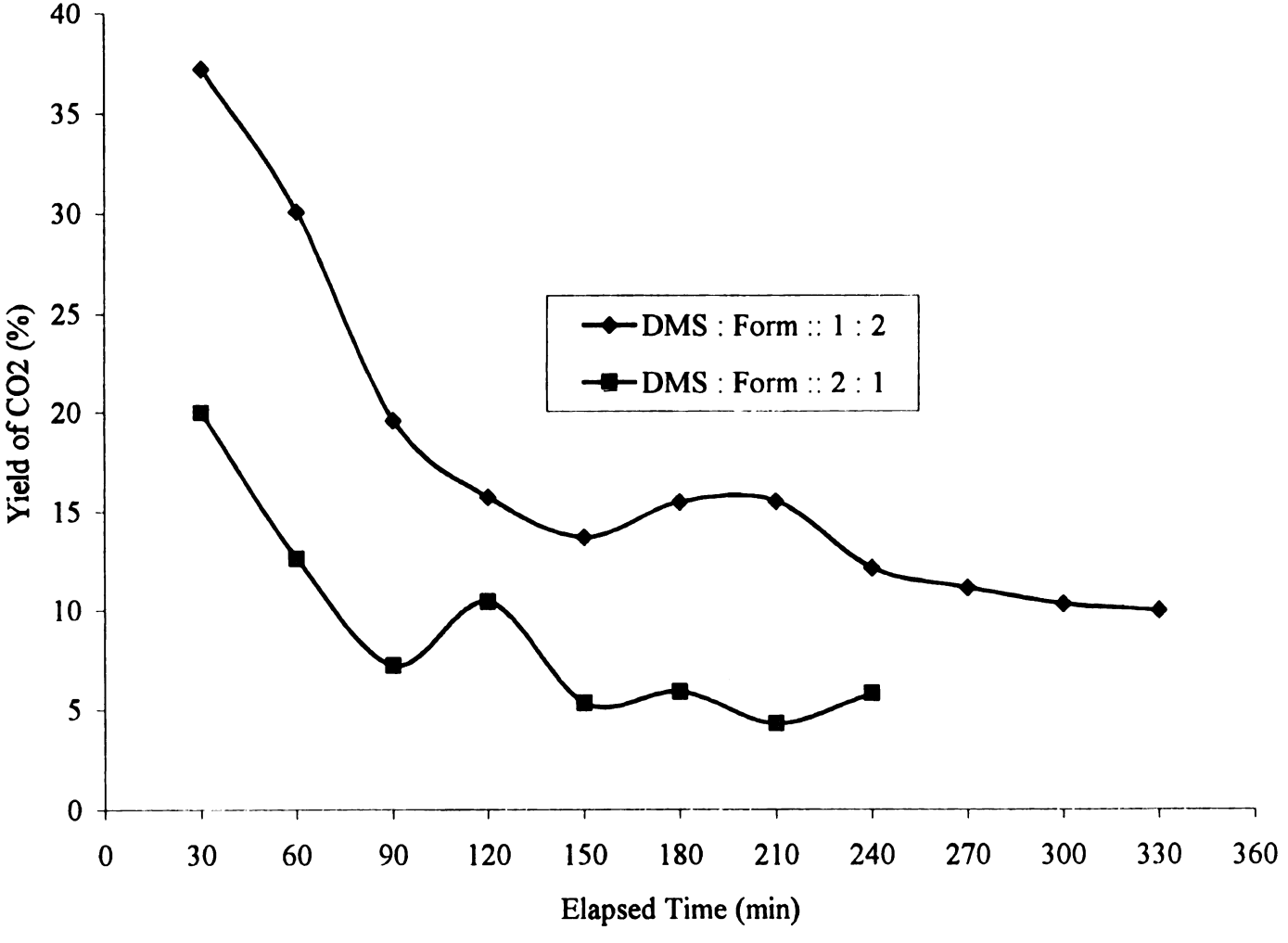


Figure 4.18. Effect of feed molar ratio on yield of CO2

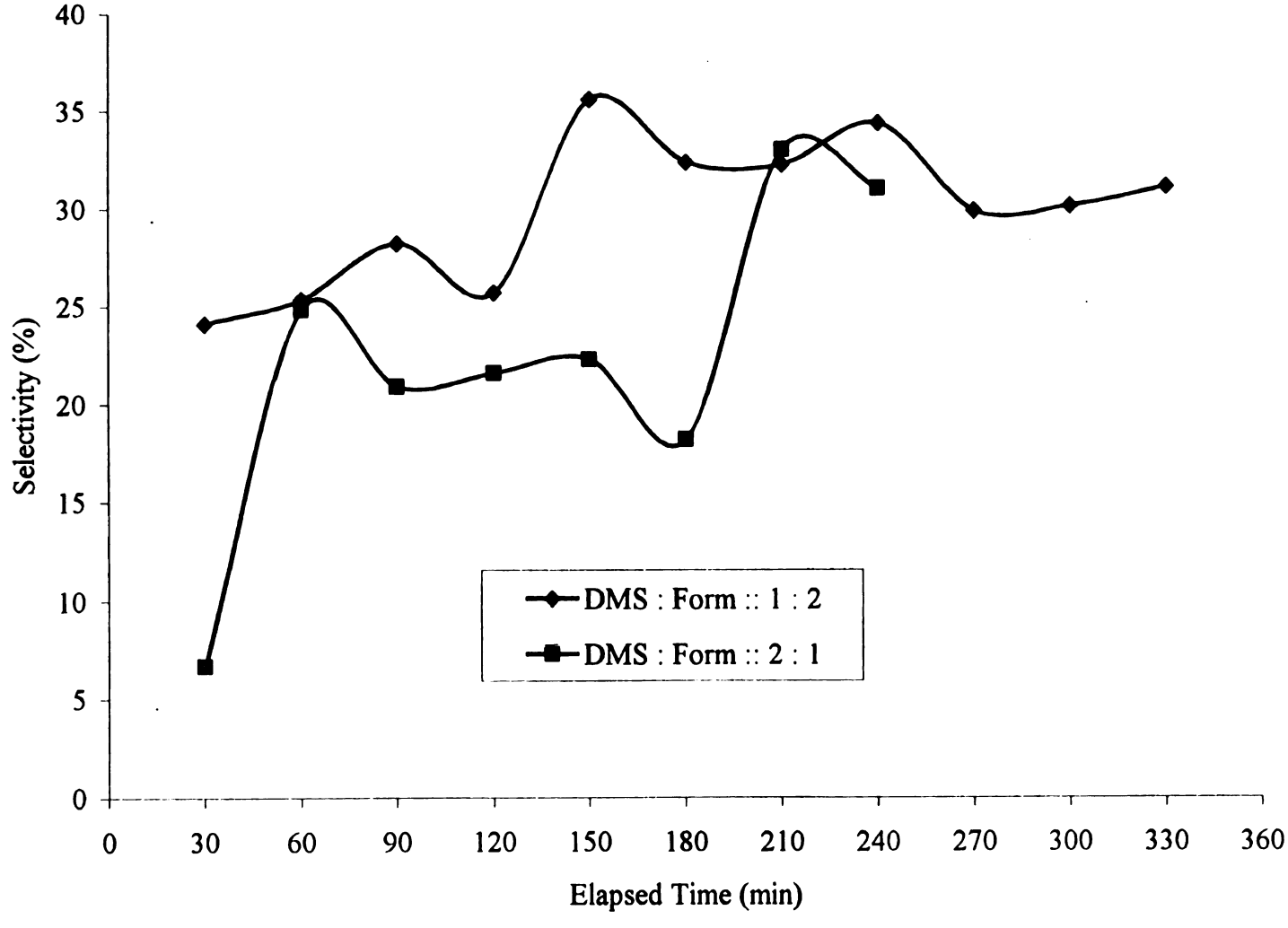


Figure 4.19. Effect of feed molar ratio on selectivity

4.9. Hydrolysis of Products

The raw product exiting the reactor was a mixture of citraconic anhydride, citraconic acid, monomethyl ester of citraconic acid, and dimethyl citraconate. To clearly evaluate product yields and selectivity, it was necessary to hydrolyze the product mix in aqueous H_2SO_4 solution to recover all species as the free acid. Usually, about 20% of the citraconate was in the form of monomethyl or dimethyl ester, so reported yields for unhydrolyzed mixtures were lower than the actual values. In Run 65 (DMS + TO, SA3177), 35% yield of citraconic acid was observed following hydrolysis of the product. Figure 4.20 shows how the yields of citraconic anhydride formation increased after hydrolyzing the product. The first column in Figure 4.20 shows the unhydrolyzed yield of citraconic anhydride. The second column represents the yield of citraconates after hydrolysis but not severe hydrolysis; the sample was prepared in the HPLC mobile phase on the experiment day but was injected after one month. The acidic mobile phase hydrolyzes the reaction product to some extent over time. The yield of citraconates after the severe hydrolysis of the product mixture (refluxing the sample in the mobile phase used in HPLC analysis plus 5-7 drops of concentrate sulfuric acid for twenty-four hours) is represented by the third column of the Figure 4.20.

4.10. Extended Run

The full time scale of catalyst deactivation is shown in an extended time experiment in Figure 4.21 (unhydrolyzed complete results) and Table 4.7 (hydrolyzed results). Trioxane and dimethyl succinate were feed materials and SA3177 alumina was used as the catalyst. It is clear that conversion of succinate and yield of citraconate (hydrolyzed

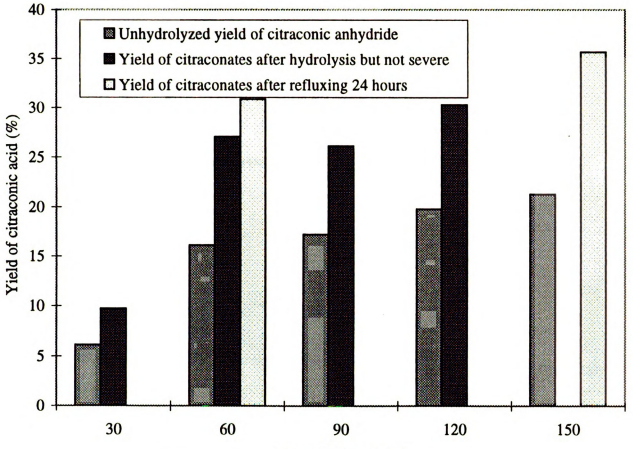


Figure 4.20. Yield of citraconic acid after hydrolysis (SA3177)

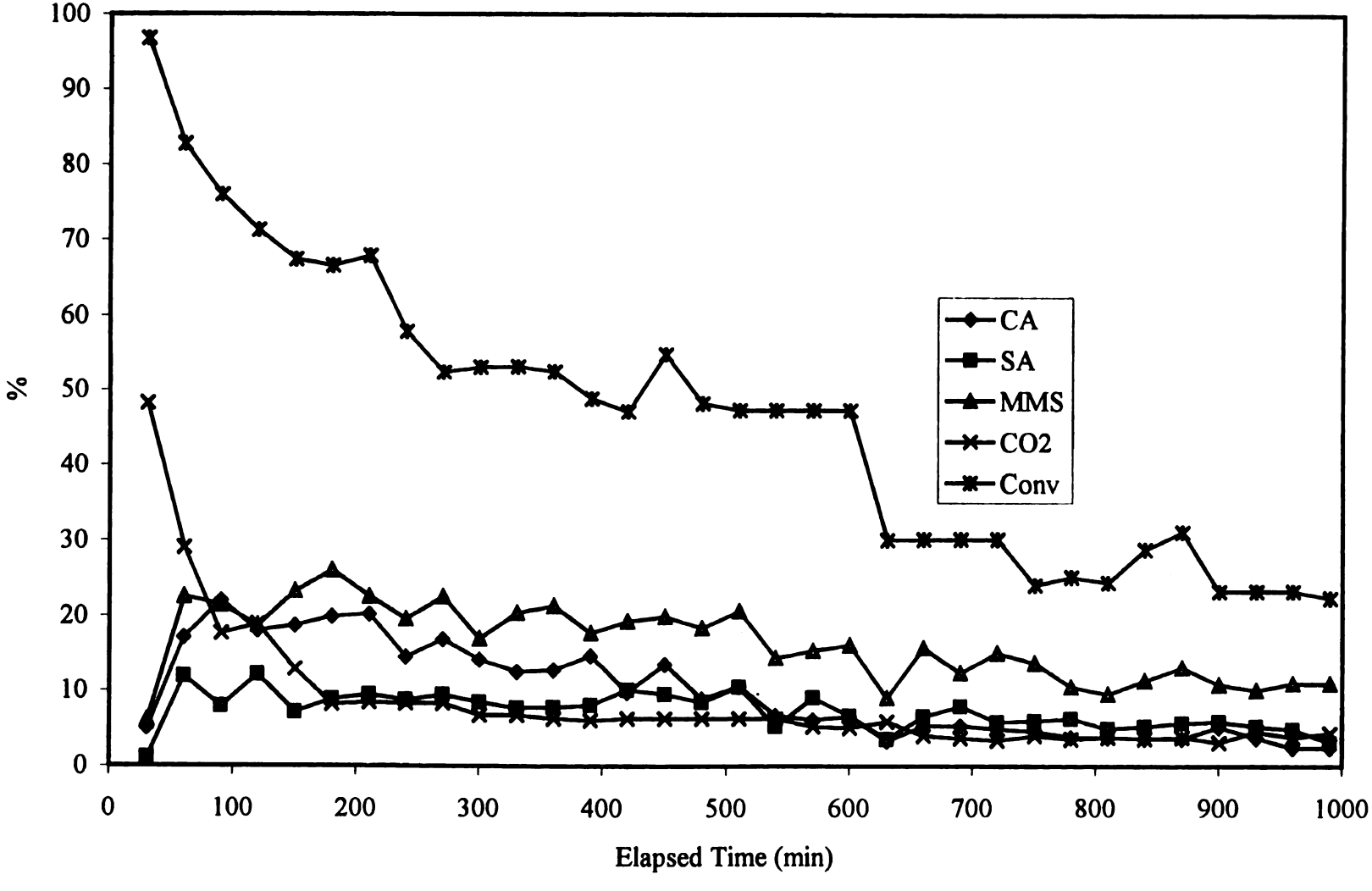


Figure 4.21. Results from extended time experiment before hydrolysis

results) decayed over the 17 hour run. Selectivity in this run, however, was consistently high at between 70% and 80%. The carbon recovery ranges from 80% to 95%, indicating that the experiments were of good quality. It is noteworthy that deficit in carbon recovery results in lower yields and selectivities; if all carbon were accounted for the values of yield and selectivity reported can only increase.

Table 4.7. Results from extended run (17 hrs)[a]

Elapsed Time (min)	Yield of Citraconates (%)	Conversion of Succinates (%)	Selectivity[b] (%)	Yield of CO_2 (%)	Carbon Recovered[c] (%)
90	32.8	45.6	71.9	21.1	85.5
120	30.0	40.2	74.6	22.6	89.1
150	26.0	36.6	71.0	15.4	84.6
180	23.0	30.1	76.4	9.9	81.0
210	22.2	29.0	76.6	10.2	78.0
300	19.6	24.7	79.4	8.1	78.0
420	17.6	20.7	85.0	7.5	95.0
540	7.5	15.5	48.4	8.5	82.0
750	6.0	6.5	92.3	4.8	92.3
960	3.6	7.3	49.3	4.5	87.0

a. Reaction temperature = 380° C; pressure = 60 psi; feed = DMS + 1,3,5-Trioxane (TO) liquid feed flow rate = 0.10 ml/min; molar ratio = 2/3 to 1 (TO to DMS).
b. Selectivity of Citraconates = Yield of Citraconates*100/(Conv of DMS - Yield of SA - Yield of MMS).
c. Carbon recovered (%) = 100-(moles of C in - moles of C out)*100/moles of C in.

4.11. Catalyst Deactivation

The rate of formation of citraconic anhydride in the reactor declines after several hours on line as the catalyst cokes and thus deactivates. In early stages of the reaction, catalysts appeared to be very active, resulting in cracking of succinates and lower yield of desired citraconates. The production of carbon dioxide and carbon monoxide was also very high early in the reaction, and then declined to small values after about 60 min. The yield of citraconic anhydride started to decrease after reaching a maximum in 3rd or 4th product samples depending on the temperature of the reaction (Figure 4.6).

It was obvious from control experiments that coking involved the reactants, succinate and formaldehyde, and the product, citraconic anhydride. After completion of the reaction, catalyst weight gain was observed which also suggests that coking occurred during the reaction. The rate of coking was high early in the reaction, according to weight gain of the catalyst taken at different times during the reaction. Table 4.8 gives the catalyst weight gain and the surface area of the used catalyst taken at different times during the reaction. Interestingly, the surface area of SA3177 increased after the reaction of dimethyl succinate and trioxane. Surface area of SA3177 after the reaction also increased with the increase in the duration of the reaction. The used SA3177 was calcined at 500 °C for five hours and it was found that the surface area of the used SA3177 after calcination was the same as the surface area of the fresh SA3177. As discussed in the following section, fresh SA3177 and regenerated SA3177 both gave identical results at identical conditions. The surface area of zeolites significantly decreased after two hours of the reaction due to coke formation and could not be recovered completely after the calcination in the presence of air at 600 °C for 5-6 hours.

However, the surface areas of alumina-in-house and SA6173 were remained unchanged after the reaction of dimethyl succinate and trioxane.

We postulate that the high surface area carbon on the surface of the SA3177 is produced by the cracking of reactants and products during the reaction, and this is why we observed the increase in the surface area of SA3177 after the reaction. We also infer that the surface area of activated carbon produced by the cracking is not high enough to affect the surface area of high surface area catalyst materials such as SA6173 and alumina-in-house. The decrease in the surface area suggests that the some of micropores in zeolite were likely collapsed by the coke formation and these pores were not subject to regeneration.

Table 4.8. Effect of coking on catalyst weight gain and surface area of the catalyst[1]

Catalyst	Duration of the reaction (hr)	Weight gain (g)	Surface area of fresh catalyst (m^2/g)	Surface area of used catalyst (m^2/g)
SA3177	2.5	1.0	97	-
SA3177	5.5	1.4	97	142
SA3177	17	2.0	97	152
SA6173	5	2.1	220	226
AIH[2]	5	0.8	143	138
Zeolite	2	1.5	454	219[3]

[1]Results are at the base case conditions.
[2]AIH = Alumina-In-House
[3]Surface area of regenerated zeolite was 339 m^2/g.

4.12. Catalyst Regeneration

Following one experiment where the catalyst deactivated, air was passed through the reactor at 500 °C to remove coke residing on the used catalyst. The Riken gas analyzer was showing substantial amount of CO_2 in the outlet during this time, indicating that the catalyst was being regenerated. The above regeneration process was stopped when the CO_2 reading approached zero, i.e., oxidation of coke present on the surface of support was complete. An experiment was then rerun at identical conditions using the regenerated catalyst. Yields of citraconic anhydride and conversion of succinates were identical for both fresh and regenerated catalysts (Table 4.9). This suggests that coke residual on catalyst surface decreases the activity of our catalysts and also indicates that other means of deactivation are less probable.

Table 4.9. Yield of citraconic anhydride[a] before and after the regeneration of catalyst

Elapsed Time (min)	Yield of Citraconic Acid (%)		Yield of CO_2 (%)		Conversion of DES (%)	
	Before	After	Before	After	Before	After
30	7	3	30	61	87	
60	17	17	12	7	81	
90	14	12	20	7	74	
120	11		5		74	

[a]Reaction temperature = 410° C; pressure = 60 psi; feed = DES + 1,3,5-Trioxane; liquid feed flow rate = 0.10 ml/min; molar ratio = 2 to 1 (formaldehyde to DES)

4.13. Summary

The nature of sites on the support played important role in the formation of citraconates in the vapor phase reaction. Neither highly acidic (e.g. CPGs and zeolites) nor basic (talicites, zirconia, and iron oxides) sites on the support favored the reaction. In contrast, alumina, a mildly acidic support in nature, without any salt added showed significant activity for the formation of citraconates from succinates. A maximum 35% yield of all citraconates at 48% conversion of dimethyl succinate over intermediate surface area γ-alumina, SA3177, was observed at the base case conditions and thus a selectivity of 70% of citraconates formation from dimethyl succinate. The highly acidic supports were found to be very active for cracking dialkyl succinate into carbon dioxide and carbon monoxide, but not for condensation to citraconic anhydride. Also, coke forming tendency is directly related to acidity of supports. Coke also formed on silica, zeolites, alumina, and other acidic supports. Alumina supports, in contrast, hold promise because of their ability to take on either acidic or basic character. For all alumina supports, heavy cracking of dialkyl succinates to carbon dioxide and carbon monoxide accompanied the early stages of reaction, indicative of initial high support acidity which is deactivated by coking after exposure to dialkyl succinates. Citraconic anhydride yield stabilizes following acid site deactivation. The basic supports gave little citraconic anhydride but catalyzed the Cannizzaro reaction of formaldehyde to methanol and formic acid. No citraconic anhydride is produced from a base supported on SA3177 because base poisons all acidic sites on SA3177 and makes it basic in character.

We can draw conclusions about the surface acidity/basicity properties required for an active catalyst. First, the active catalyst must have a significant concentration of

mildly or weakly acidic surface sites. Strong acid sites only, such as those found on the zeolite-13X, lead primarily to cracking of dimethyl succinate to carbon dioxide. The second requirement is that the catalyst does not have a high concentration of strong basic sites. These strong basic sites catalyze the Cannizzaro reaction of formaldehyde to form ultimately carbon dioxide and methanol, thus preventing formaldehyde from participating in the desired condensation.

Citraconic anhydride yields are clearly highest at 380 °C; at temperatures above 380 °C secondary reactions and competing reactions, especially the cracking reaction of formaldehyde, predominate over the desired condensation. At lower temperature the conversion of succinates is lower. It is worth noting that selectivity to citraconic anhydride is highest at 350 °C. The reactor pressure does not have any effect on citraconic anhydride yields.

CHAPTER 5

CONDENSATION OF SUCCINIC ANHYDRIDE AND TRIOXANE TO CITRACONIC ANHYDRIDE

5.1. Introduction

The use of succinic anhydride as a feed for the reaction has been investigated in detail. Succinic anhydride (mp = 119 °C) and trioxane (mp = 63 °C), as a source of formaldehyde, are both solids at room temperature. It is essential for the continuous process to feed these solid reactants in the molten phase or to use a solvent to make a feed solution. Section 5.2 enumerates the series of experiments in which succinic anhydride and trioxane were fed into the reactor in the molten phase. Section 5.3 discusses the experiments in which succinic anhydride and trioxane was mixed with methanol and then fed into the reactor.

5.2. Succinic Anhydride and Trioxane in Molten Phase

To accommodate the requirements of feeding succinic anhydride and trioxane, the liquid feed system, including pre-heating of feed, and the product collection system were re-designed. The feed, a molten mixture of succinic anhydride and trioxane, was

maintained at 120°C in a syringe pump before being fed to the reactor. These feed preparation methods are discussed comprehensively in Chapter 2.3.3.

It is already established that the intermediate surface area γ-alumina, SA3177, is an optimal catalyst material for the formation of citraconic anhydride from succinates and formaldehyde. The focal point of this study was to obtain a set of optimal conditions for the desired reaction using γ-alumina, SA3177, as a catalyst material and trioxane and succinic anhydride as a feed. The reactor temperature, liquid feed flow rate, and the carrier gas flow rate were the key parameters investigated.

5.2.1. Reaction Conditions

A series of experiments were carried out in a continuous fixed bed reactor to study the condensation reaction of succinic anhydride and trioxane. The reaction conditions are summarized in Table 5.1.

Succinic anhydride melts at 119 °C and trioxane vaporizes at 120 °C, so the temperature of the feed line and syringe pump barrel was strictly kept at 120 °C. The feed system configuration is discussed in Section 2.5 in detail. Product collection was carried out in collection traps containing dimethyl sulfoxide (DMSO) immersed in boiling water to avert solidification of the unreacted succinic anhydride and paraformaldehyde resulting from polymerization of formaldehyde in the collection trap.

Mostly experiments were carried out for three hours and samples were taken after each 30 minutes. Helium was used as a carrier gas.

Table 5.1. Reaction conditions

S.N.	Condition	Range	Base case condition
1	Reaction temperature (°C)	320 – 380	350
2	Reactor pressure (psi)	60-80	60
3	Pre-heat temperature (°C)	200 – 340	200
4	Feed molar composition (mol%)		
	Succinic anhydride	11.2 - 20.3	20.3
	Trioxane	28.9 - 55.3	40.6
	(formaldehyde equivalent)		
	Helium	33.5 - 56.7	39.1
5	Liquid feed flow rate (ml/min)	0.10 - 0.17	0.10
6	Outlet gas flow rate (ml(STP)/min)	27 – 82	27

5.2.2. Base Case Results over γ-Alumina (SA3177)

The condensation reaction of succinic anhydride and trioxane was studied comprehensively over intermediate surface area alumina (SA3177). Results of a typical experiment are given in Table 5.2; reaction conditions are at the base case values with trioxane as the formaldehyde and SA3177 as the catalyst. The yield of citraconic anhydride was as high as 43% of theoretical, with selectivity ranging from 50-70% except at the very beginning and at the end of the experiment. The yield of carbon dioxide was significantly higher using succinic anhydride than with dimethyl succinate, resulting in lower selectivities. The only other succinate formed was monomethyl

succinate (MMS), resulting from the reaction of succinic anhydride with methanol formed from formaldehyde via the Cannizzaro reaction.

Table 5.2. Results from succinic anhydride and trioxane using SA3177[1]

Elapsed time (min)	Yield of citraconic acid (%)	Conv of succinic anhydride(%)	Selectivity[2] (%)	Yield of MMS (%)	Carbon Recovery[3] (%)	Yield of CO_2[4] (%)	Conv of TO (%)
30	25	84	31	3	46	29	95
60	43	80	58	6	69	23	87
90	43	76	62	6	74	16	87
120	28	41	71	7	96	16	61
150	18	63	32	6	62	14	75

[1]Reaction conditions: Temperature = 380 °C; pressure = 60 psi; feed = succinic anhydride and trioxane (1 to 2/3 molar ratio); liquid feed flow rate = 0.10 ml/min; outlet gas flow rate = 27 ml(STP)/min; pre-heat temperature = 200 °C.
[2]Selectivity of citraconic acid = Yield of citraconic acid * 100/(Conversion of succinic anhydride – Yield of monomethyl ester of succinic acid).
[3]Succinate carbon recovery = 100 – (moles of succinate in – moles of succinate out – moles of citraconic anhydride out)/moles of succinate in.
[4]Yield of carbon dioxide (%) = moles of CO_2 evolved * 100/ (2 * moles of succinic anhydride fed)

The experiment could not be continued for five hours due to reactor plugging. Succinic anhydride has a very high boiling point (269 °C) and solidifies on any cold surface. This led to frequent plugging of the Valco product switching valve and the collection traps during experiments. Excessive cracking of succinic anhydride also caused plugging of the reactor top.

5.2.3. Parametric Studies over γ-Alumina (SA3177)

The effect of various parameters in the condensation reaction was studied in detail using γ-alumina, SA3177, and is discussed in the following sections.

5.2.3.1. Temperature

The condensation reaction of succinic anhydride with trioxane was performed over SA3177 at a series of temperatures of 320 - 380 °C. The effect of temperature on citraconic anhydride yield, succinic anhydride conversion, selectivity of citraconic anhydride, and carbon dioxide yield may be seen in Figure 5.1, Figure 5.2, Figure 5.3, and Figure 5.4, respectively.

The conversion of succinic anhydride was found to be insensitive to the reactor temperature. Conversion of succinic anhydride ranged from 95% after half an hour of reaction to 56% after 2.5 hours of reaction at all temperatures studied. However, yield of citraconic anhydride increased with increasing temperature. The effect of temperature on citraconic anhydride yield was not pronounced from 350 °C to 380 °C. Yield of citraconic anhydride was 43% at 380 °C and 38% at 350 °C after one hour of the reaction. This yield decreased precipitously with decreasing temperature to 18% at 320 °C. A steep decline in yield of citraconic anhydride was noticed after one hour of reaction at higher temperatures (350 °C to 380 °C), but citraconic anhydride yields almost stabilized after one hour of reaction at 320 °C. Yield of carbon dioxide evolved from the reaction due to cracking of succinic anhydride or from the Cannizzaro reaction did not follow any significant trends with temperature.

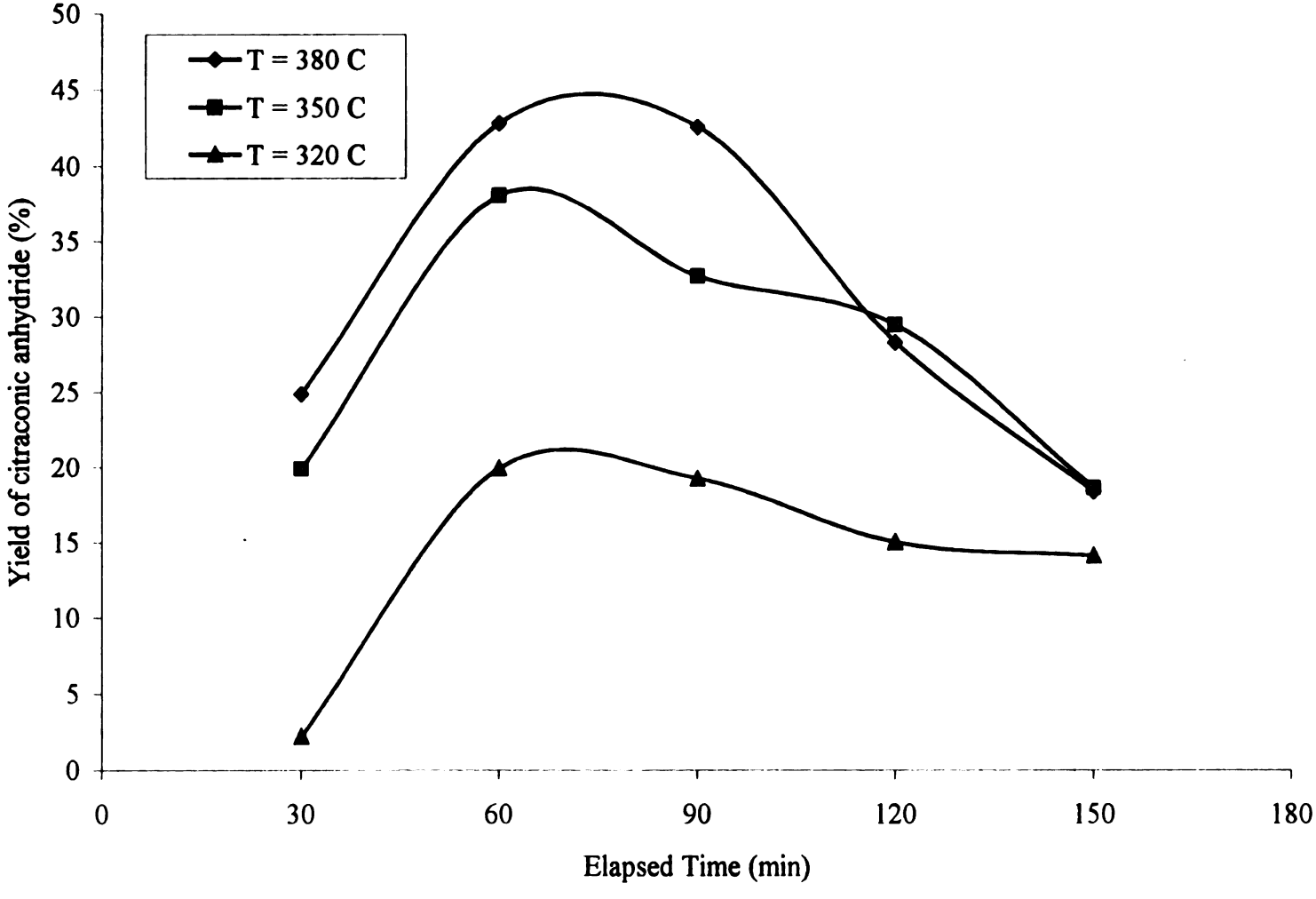


Figure 5.1. Effect of temperature on yield of citraconic anhydride

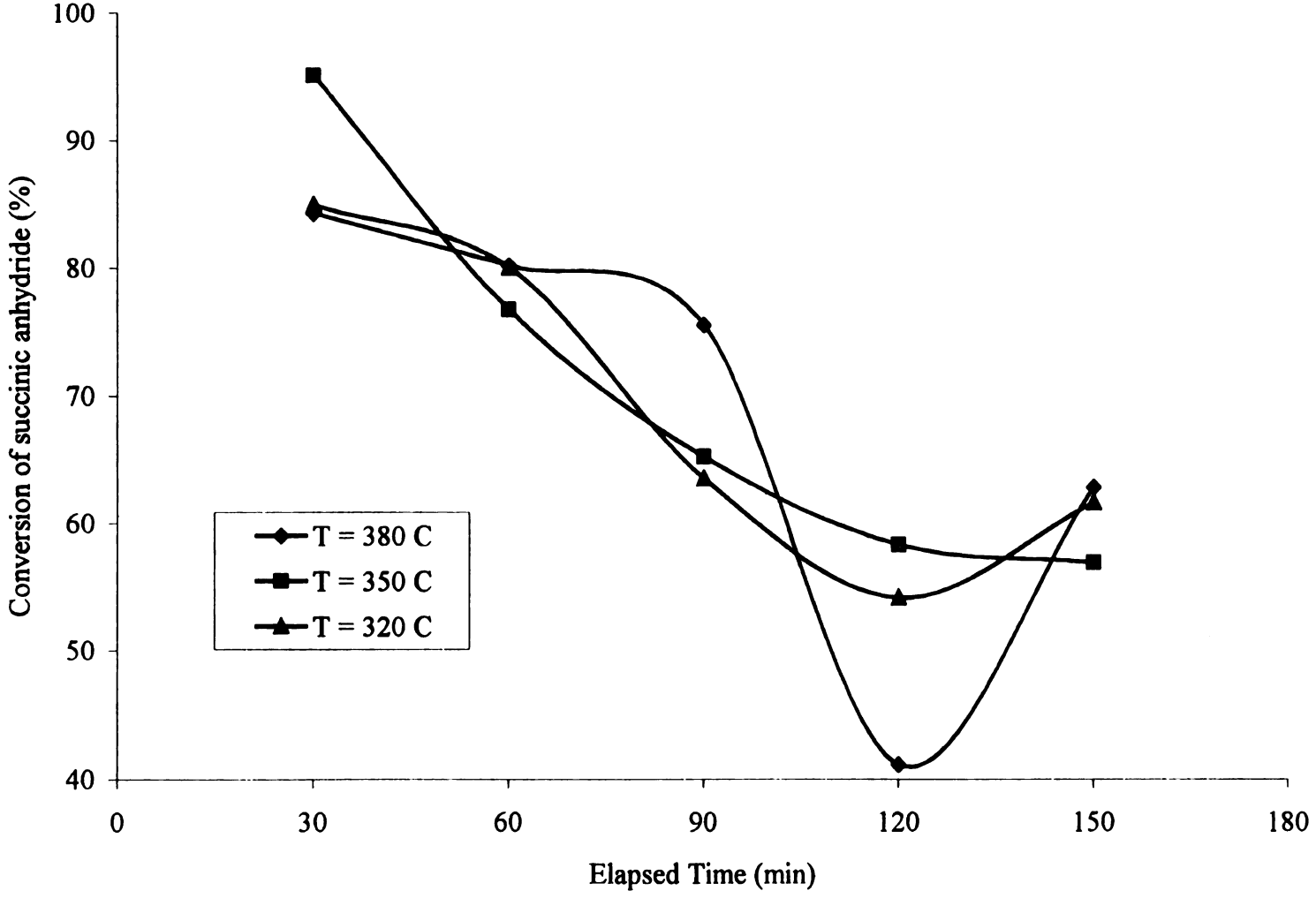


Figure 5.2. Effect of temperature on conversion of succinic anhydride

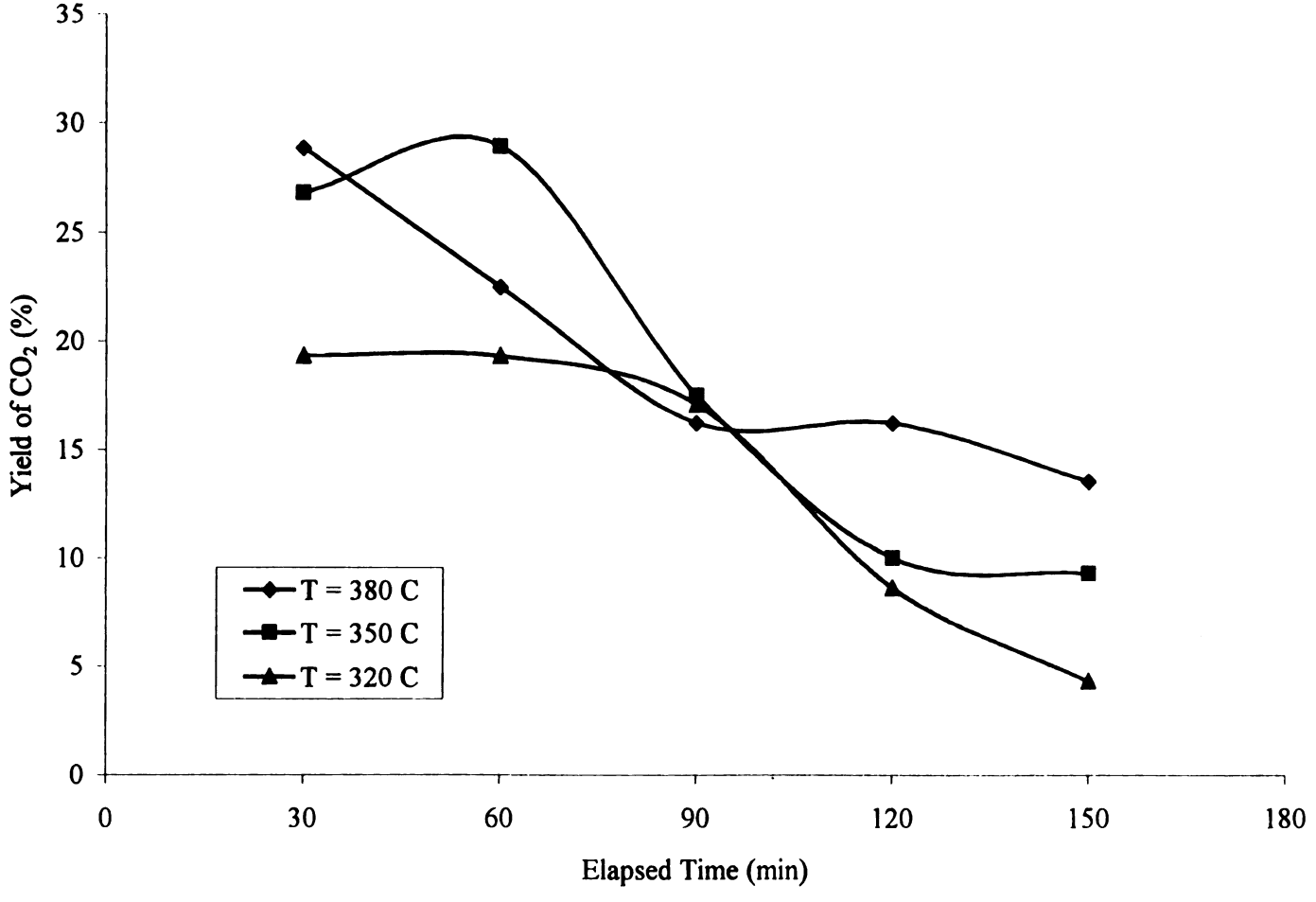


Figure 5.3. Effect of temperature on CO_2 yield

Figure 5.4. Effect of temperature on selectivity of citraconic anhydride formation

5.2.3.2. Feed Molar Ratio

The molar ratio of 5:1 of formaldehyde to succinic anhydride was also examined for the reaction besides the base case molar ratio of 2:1 of formaldehyde to succinic anhydride. Results from the reaction of succinic anhydride and trioxane at different feed molar ratio are given in Table 5.3. There was no significant trend found in results of the condensation reaction of succinic anhydride and formaldehyde from different molar ratios. Succinic anhydride conversion was 87% at 5:1 molar ratio compare to 80% at 2:1 molar ratio after one hour of the reaction. Higher conversion of succinic anhydride at 5:1 resulted in higher yield (26%) of carbon dioxide compare to 23% yield of carbon dioxide at 2:1 molar ratio. However, yield of citraconic anhydride was lower, 32%, at 5:1 molar ratio, whereas the yield was 43% at 2:1 molar ratio. Thus, higher selectivity was observed at 2:1 molar ratio than 5:1. The molar ratio study could not be conducted in detail due to cumbersome process of feeding succinic anhydride and trioxane in the molten phase.

5.2.3.3. Liquid Feed Flow Rate

The condensation reaction of succinic anhydride and trioxane was carried out at liquid feed flow rates of 0.10 ml/min (6ml/hr) and 0.17 ml/min (10 ml/hr), keeping other parameters unchanged. Figure 5.5, Figure 5.6, Figure 5.7, and Figure 5.8 present yield of citraconic anhydride, conversion of succinic anhydride, selectivity of citraconic anhydride, and the yield of carbon dioxide evolved from the reaction, respectively, at the two different liquid feed flow rates.

Table 5.3. Results at different feed molar ratios[1]

Elapsed time (min)	Yield of citraconic anhydride (%)		Conversion of succinic anhydride (%)		Yield of CO_2 (%)[3]	
	2:1[2]	5:1[2]	2:1[2]	5:1[2]	2:1[2]	5:1[2]
30	25	32	84	83	29	34
60	43	26	80	87	23	26
90	43	34	76	80	16	31
120	28		41		16	
150	18		62		14	

[1]Reaction conditions: Temperature = 380 °C; pressure = 60 psi; feed = succinic anhydride and trioxane; liquid feed flow rate = 0.10 ml/min; outlet gas flow rate = 27 ml(STP)/min; pre-heat temperature = 200 °C.
[2]Feed molar ratio: succinic anhydride to formaldehyde
[3]Yield of carbon dioxide (%) = moles of CO_2 evolved * 100/ (2 * moles of succinic anhydride fed)

Conversion of succinic anhydride was significantly affected by increasing liquid feed flow rate, which is expected according to simple reaction kinetics. The conversion of succinic anhydride at higher liquid feed flow rate (10 ml/hr) was always ~20% less than the conversion at lower liquid feed flow rate (6 ml/hr). The lower conversion of succinic anhydride at 10 ml/hr was reflected in lower yield of citraconic anhydride and carbon dioxide at that flow rate. Yields of carbon dioxide evolved from the reaction also follows succinic anhydride conversion trends. There was always a 6-percentage points lower yield of carbon dioxide at higher liquid feed flow rate than at lower liquid feed flow rate. Selectivities for citraconic anhydride formation from succinic anhydride were higher at the higher liquid feed flow rate of 10 ml/hr.

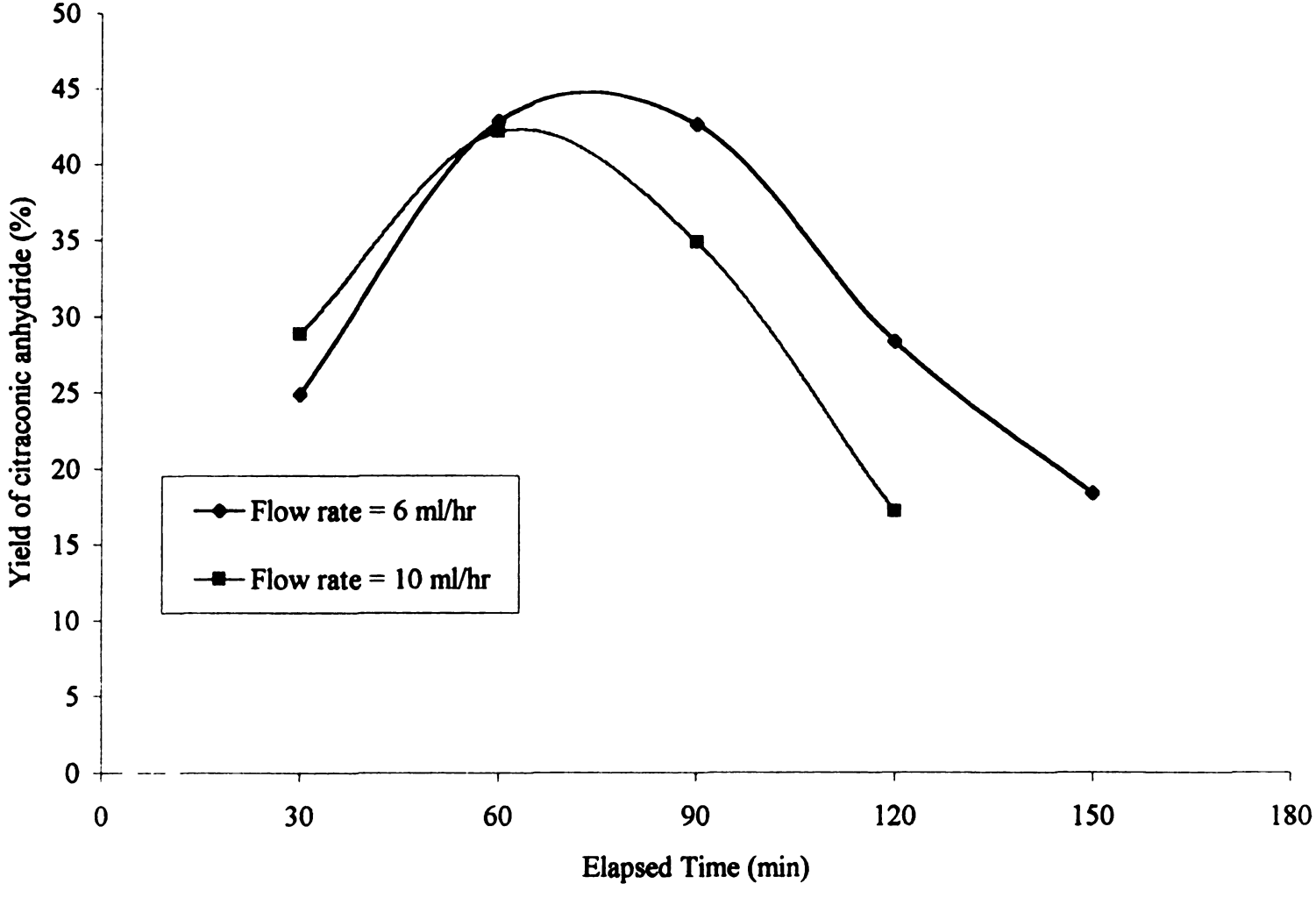


Figure 5.5. Effect of liquid feed flow rate on yield of citraconic anhydride

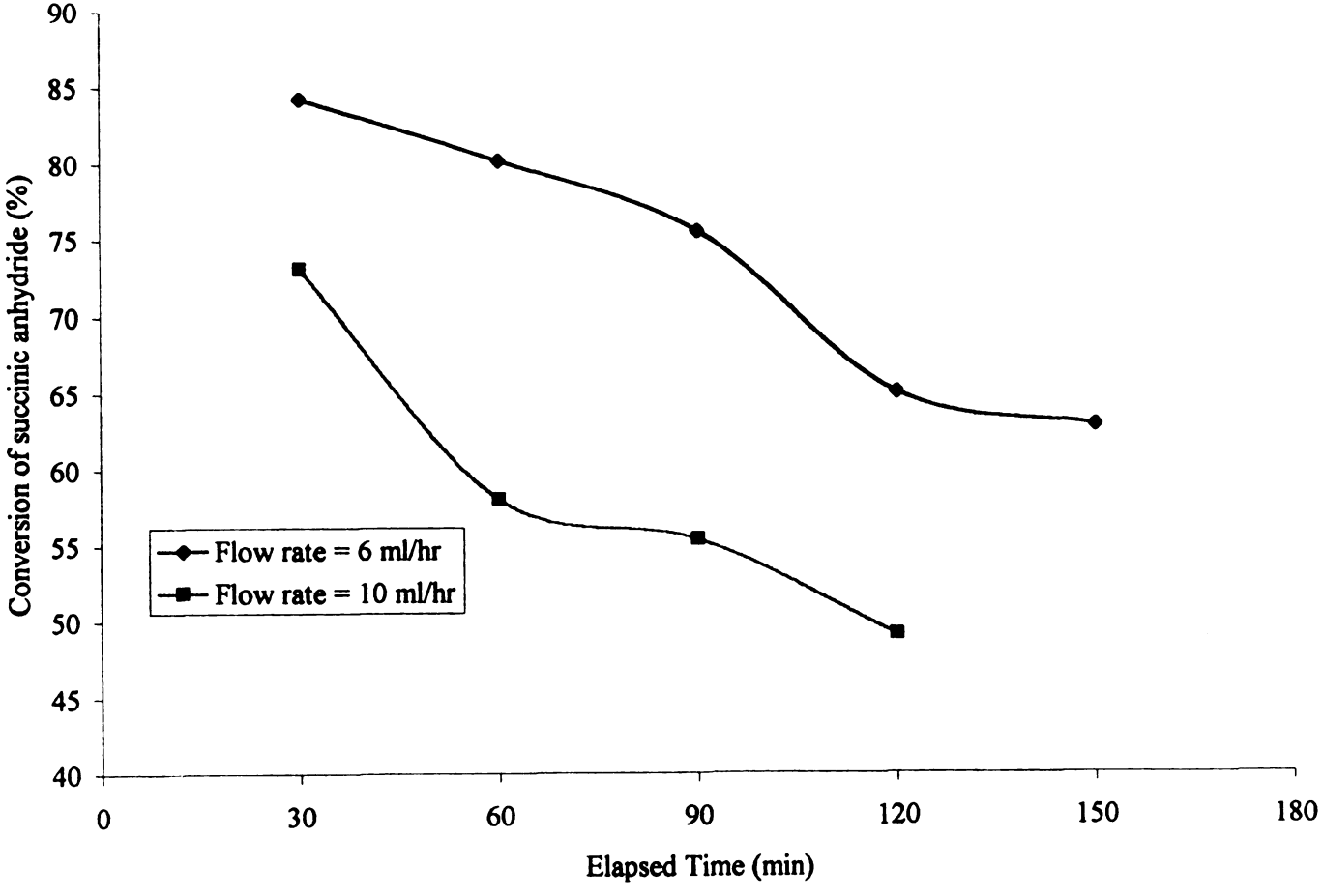


Figure 5.6. Effect of liquid feed flow rate on conversion of succinic anhydride

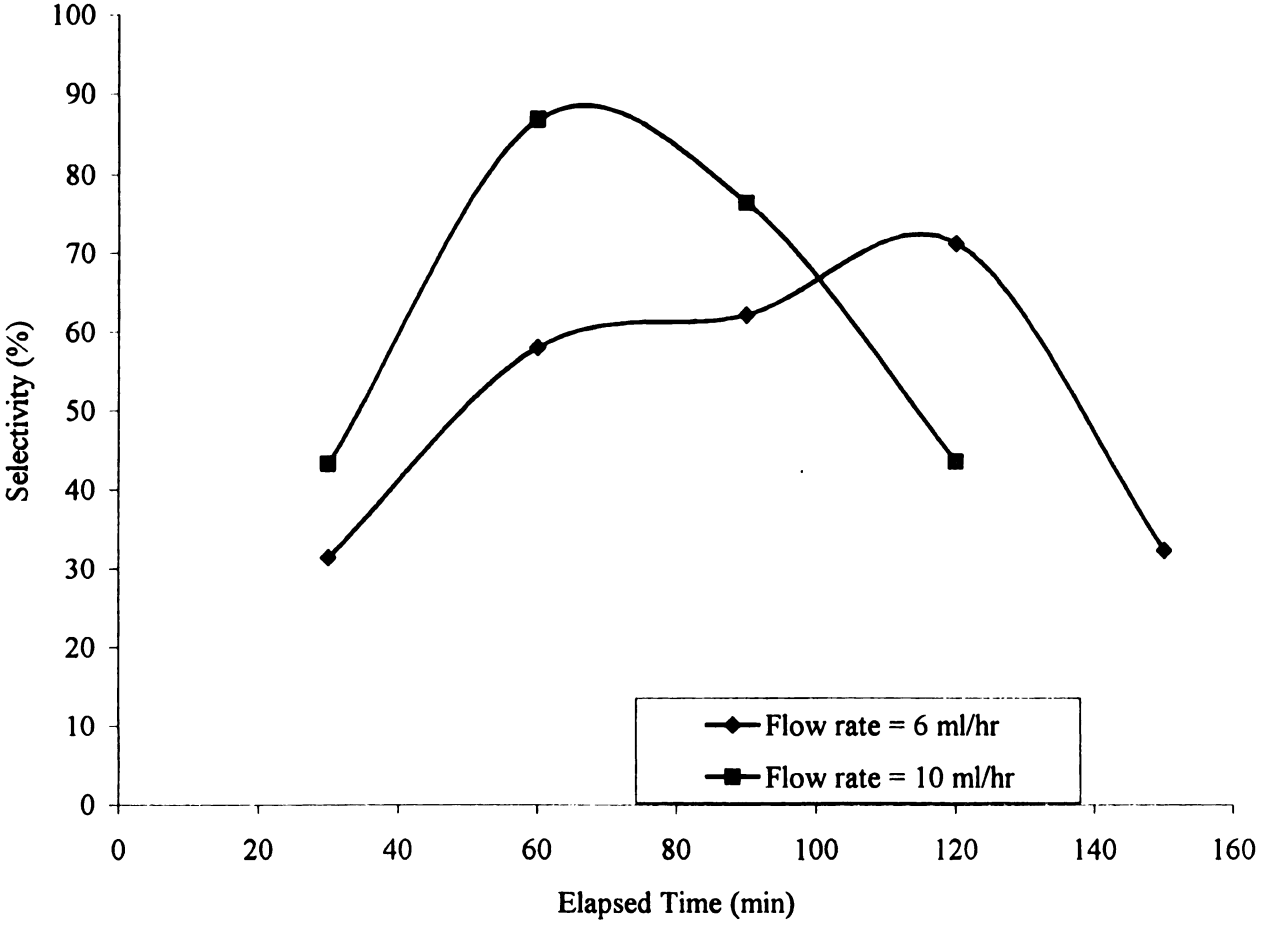


Figure 5.7. Effect of liquid feed flow rate on selectivity of citracinic anhydride formation

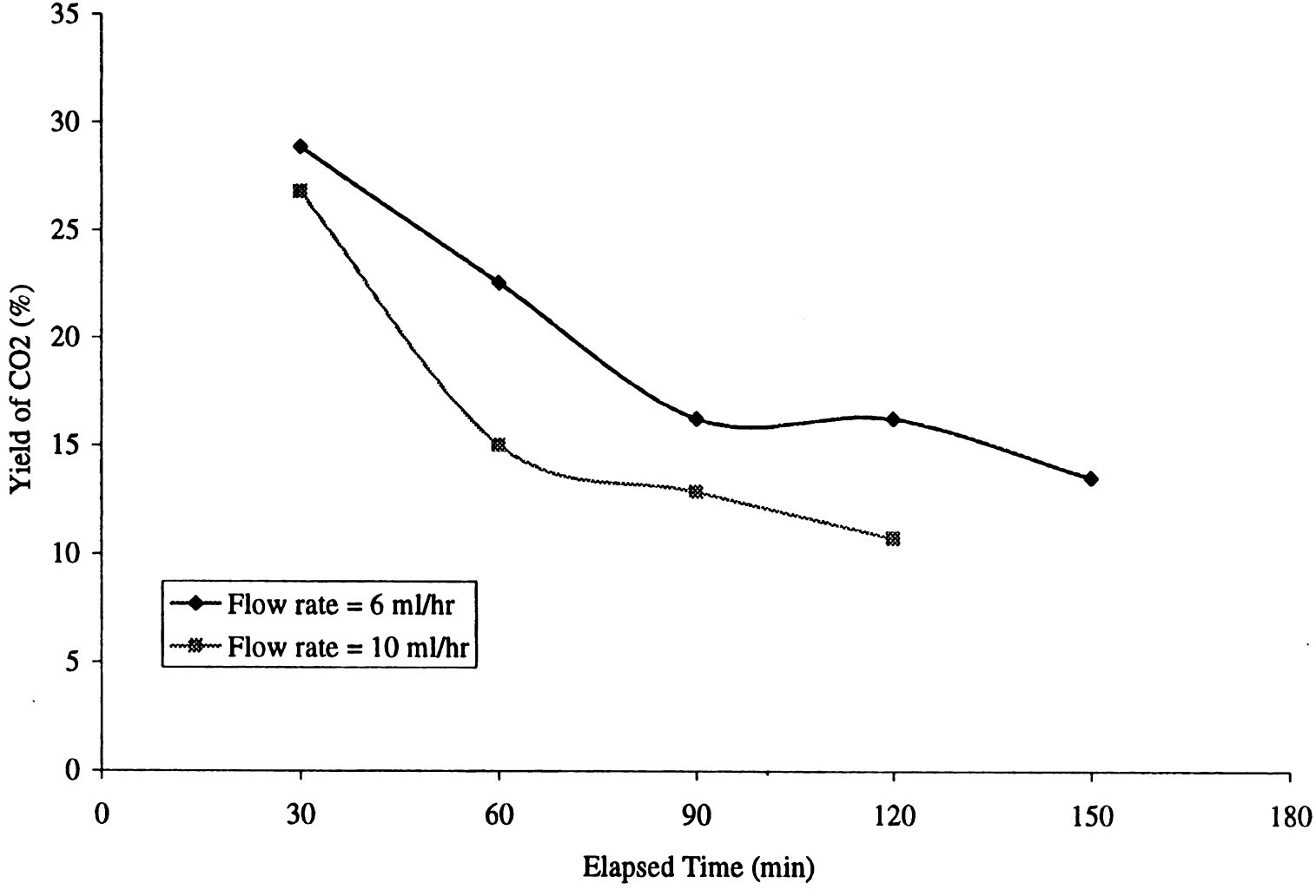


Figure 5.8. Effect of liquid feed flow rate on CO2 yield

5.2.3.4. Carrier Gas Flow Rate

The flow rate of helium was also varied in some experiments to see its effect on yield of citraconic anhydride and conversion of succinic anhydride from the reaction of succinic anhydride and trioxane over SA3177. In the first set of experiments, reactions were carried out at the helium flow rates of 27 ml(STP)/min and 55 ml(STP)/min, keeping the reactor temperature of 380 °C and liquid feed flow rate of 0.10 ml/min (6 ml/hr). In the other set of experiments, the helium flow rate was varied from 55 ml(STP)/min to 82 ml(STP)/min, whereas the reaction temperature was kept at 350 °C and the liquid feed flow rate was fixed at 0.167 ml/min (10 ml/hr). Table 5.4 gives the results at different helium flow rates.

Although the first set of experiments did not give any conclusive results, it is clear from the second set of data that conversion of succinic anhydride at higher helium flow rate (82 ml(STP)/min) was significantly lower than the conversion at lower helium flow rate (55 ml(STP)/min). The yield of citraconic anhydride was also lower at higher helium flow rate in the same proportion as the conversion of succinic anhydride and, thus, the selectivity remained the same at both helium flow rates employed for the reaction.

Table 5.4. Effect of outlet helium flow rate on results[1]

Elapsed Time (min)	Yield of citraconic anhydride (%)				Conversion of succinic anhydride (%)			
	T = 350 °C		T = 380 °C		T = 350 °C		T = 380 °C	
	55 ml/min	82 ml/min	27 ml/min	55 ml/min	55 ml/min	82 ml/min	27 ml/min	55 ml/min
30	30	27	25	17	95	80	84	95
60	38	30	43	42	77	61	80	74
90	33	27	43		65	54	76	
120	30		28		58		41	
150	19		18		57		62	

[1]Reaction conditions: Pressure = 60 psi; feed = succinic anhydride and trioxane (1 to 2/3 molar ratio); liquid feed flow rate = 0.10 ml/min; pre-heat temperature = 200 °C.

5.2.3.5. Longer Reactor Catalyst Bed

The condensation reaction of succinic anhydride with trioxane was also carried out with a longer reactor catalyst bed (11 g catalyst weight vs. 5.2 g catalyst weight) to see the effects of increasing weight hourly space velocity (WHSV) on the desired results. The diameter of the reactor was the same. The experiment with the longer reactor was conducted at the base case conditions and results from the longer reactor are compared with the regular reactor in Table 5.5.

A higher conversion of succinic anhydride and a significantly lower yield of citraconic anhydride, coupled with the almost doubled yield of carbon dioxide using the longer reactor, suggests that the extra length of the reactor bed contributed to cracking of citraconates and succinates.

Table 5.5. Comparison of results from longer reactor with regular reactor[1]

Elapsed Time (min)	Yield of citraconic anhydride (%)		Conversion of succinic anhydride (%)		Yield of CO_2 (%)	
	11.0 g[2]	5.2 g[2]	11.0 g[2]	5.2 g[2]	11.0 g[2]	5.2 g[2]
30	5	30	99	95	54	27
60	21	38	86	77	43	29
90	20	33	85	65	47	18
120		30		58		10
150		19		57		9

[1]Reaction conditions: Temperature = 350 °C; pressure = 60 psi; feed = succinic anhydride and trioxane (1 to 2/3 molar ratio); liquid feed flow rate = 0.10 ml/min; outlet gas flow rate = 27 ml(STP)/min; pre-heat temperature = 200 °C.
[2]Catalyst weight taken into the reactor bed

5.2.3.6. Hydrolysis

Hydrolysis of the reaction products from the reaction of succinic anhydride and trioxane was carried out to convert all citraconates to citraconic acid and succinates to succinic acid. Results from succinic anhydride and trioxane after and before hydrolysis are shown in Table 5.6. Yield of citraconates and the conversion of succinates were not changed much after hydrolysis of the reaction products from the reaction of succinic anhydride and trioxane over SA3177. Again, this is because no methanol is produced in the reaction to facilitate ester formation.

Table 5.6. Results[1] from succinic anhydride and trioxane after and before hydrolysis

Elapsed Time (min)	Yield of Citraconates (%)		Conv of succinates (%)	
	Before	After	Before	After
60	43	43	73	74
90	43	44	67	67

[1]Reaction conditions: Temperature = 380 °C; pressure = 60 psi; feed = succinic anhydride and trioxane (1 to 2/3 molar ratio); liquid feed flow rate = 0.10 ml/min; outlet gas flow rate = 27 ml(STP)/min; pre-heat temperature = 200 °C.

5.2.3.7. Deactivation Studies

The rate of catalyst deactivation was very high with succinic anhydride and trioxane feed compared to dimethyl succinate and trioxane feed. The deactivation of catalyst was caused by coking on the surface of the catalyst resulting from cracking of reactants and products at the reaction conditions employed. Higher yields of carbon dioxide evolved from the reaction were observed due to excessive cracking. The yield of citraconic anhydride dropped drastically to lower values after peaking in the 2nd and 3rd product samples. The conversion of succinic anhydride also decreased sharply over time. This is in contrast to dimethyl succinate as the feed, where the yield of citraconic anhydride and the conversion of dimethyl succinate almost stabilized after two hours of reaction. The lower conversion and thermal decomposition of succinic anhydride also caused the plugging problem in the reactor downstream and difficulties in product analysis. The larger portion of unreacted succinic anhydride, coupled with paraformaldehyde formation resulting from polymerization of formaldehyde, solidified inside the tiny ports of the switching valve or inside the tubing at any cold spot and caused the reactor-plugging problem. The catalyst weight gain was 2.1 g after three

hours of reaction of succinic anhydride and trioxane, whereas the catalyst gain was 1.5 g after five hours of the reaction of dimethyl succinate and trioxane. As discussed earlier, coking was observed from succinic anhydride feed even with an inactive material, glass beads. It was obvious from control experiments that coking involved the reactants, succinate and formaldehyde, and the product, citraconic anhydride.

5.2.4. Other Catalysts Used

Intermediate surface area alumina, SA3177, was found to be the best catalyst material for this condensation reaction, so it was primarily used for studies with succinic anhydride and trioxane. But, some experiments were also carried out with catalyst material having different catalyst characteristics than SA3177 to confirm our postulates about particular characteristics. For example, a reaction was conducted with a basic support, iron oxide (Fe_2O_3), to confirm the postulate that a base catalyst without having any acidic sites does not work for the desired reaction. Similarly, the empty reactor and glass beads were used to test the thermal stability of succinic anhydride and trioxane over a material that has very low surface area and acidic/basic site concentration.

5.2.4.1. Empty Reactor

Succinic anhydride and trioxane were passed through the empty reactor to see any reactivity of reactants at the reaction conditions in the absence of any catalyst material. Although no yield of citraconic anhydride was observed, 15% conversion of succinic anhydride was noticed. It was inferred from the empty reactor reaction that the condensation reaction of succinic anhydride and trioxane to form citraconic anhydride is

not a simple thermal reaction and succinic anhydride is not thermally stable at elevated temperatures.

5.2.4.2. Glass Beads

Glass beads, 0.5 mm diameter (Quackenbush Company, Inc.), discussed in Section 4.5.1 and Section 6.5.7, were placed in the reactor to characterize the thermal stability of succinic anhydride and trioxane over an inert material. A 13% yield of citraconic anhydride at 78% conversion of succinic anhydride over glass beads was observed with 60% product recovery. High yield of carbon dioxide, 54%, was also noticed due to excessive cracking of reactants. The run with succinic anhydride and trioxane over glass beads was repeated to verify reproducibility.

Succinic anhydride decomposes like other acid anhydrides at elevated temperature (<320 °C) (9-13). The decomposition of succinic anhydride produces a coating of activated carbon on the glass bead surface. We postulate that the activated carbon produced by cracking of succinic anhydride provided a platform for the condensation reaction of succinic anhydride and trioxane to form citraconic anhydride and this is why we observed citraconic anhydride in the product.

Interestingly, no monomethyl ester of succinic acid was seen in the product. Monomethyl ester of succinic acid is formed from the reaction of succinic anhydride with methanol, where methanol is generated from the Cannizzaro reaction of formaldehyde in the presence of basic sites on the catalyst. But, the Cannizzaro reaction does not occur over glass beads. First, the basic or acidic sites required for the Cannizzaro reaction are not present on inert glass bead surface. The occurrence of the Cannizzaro reaction has

been seen over activated carbon which does contain acidic and basic sites, from the reaction of dimethyl succinate and Formalin (see Section 6.5.6). Second, not enough water, which is also required for the Cannizzaro reaction, is available, because no water was fed to the reactor. Some water maybe produced from the formation of citraconic anhydride from succinic anhydride and formaldehyde, but that is likely consumed by formaldehyde to polymerize into paraformaldehyde instead of facilitating the Cannizzaro reaction.

5.2.4.3. Iron Oxide

Reactions of succinic anhydride with trioxane were also performed over iron oxide (Fe_2O_3) (Aldrich). Because glass beads gave 13% citraconic anhydride from succinic anhydride, it was decided to test iron oxide, a very basic catalyst without any acidic characteristics, for the desired reaction. Complete conversion of succinic anhydride was observed over iron oxide (compared to 30% conversion of dimethyl succinate at similar conditions). Complete conversion of succinic anhydride over ferric oxide suggests that succinic anhydride is not stable at elevated temperature in the presence of basic material. The carbon dioxide meter was out of range in the reaction of succinic anhydride with trioxane. Formaldehyde was entirely converted into methanol and carbon dioxide via the Cannizzaro reaction.

5.3. Succinic Anhydride and Trioxane in Solution

Succinic anhydride is a good feed material for the reaction, as the highest yields of citraconates were achieved with very good selectivities. There were several problems

associated with the use of succinic anhydride as a feed material, e.g., faster catalyst deactivation, reactor tube plugging, and difficulties in product and reactant handling. To attempt to get rid of these problems caused by succinic anhydride as the feed, succinic anhydride and trioxane were mixed with methanol to make a feed solution of monomethyl succinate and trioxane.

5.3.1. Reaction Conditions

Reaction conditions employed for monomethyl succinate and trioxane in methanol were also readjusted due to the nature of the feed. Reactants became very dilute because of the excessive amount of methanol needed to solubilize them in methanol. The liquid feed flow rate was therefore increased to maintain the same succinate feed rate as with other feeds. Product samples were taken every 15 minutes and only every other sample was analyzed. Helium was used as a carrier gas, but some experiments were carried out without any helium. The product collection traps were immersed in cold water to collect methanol. The standard reaction conditions are summarized in Table 5.7.

5.3.2. Base Case Results

Results from the condensation reaction of monomethyl succinate (MMS) and formaldehyde in methanol before hydrolysis are given in Table 5.8 along with those over KH_2PO_4/SA3177 discussed in the next section; succinate conversion was lower with this feed mixture and conditions but selectivity (citraconates formed/succinate converted) was better at 75-80%. After hydrolysis, a maximum of 31% yield of citraconates after was observed at 40% conversion of succinates. Dimethyl succinate and succinic acid were

Table 5.7. Reaction conditions

S.N.	Condition	Value
1	Reaction temperature (°C)	350
2	Reactor pressure (psi)	60
3	Pre-heat temperature (°C)	200
4	Feed molar composition (mol%)	
	Monomethyl succinate	9.7
	Trioxane	18.8
	(formaldehyde equivalent)	
	Methanol	60.0
	Helium	11.5
5	Liquid feed flow rate (ml/min)	0.3
6	Carrier gas flow rate (ml(STP)/min)	20

also found in products. The dimethyl succinate was formed from the esterification of monomethyl succinate. The catalyst performance was very consistent after the first 30 minutes of the reaction and the product composition in each sample collected was reproducible at that time. 70% conversion of monomethyl succinate, 23% yield of citraconic anhydride, 30% yield of dimethyl succinate, and 11% yield of succinic acid were observed consistently after the first 30 minutes of the reaction.

Table 5.8. Results from MMS and trioxane feed in methanol[1]

Elapsed Time (min)	Yield of CA (%)		Conv of MMS (%)		Yield of DMS (%)		Yield of SA (%)		Yield of CO_2 (%)	
	A[2]	B[3]	A	B	A	B	A	B	A	B
30	20	6	72	94	23	55	5	0	16	4
60	26	5	70	86	29	78	10	0	10	7
90	23	3	70	93	30	74	11	0	6	5
120	22		70		25		11		8	

[1]Reaction conditions: Temperature = 350 °C; pressure = 60 psi; feed = monomethyl succinate and trioxane (1 to 2/3 molar ratio) in methanol; liquid feed flow rate = 0.30 ml/min; outlet gas flow rate = 20 ml(STP)/min; pre-heat temperature = 200 °C.
[2]A = Catalyst is unsupported SA3177
[3]B = Catalyst is 0.15 mmol KH_2PO_4/g SA3177

In one another separate experiment, only monomethyl succinate in methanol was fed into the reactor at the reaction conditions described above. Yields of dimethyl succinate and succinic acid were 54% and 6% respectively at 64% conversion of monomethyl succinate. The yield of carbon dioxide was always less than 1% and, hence, very little coking was found on the catalyst after the reaction. 90% of feed by mass was recovered in the product after the reaction. Some methanol lost during the reaction in the form of dimethyl ether, which passed through the product trap.

5.3.2.1. Effect of Temperature

The effect of temperature on the formation of citraconic anhydride from monomethyl succinate and trioxane over SA3177 was also studied. Reactions were performed at 350 °C and 380 °C keeping all other reaction conditions unchanged. Yield

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Table 5.9.

Elapsed Time (min)	Y H m
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120	

[1]Reaction con
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of citraconic anhydride and conversion of monomethyl succinate were insensitive to temperature.

5.3.2.2. Effect of Carrier Gas

Conversion of monomethyl succinate and trioxane in methanol was also carried out without using helium as a carrier gas to increase concentrations of reactants at the reactor inlet. Complete results with and without helium as a carrier gas are presented in Table 5.9. After hydrolysis, a maximum 22% yield of citrconates at 30% conversion of succinates after hydrolysis was achieved at the base case conditions without any carrier gas, compared to a maximum of 31% yield of citraconates at 40% conversion of succinates with helium as a carrier gas. Higher yields of dimethyl succinate and succinic

Table 5.9. Effect of carrier gas on results (before hydrolysis)[1]

Elapsed Time (min)	Yield of CA (%)		Conv of MMS (%)		Yield of DMS (%)		Yield of SA (%)	
	He@20 ml/min	No He carrier	He@20 ml/min	No He carrier	He@20 ml/min	No He carrier	He@20 ml/min	No He carrier
30	20	16	72	78	23	47	5	11
60	26	18	70	78	29	45	10	13
90	23	16	70	83	30	54	11	15
120	22	18	70	84	25	52	11	13

[1]Reaction conditions: Temperature = 350 °C; pressure = 60 psi; feed = monomethyl succinate and trioxane (1 to 2/3 molar ratio) in methanol; liquid feed flow rate = 0.30 ml/min; pre-heat temperature = 200 °C.

acid were observed with no carrier gas, compared to yields of dimethyl succinate and succinic acid with carrier gas; this is likely because of longer residence time.

5.3.2.3. Hydrolysis

The raw product coming from the reactor was also hydrolyzed to quantify all citraconates present in the product. Succinates were converted into succinic acid in the hydrolysis. Table 5.10 shows results where all yields, conversions, and selectivities are based on hydrolyzed results. The yield of citraconates after hydrolysis was usually increased by 20% of unhydrolyzed yields.

Table 5.10. Results before and after hydrolysis of product[1]

Elapsed Time (min)	Yield of citraconates (%)		Conv of Succinates (%)		Selectivity[2] (%)
	Before	After	Before	After	
30	20	25	45	46	54
60	26	31	31	40	78
90	23	25	30	33	76

[1]Reaction conditions: Temperature = 350 °C; pressure = 60 psi; feed = monomethyl succinate and trioxane (1 to 2/3 molar ratio) in methanol; liquid feed flow rate = 0.30 ml/min; outlet gas flow rate = 20 ml(STP)/min; pre-heat temperature = 200 °C.
[2]Selectivity is based on hydrolyzed products.

5.3.2.4. Deactivation Studies

Coking of the catalyst was observed from monomethyl succinate and trioxane feed in methanol, but not at a significant level as with succinic anhydride feed. The catalyst weight gain was only 0.66 g after three hours of reaction from monomethyl succinate and

trioxane feed, whereas the catalyst weight gain was 2.1 g after three hours of reaction of succinic anhydride and trioxane feed. First, monomethyl succinate does not have thermal stability problems as does succinic anhydride at elevated temperatures. Second, a very dilute solution of monomethyl succinate in methanol was used.

Catalyst performance was very steady with monomethyl succinate as a feed. The conversion of monomethyl succinate and yield of citraconic anhydride stabilized after fifteen minutes of reaction for the rest of the reaction time

5.3.3. Other Catalyst Used

Most of the experiments with monomethyl succinate feed were carried out with intermediate surface area alumina, SA3177, but high surface area alumina, SA6173, high surface area silica, CPG-75, and KH_2PO_4 supported on SA3177 were also employed for the reaction. Results from different catalysts are discussed in the following sections.

5.3.3.1. KH_2PO_4/SA3177

Detailed results before hydrolysis from KH_2PO_4 supported on SA3177 are given in Table 5.8. Conversion of monomethyl succinate and trioxane was also performed over KH_2PO_4 supported on SA3177. KH_2PO_4 was used here to poison strong acidic sites on alumina, which are responsible for coking on the catalyst. Loading of 0.15 mmol KH_2PO_4/g SA3177 was taken for the reaction because it corresponds to the density of strong acidic sites on SA3177. A maximum 5% yield of citraconic anhydride was obtained over KH_2PO_4 supported on SA3177 from the reaction of monomethyl succinate and formaldehyde in methanol. Higher conversion of monomethyl succinate (86%) was

observed over KH_2PO_4 supported on SA3177, compared to 70% conversion with SA3177 alone. Interestingly, KH_2PO_4 supported on SA3177 overwhelmingly catalyzed the esterification of monomethyl succinate to dimethyl succinate. A higher yield (78%) of dimethyl succinate was obtained, compared to 30% yield of dimethyl succinate from SA3177 alone. The absence of succinic acid in the product suggests that de-esterification of monomethyl succinate was completely halted due to the absence of acidic sites on the catalyst. Amount of carbon dioxide evolved from the reaction due to cracking was also very low over KH_2PO_4 supported on SA3177.

5.3.3.2. CPG-75

In the early part of this study, silica (CPG) was comprehensively studied for the reaction of diethyl succinate and trioxane, but no experiment was carried out with unsupported high surface area silica (CPG-75). High loading of KH_2PO_4 (2 mmol/g) over CPG-75 was employed for the reaction of diethyl succinate and trioxane and the yield of citraconic anhydride was less than one percent at higher conversion of dimethyl succinate. It was well established that a base loading on any active catalyst kills the desired reaction, so it was decided to conduct one experiment of monomethyl succinate and trioxane without loading any bases on a high surface area silica, CPG-75.

The reaction of monomethyl succinate and trioxane in methanol solvent over unsupported CPG-75 was conducted at 350 °C and 400 °C. No citraconic anhydride was formed at 350 °C, and 3% yield of citraconic anhydride was achieved at 400 °C. Esterification of monomethyl succinate was dominant over CPG-75 and yields of dimethyl succinate were 79% and 60% at 350 °C and 400 °C, respectively. CPG-75 gave

monomethyl succinate conversions of 91% at 350 °C and 92% at 400 °C. No succinic acid was formed at any temperature used for the reaction.

5.3.3.3. SA6175

High surface area alumina, SA6175, (235 m^2/g) was also employed for the reaction of monomethyl succinate and trioxane at the base case conditions. A maximum citraconate yield of 18% after hydrolysis was obtained at 30% conversion of succinates. Coking was also observed on the catalyst surface.

5.4. Summary

The use of succinic anhydride and trioxane as a feed for the formation of citraconic anhydride over various catalysts was studied. Succinic anhydride and trioxane were fed into the reactor in the molten phase or as a feed solution in methanol. Optimization of reaction conditions was also conducted to maximize citraconic anhydride yields. These optimization studies involved temperature, feed compositions, liquid feed and gas flow rate, and catalyst bed length.

The yield of citraconic anhydride from the reaction of succinic anhydride and trioxane over SA3177 was as high as 43% of theoretical at selectivity ranging from 50-70%. The rate of catalyst deactivation was very high with succinic anhydride and trioxane feed and thus the yield of citraconic anhydride and conversion of succinic anhydride decreased sharply over time; this is likely caused by coking on the surface of the catalyst resulting from the thermal decomposition of highly unstable succinic anhydride at elevated temperatures. Citraconic anhydride formation was even noticed

with the glass beads (an inactive material), likely because of the activated carbon produced from the decomposition of succinic anhydride.

The hydrolysis of reaction products from the reaction of succinic anhydride and trioxane did not affect yield of citraconates, because no methanol is produced in the reaction to facilitate ester formation. The yield of citraconic anhydride from succinic anhydride and trioxane increased with increasing temperature, but decreased with increasing feed molar ratio of formaldehyde to succinic anhydride. The conversion of succinic anhydride sharply decreased with decreasing liquid feed flow rate, but yield of citraconic anhydride did not decrease with decreasing liquid feed flow rate in the same proportion as conversion of dimethyl succinate. Thus, the reaction is highly selective at the higher liquid feed flow rate. A higher conversion of succinic anhydride and a significantly lower yield of citraconic anhydride were observed from the longer catalyst bed.

After hydrolysis of raw products from the reactor, a maximum 31% yield of citraconates at 40% conversion of succinates from the reaction of monomethyl succinate and trioxane over SA3177 was achieved at the base case conditions. The reaction of monomethyl succinate and trioxane was not affected much by the reaction temperature. With no carrier gas used for the reaction of monomethyl succinate and trioxane, the yield of citraconic anhydride decreased, while the yield of dimethyl succinate significantly increased.

Succinic anhydride is a good feed material for the reaction, as the highest yields of citraconate were achieved with very good selectivities. In the laboratory, reactions are somewhat more difficult to conduct with succinic anhydride, because it has a very high

boiling point (269 °C) and solidifies on any cold surface. This led to frequent plugging of reactor tubes and collection traps during experiment. On a commercial scale, the properties of succinic anhydride should pose less of a problem. Coking on the catalyst was not significant from the reaction of monomethyl succinate and trioxane and, hence, results were stabilized over time.

Monomethyl succinate was also proved to be a good feed material for the reaction, as the highest selectivities of citraconates were achieved and the catalyst deactivation was also minimal. Dilution of monomethyl succinate feed in methanol may make it an economically unfavorable process, because excessive methanol would impart an increase in the reactor, heating, and the separation costs of the process. A small amount of methanol is also lost in the reactor at reaction temperatures as dimethyl ether.

Dimethyl succinate is produced by esterification of succinic acid and succinic anhydride can be produced by heating succinic acid. Production of monomethyl succinate from succinic acid requires one additional step, first forming succinic anhydride from succinic acid, and then its esterification. Monomethyl succinate does not have any significant advantage over dimethyl succinate.

CHAPTER 6

CONDENSATION OF DIMETHYL SUCCINATE AND FORMALDEHYDE IN AQUEOUS SOLUTIONS TO CITRACONIC ANHYDRIDE

6.1. Introduction

This chapter presents the studies of the condensation reaction of dimethyl succinate with formaldehyde in the vapor phase over various catalysts where the source of formaldehyde is a commercially available formaldehyde solution. Earlier in this work, 1,3,5 trioxane, the cyclic trimer of formaldehyde, was used as a source of formaldehyde for the reaction because of its ease in handling. But trioxane is not commercially available, so it is necessary to look to other sources of formaldehyde for the reaction which are commercially available. Formalin, a mix of 37 wt% formaldehyde, 10 wt% methanol, and 53 wt% water, is a readily available formaldehyde solution and is widely used in this study. One another commercially available source of formaldehyde, Formcel, produced by Celanese, was also used in this study. Formcel solutions are blends of 55 wt% formaldehyde, 35 wt% methanol, and 10 wt% water.

6.2. Reaction Conditions

The reaction studies involve primarily dimethyl succinate and formaldehyde solution as the feed with helium as a carrier gas. Most experiments were carried out for five hours at steady state, with samples taken in 30-minute intervals. Typical reactor operating conditions are given in Table 6.1.

Table 6.1. Reactor Operating Conditions

S.N.	Condition	Range	Base case condition
1	Reaction temperature (°C)	380 - 380	380
2	Reactor pressure (psi)	60	60
3	Pre-heat temperature (°C)	200 - 250	250
4	Feed molar composition (mol%)		
	Dimethyl succinate	7.4 – 14	9.5
	Formaldehyde	4.4 – 34.6	18.8
	Methanol	4.2 – 40.6	4.8
	Water	8.9 - 42.0	45.1
	Helium	21.9 – 31.5	21.9
5	Liquid feed flow rate (ml/min)	0.14 – 0.42	0.15
6	Outlet gas flow rate (ml(STP)/min)	27 - 82	27

6.3. Control Experiments of Formalin

Formalin was passed through the empty reactor to characterize its stability at the normal reaction temperature. The recovery of formaldehyde solution after the reaction

was complete, which suggests that formaldehyde does not escape from the solution even at higher temperatures. The sodium sulfite method (discussed in Section 2.6.3) was used for the determination of formaldehyde concentration in control experiments of Formalin.

Complete (100%) conversion of formaldehyde was obtained when Formalin itself was passed over γ-alumina (SA3177) at the base case conditions. The catalyst activity was not changed over the five-hour reaction time because the water present in Formalin oxidized any coke formed from the cracking of formaldehyde. A significant amount of carbon monoxide was observed due to the decomposition of formaldehyde at the reaction temperature. A 16% yield of carbon dioxide and methanol, Cannizzaro products, was observed.

Reactions with Formalin were also done at 200 °C using different catalysts such as γ-alumina, SA3177, $AlPO_4$, and hydrotalcites (36% Al + 64% Mg, also identified as AM-36). The formation of carbon dioxide, carbon monoxide, and methanol was monitored. Methanol is a product of the Cannizzaro reaction of formaldehyde, and formic acid formed decomposes to give carbon dioxide and hydrogen at the reaction conditions. Base catalysts are responsible for the Cannizzaro reaction. The acid sites on the catalysts are responsible for the cracking reaction. With SA3177 alumina, the initial 30 minutes reaction gave only cracking products and most of the formaldehyde was destroyed. Analysis of gas samples revealed C_1, C_2, and C_3 hydrocarbons. In another experiment, the acidic sites on SA3177 were poisoned by base addition to block the initial activity. In this case, the products were substantially methanol. Carbon dioxide was also prominent. Substantial methanol was formed when AM-36 was used as catalyst. Carbon dioxide generation was very high. In $AlPO_4$, there was hardly any

methanol produced, carbon monoxide was detected in the reactor outlet gas, and much of the formaldehyde was recovered. The basic sites in $AlPO_4$ were responsible for the conversion of formaldehyde to methanol, and the acidic sites tended to preserve the formaldehyde for the necessary reaction.

6.4. Base Case Results

Intermediate surface area alumina being identified as an optimal catalyst material for the desired reaction, was extensively used in this study. Commercial available γ-alumina, SA3177 (Alundum), and alumina-in-house, prepared in the laboratory, both were used as intermediate surface area aluminas. Results from alumina-in-house were very similar to the results from SA3177 and, hence, it was decided to use readily available SA3177 to avoid the tedious preparation of alumina-in-house. Most experiments with SA3177 were carried out without any salt impregnated. Supported SA3177 was also used in some experiments to accomplish some specific task; this is discussed in later sections.

Yields of citraconic anhydride, conversions of dimethyl succinate, selectivities of citraconic anhydride from dimethyl succinate, yields of monomethyl succinate, and yields of carbon dioxide evolved from the reaction of dimethyl succinate and Formalin over SA3177 are given and compared with other sources of formaldehyde in Figure 6.1, Figure 6.2, Figure 6.3, Figure 6.4, and Figure 6.5 respectively. Section 4.7.2.1 discusses results of trioxane and dimethyl succinate feed. Results from Formcel are discussed in Section 6.6.1. The use of Formalin as a source of formaldehyde for the reaction is discussed in the following paragraphs.

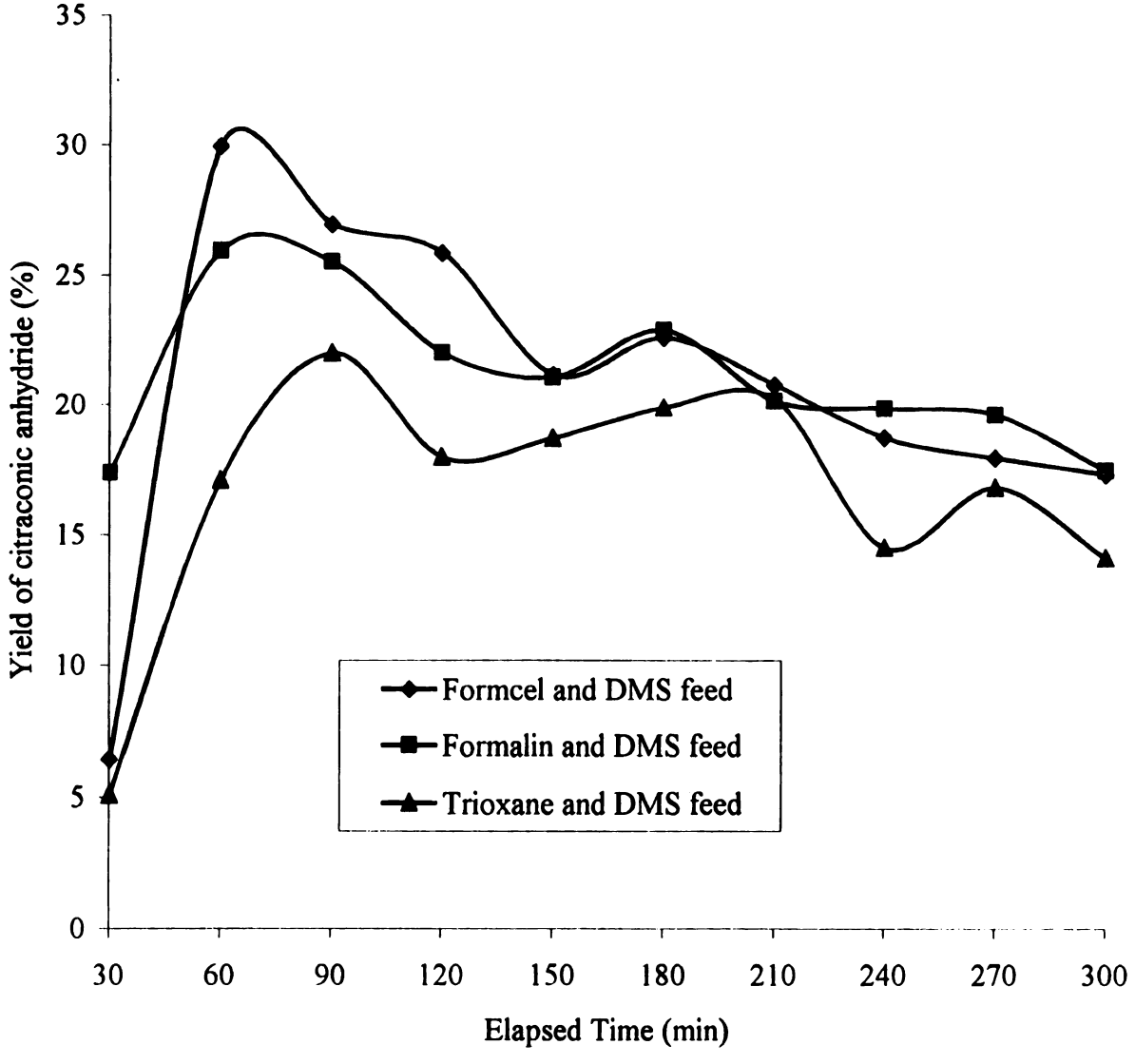

Figure 6.1. Citraconic anhydride yield from different formaldehyde sources

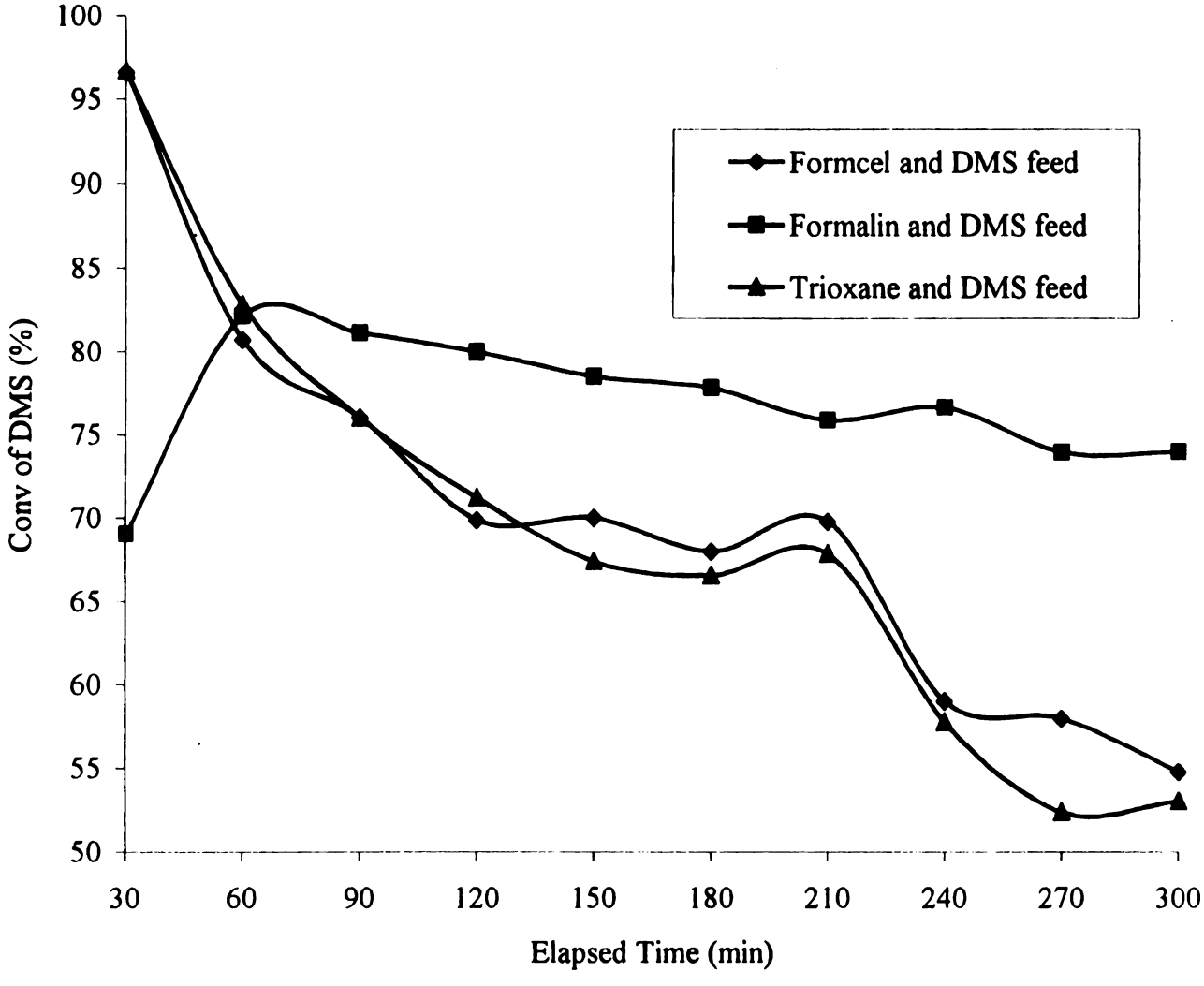

Figure 6.2. Conversion of DMS from different formaldehyde sources

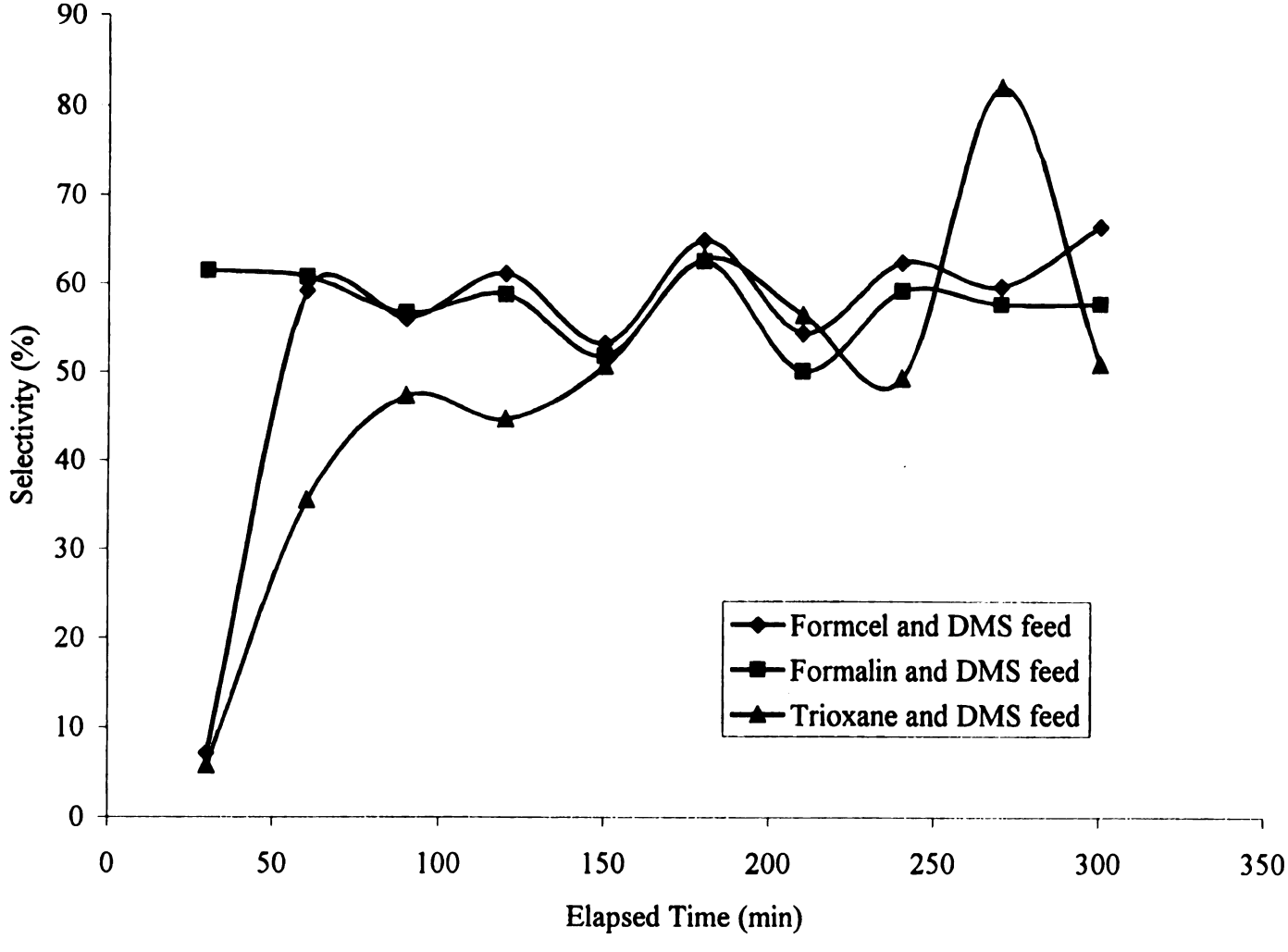

Figure 6.3. Selectivity from different formaldehyde sources

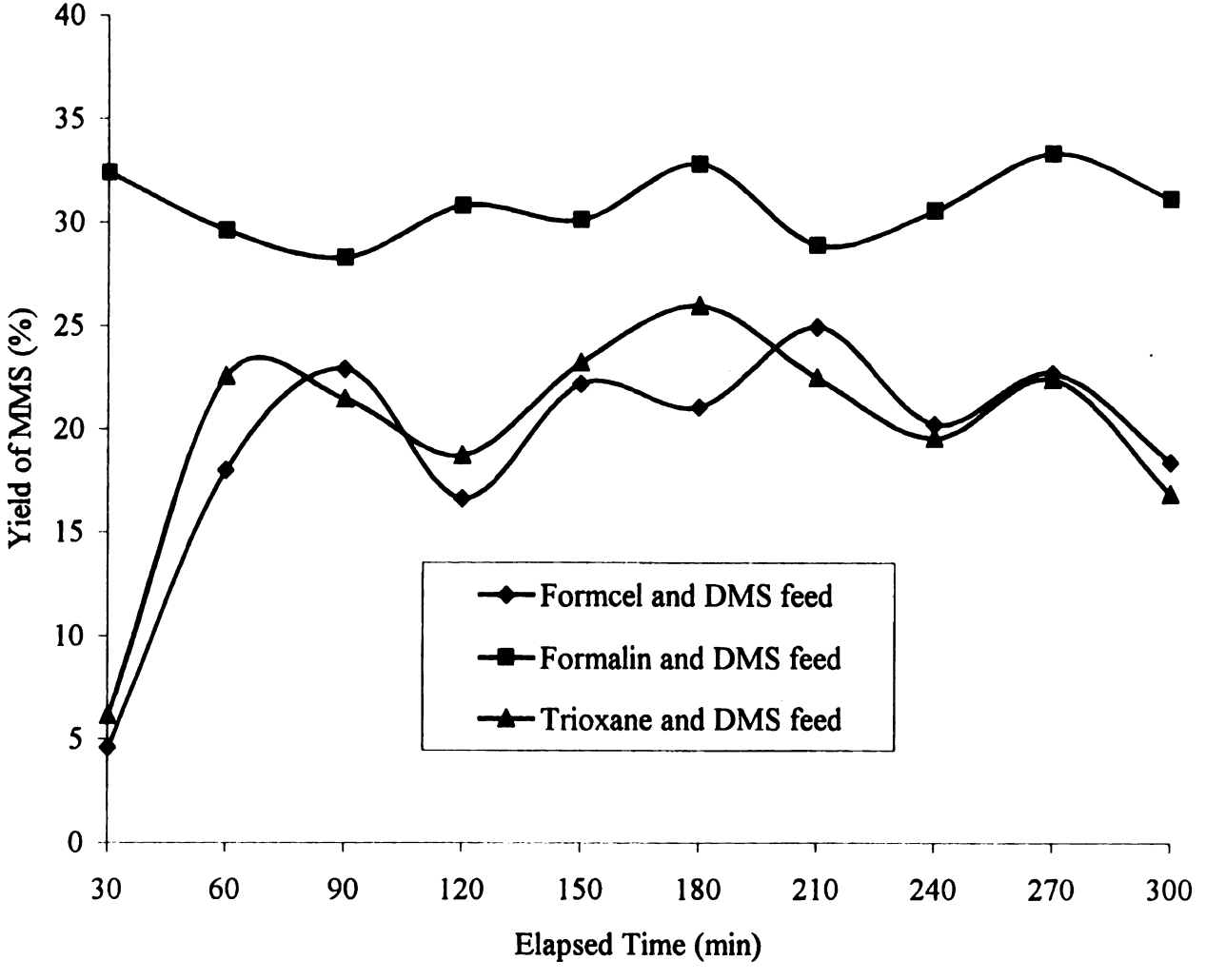

Figure 6.4. Yield of MMS from different formaldehyde sources

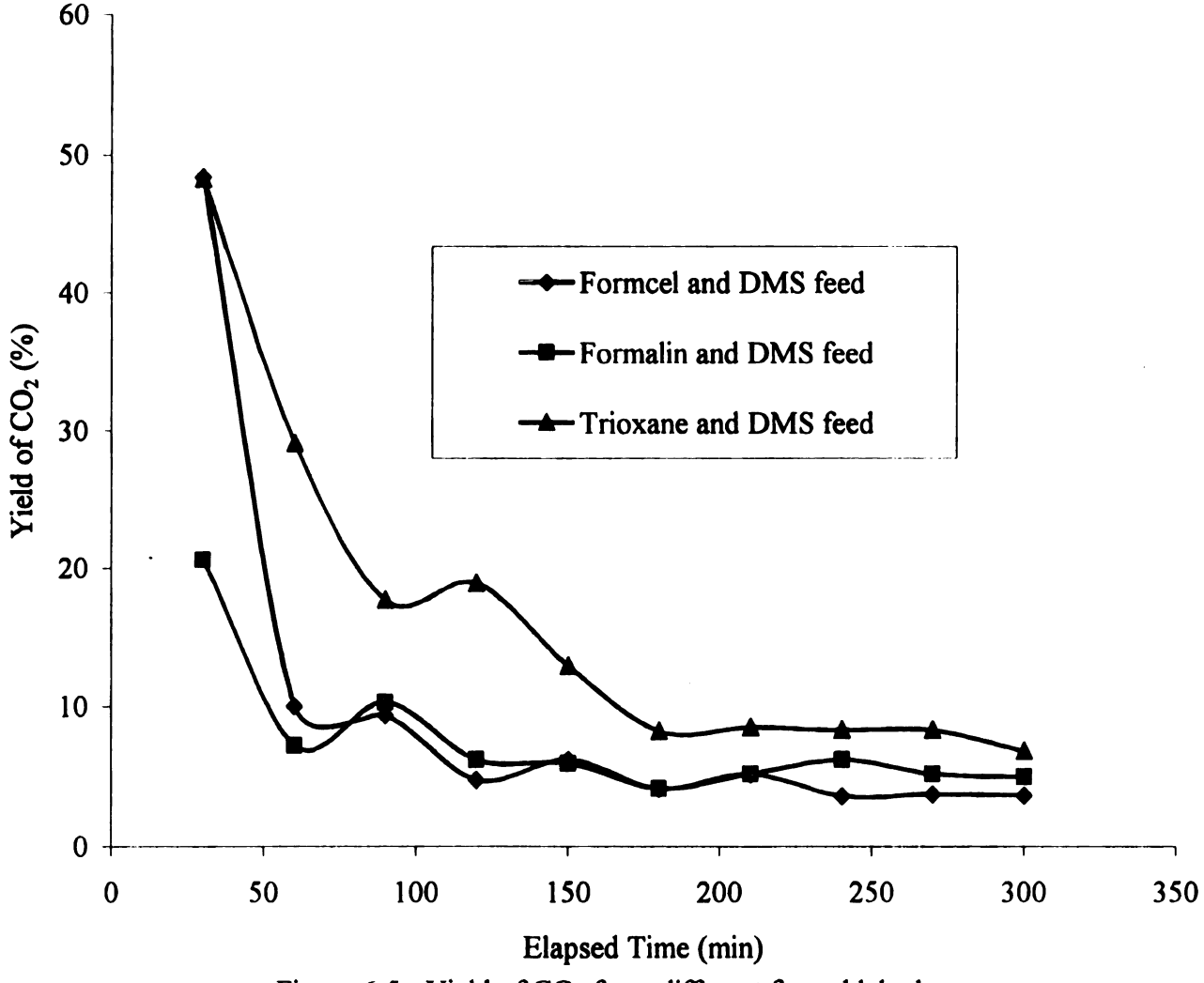

Figure 6.5. Yield of CO_2 from different formaldehyde sources

The condensation reaction of dimethyl succinate with Formalin over SA3177 was conducted at the base case conditions. A maximum 26% yield of citraconic anhydride at 82% conversion of dimethyl succinate was observed. After hydrolysis of product samples, 42% conversion of succinates was achieved with a citraconates yield of 29%, hence, a selectivity of about 70%. Conversions of dimethyl succinate were higher with Formalin as compared to other formaldehyde sources (see Figure 6.2). Higher conversion of dimethyl succinate was a result of hydrolysis of dimethyl succinate during the reaction over acidic alumina in the presence of the excess water from Formalin. Consequently, higher yields (see Figure 6.5) of monomethyl succinate and succinic anhydride were obtained. Yields of monomethyl succinate and succinic acid from Formalin and dimethyl succinate feed were about 30% and 10%, respectively at 80% conversion of dimethyl succinate.

Two advantages of using Formalin are apparent: first, the decay in catalyst activity was much slower with Formalin. Yields of citraconic anhydride and conversion of dimethyl succinate dropped off very slowly over time for reaction times out to five hours. Yields of monomethyl succinate remained almost constant at 30% throughout the reaction time of five hours. Similarly, yields of carbon dioxide evolved from the cracking of reactants stabilized after starting at a maximum in the first sample (Figure 6.5). Second, the gain in the catalyst weight due to coking was much less with Formalin, likely because the water present steam-cleaned the catalyst during the reaction.

6.5. Other Catalysts Used

Intermediate surface area alumina has been already established as an optimal catalyst material for citraconic anhydride production, so it was used for the process optimization study. However, several additional catalyst materials such as high surface area aluminas, aluminum phosphates, hydrotalcites, glass beads, and activated carbon were also used for the reaction of dimethyl succinate and Formalin. The most significant effort of this study was to tailor the catalyst acidic-basic sites by changing magnesia content in alumina-magnesia mixed catalyst and then to correlate the support characteristics with the yield of citraconic anhydride and the conversion of dimethyl succinate.

6.5.1. Intermediate Surface Area Alumina

6.5.1.1. Salts Supported on SA3177 Alumina

Conversion of dimethyl succinate and Formalin was also performed over ceric sulfate ($Ce_2(SO_4)_3$) and KH_2PO_4 supported on SA3177. Reactions with ceric sulfate supported on SA3177 were conducted in the early part of this study. There were two reasons behind the selection of ceric sulfate as a catalyst for the formation of citraconic anhydride. One, initially, thorium sulfate was selected as a salt additive because thorium sulfate supported alumina was successfully used, in a prior art, for this reaction (33). But, the radioactive nature of thorium sulfate made its intended uses difficult, so ceric sulfate, similar compound to thorium sulfate, became our choice. Two, cerium salts are widely used as coking reducers in industry. A maximum 16% yield of citraconic anhydride at 75% conversion of dimethyl succinate was obtained over 0.5 mmol/g ceric

sulfate supported on SA3177 at 410 °C and the feed molar ratio of 1 to 1.1 of dimethyl succinate to formaldehyde as Formalin. The condensation of succinates and formaldehyde was also conducted over SA3177 with ceric sulfate using diethyl succinate, different loading of ceric sulfate, and temperature of 380 °C. But the results were not significantly different from those described here.

Reaction of dimethyl succinate and Formalin was also performed over KH_2PO_4 supported on SA3177 at the base case conditions. KH_2PO_4 was impregnated onto SA3177 to selectively deactivate the strongly acidic coking sites on alumina. It has been already shown that the catalyst activity is eliminated by a base loading corresponded to the density of strong acid sites on SA3177 (0.15 mmol/g catalyst). A loading of 0.015 mmol KH_2PO_4/g SA3177 was used for the reaction of dimethyl succinate and Formalin, which is 10% of the acidic site density calculated from ammonia TPD. Figure 6.6 gives the comparison of conversion of dimethyl succinate and yield of citraconic anhydride over KH_2PO_4 supported on SA3177 and SA3177 alone. Conversion of dimethyl succinate over KH_2PO_4 supported on SA3177 was not much different than over SA3177 alone. However, the yield of citraconic anhydride over KH_2PO_4 supported on SA3177 was always 3 to 4% more than the yield of citraconic anhydride over SA3177 alone. After hydrolysis of the reaction products, a maximum 33% yield of citraconates at 43% conversion of succinates was observed over KH_2PO_4 supported on SA317, compared to 29% yield of citraconates at 43% conversion of succinates over SA3177 alone.

The comparison of yield of carbon dioxide from KH_2PO_4 supported on SA3177 and SA3177 alone is shown in Figure 6.7. Yields of carbon dioxide evolved from the reaction over KH_2PO_4 supported on SA3177 were slightly less than the yields over

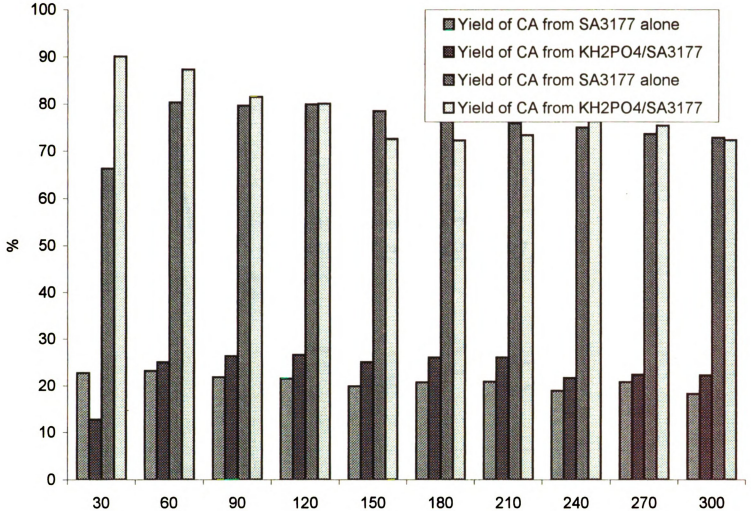

Figure 6.6. Comparison of Results from Supported and Unsupported SA3177

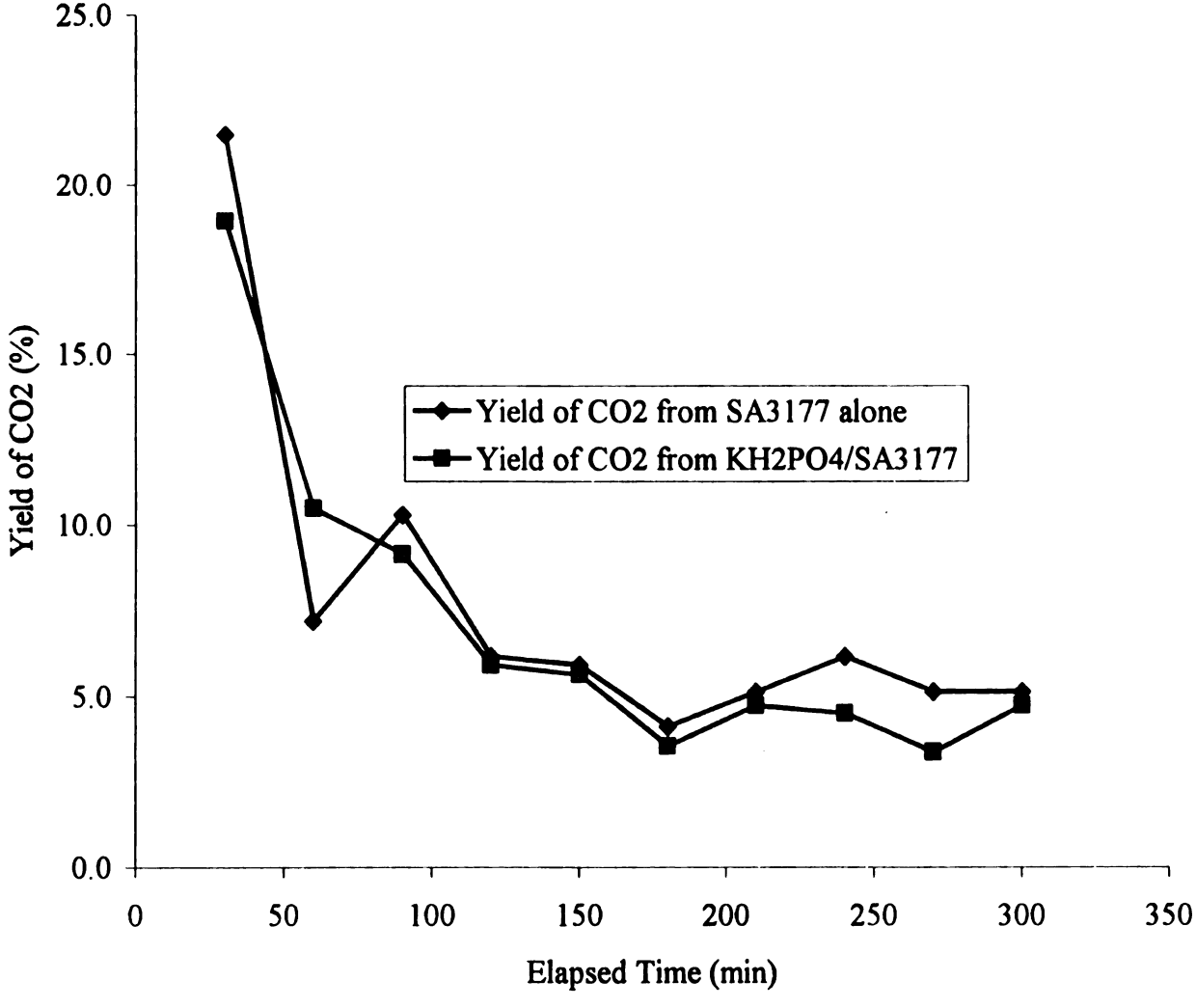

Figure 6.7. Yield of CO2 from KH2PO4/SA3177 and SA3177 only

SA3177. But catalyst weight gain with KH_2PO_4/SA3177 was 1.2 g after five hours of the reaction, compare to 1.0 g catalyst weight gain with SA3177 alone.

Summary of results from 0.015 mmol KH_2PO_4/g SA3177 compared to SA3177: conversion of dimethyl stayed the same, yields of citraconic anhydride were 3-4% points higher, yields of carbon dioxide were slightly lower, and more catalyst weight gain was observed. Results from 0.015 mmol KH_2PO_4/g SA3177 were slightly better than the SA3177 alone, but not as advantageous as anticipated.

6.5.1.2. Acid Treated SA3177

SA3177 alumina was treated with sulfuric acid to poison basic sites, which are likely responsible for the consumption of formaldehyde during the reaction via the Cannizzaro reaction. Loading of 0.15 mmol H_2SO_4/g SA3177 was taken for the reaction because it corresponds to the density of the basic sites on SA3177. The method used for loading the base was also employed for impregnation of sulfuric acid on SA3177.

The acid treated SA3177 was not active for the reaction as anticipated. The yield of citraconic anhydride over acid treated was less than 5% at low conversions of dimethyl succinate (47% in 2nd sample and 25% in 3rd sample). The conversion of formaldehyde over acid treated SA3177 was low (25%) as compared to 80% with untreated SA3177, so we were successful in reducing formaldehyde consumption. Low conversion of formaldehyde was also evident from the lower yield of methanol. The yield of succinic acid was abnormally high (18%) in the first sample because hydrolysis of dimethyl succinate was facilitated by extra acid present on the surface of the catalyst.

6.5.1.3. Alumina-In-House

γ-Alumina (alumina-in-house or AIH) prepared in our laboratory was also tested for the condensation reaction of dimethyl succinate and Formalin. Results obtained from AIH are given in Table 6.2 along with results for SA3177. Properties of the AIH may be seen in Table 4.1. AIH was found to be a more active catalyst for the cracking reaction because of its higher surface area and surface acidity. After the first sample, yields of citraconic anhydride and conversions of dimethyl succinate from AIH were comparable with yields and conversions from SA3177. Higher extent of cracking of reactants over AIH was reflected in higher yields of carbon dioxide and, therefore, lower selectivities of citraconic anhydride. The catalyst weight gain of 1.5 g was observed after 2.5 hours of the reaction. Yields of citraconates increased after hydrolysis of product samples.

Table 6.2. Comparison of results from Alumina-In-House and SA3177[1]

Elapsed Time (min)	Yield of citraconic anhydride (%)		Conversion of Succinates (%)		Yield of CO_2 (%)		Selectivity (%)	
	AIH	SA3177	AIH	SA3177	AIH	SA3177	AIH	SA3177
30	5	18	80	46	22	22	7	61
60	23	26	63	42	24	8	40	61
90	23	26	59	43	24	10	41	57
120	23	22	43	37	18	6	46	59
150	19	21	54	40	19	6	38	52

[1]Reaction conditions: Temperature = 380 °C; pressure = 60 psi; feed = dimethyl succinate + Formalin (1 to 2 molar ratio of DMS to formaldehyde); liquid feed flow rate = 0.15 ml/min; outlet gas flow rate = 27 ml(STP)/min; pre-heat temperature = 200 °C.

6.5.2. High Surface Area Alumina

The condensation reaction of dimethyl succinate and Formalin was also carried out over high surface area aluminas, SA6173 (surface area = 220 m^2/g) and SA6175 (surface area = 236 m^2/g), from Norton. Reactions over high surface area aluminas were carried out at the base case conditions except the dimethyl succinate to formaldehyde molar ratio of 1 to 1.1 was taken. A maximum 15% yield of citraconic anhydride at 92% conversion of dimethyl succinate was observed over SA6173. Results obtained from SA6175 were very similar to the results obtained from SA6173. Higher yields of carbon dioxide from the reaction of dimethyl succinate and Formalin over high surface alumina were indicative of excessive cracking of reactants. It is concluded from these reactions that the high surface area with high acid site density of aluminas facilitate the cracking reaction rather than the desired reaction.

6.5.3. Low Surface Area Alumina (SA3132)

In an earlier study, two experiments were carried out with diethyl succinate and Formalin over 0.5 mmol/g ceric sulfate supported on a low surface area alumina, SA3132 (surface area 32 m^2/g). A maximum 7% yield of citraconic anhydride at 52% conversion of diethyl succinate was observed over supported SA3132 at the base case conditions. A small amount of carbon dioxide and coking on the catalyst were also observed. The low surface area Alundum, SA3132, was found to be less active than the other aluminas used.

6.5.4. Hydrotalcites/ Magnesium-Aluminum Mixed Oxides

Hydrotalcites, mixed oxide of magnesia and alumina, are interesting catalysts for study because they can be prepared in different Mg:Al molar ratios to give different surface acidities. After calcination, these compounds lose interlayer anions and water to form mixed oxides that can be used as solid base catalysts (e.g., Mg-Al-O). The measured acidity and basicity of the hydrotalcites prepared are given in Table 4.1. As discussed in Section 1.8.3.5, the number and strength of the acid sites for calcined hydrotalcites decline as the Mg content of the hydrotalcite increases and vice versa. Hydrotalcite catalyst samples with Mg/[Al + Mg] molar ratios of 0.005, 0.01, 0.02, 0.04, 0.06, 0.12, 0.25, and 0.33 were prepared in our laboratory by the method described in Section 3.1.2 and studied comprehensively for the formation of citraconic anhydride from dimethyl succinate and Formalin. Reactions were conducted at the base case conditions.

Yields of citraconic anhydride, conversions of dimethyl succinate, selectivities of citraconic anhydride from dimethyl succinate, yields of monomethyl succinate, and yields of carbon dioxide evolved from the reaction over different hydrotalcites are given and compared with SA3177 in Figure 6.8, Figure 6.9, Figure 6.10, Figure 6.11, and Figure 6.12, respectively.

As the Mg content of the hydrotalcite increases, the conversion of dimethyl succinate and the yield and selectivity for citraconic anhydride formation decline. Yield of monomethyl succinate also decreases as the Mg content of the mixed catalysts increases because the basic catalyst does not favor the de-esterification reaction. In contrast, yields of carbon dioxide and methanol were higher for the high Mg content hydrotalcites, because the basic catalysts facilitate the Cannizzaro reaction.

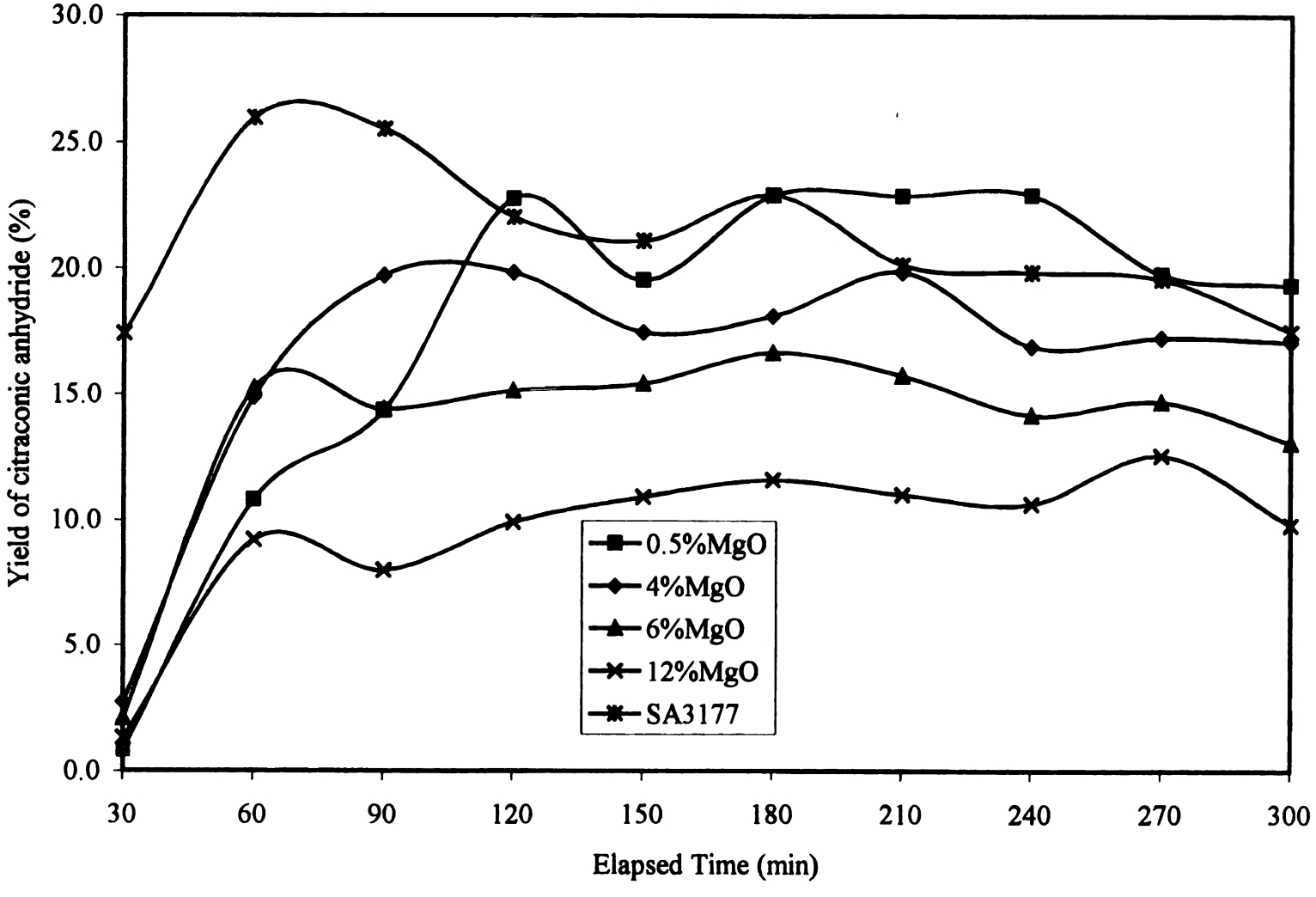

Figure 6.8. Yield of citraconic anhydride from different hydrotalcites

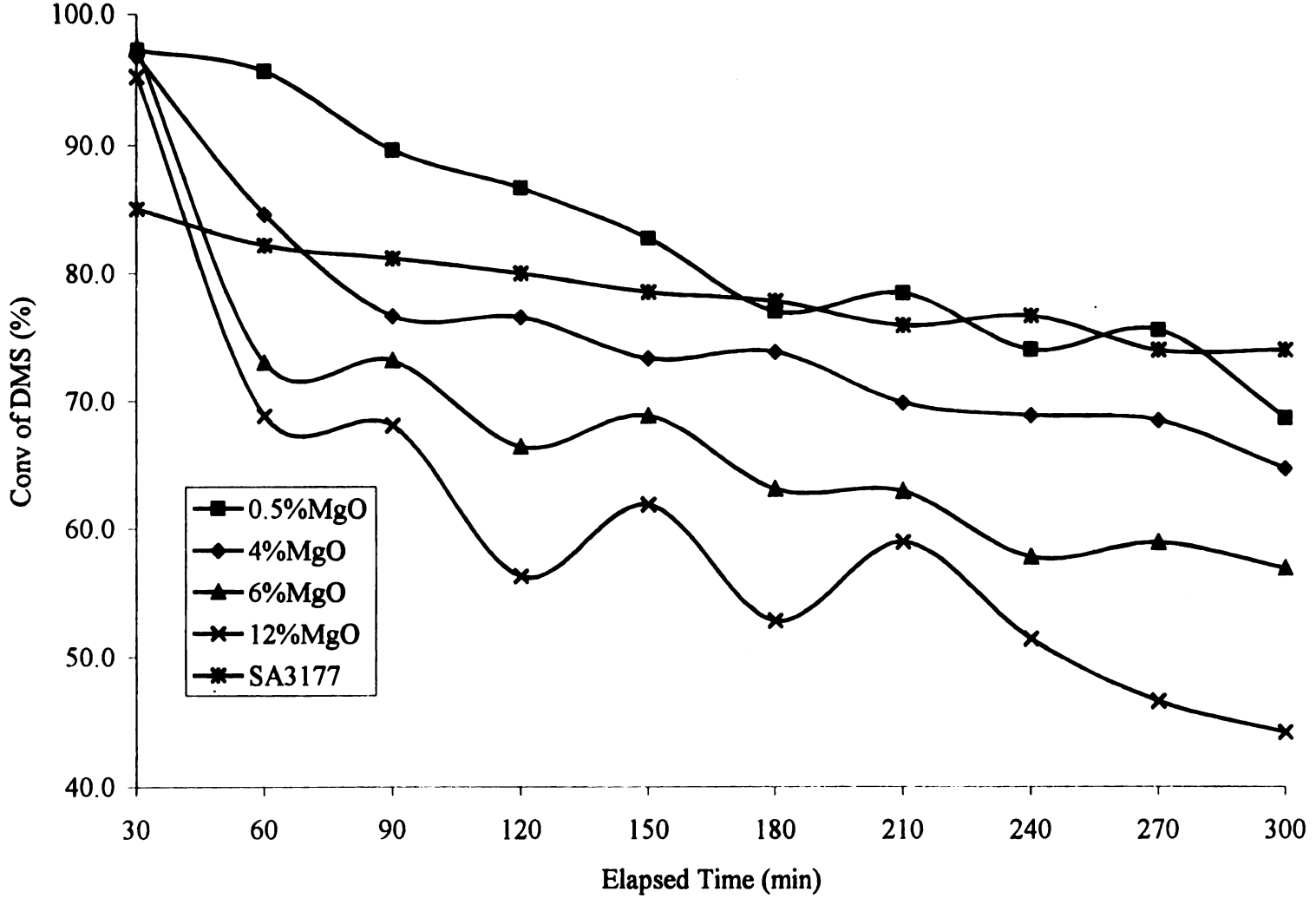

Figure 6.9. Conversion of DMS from different hydrotalcites

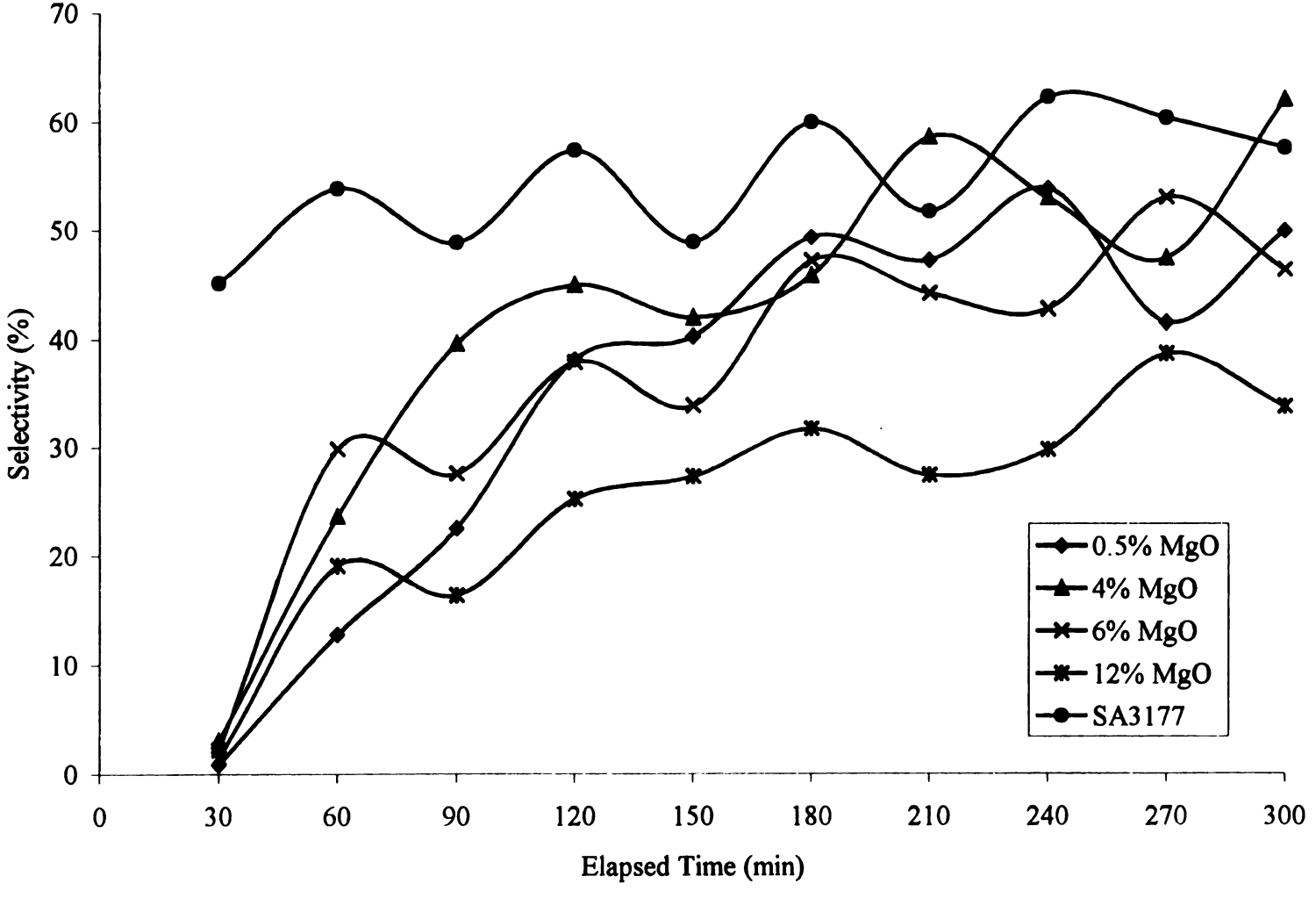

Figure 6.10. Selectivity from different hydrotalcites

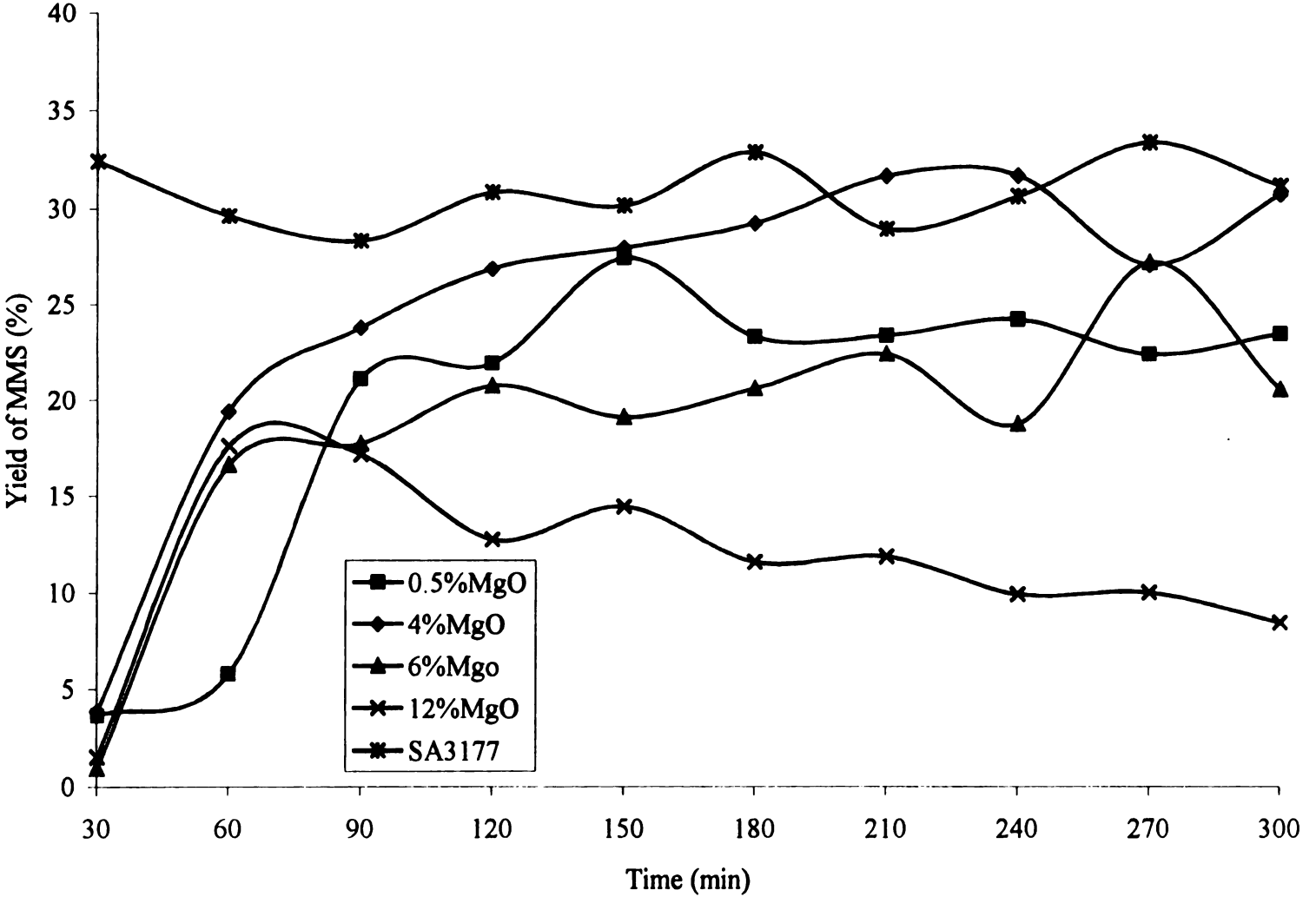

Figure 6.11. Yield of MMS from different hydrotalcites

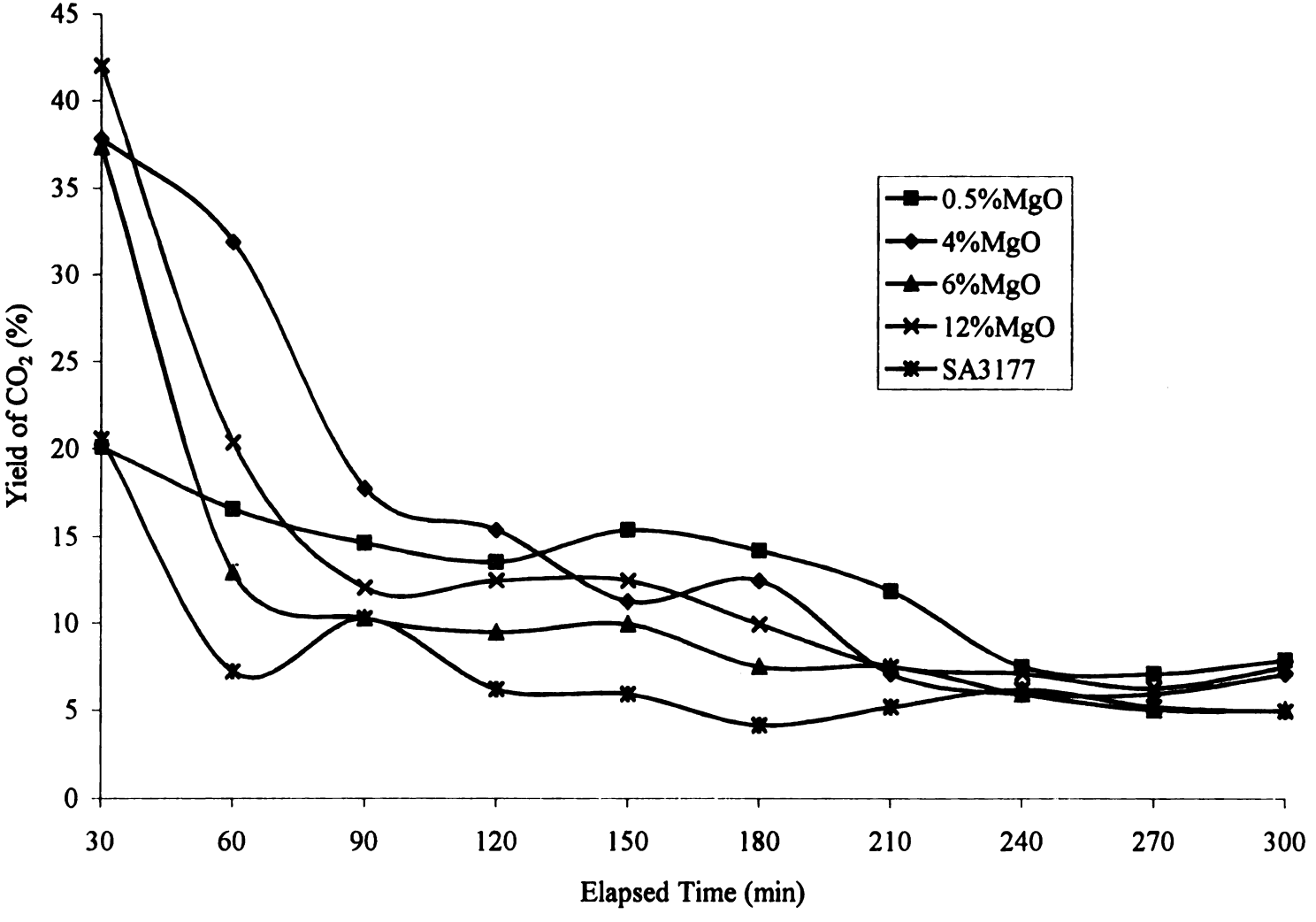

Figure 6.12. Yield of CO_2 from different hydrotalcites

A hydrotalcite containing 25% Mg gave essentially no citraconic anhydride. Hydrotalcites containing 0.5%, 1%, and 2% Mg gave almost the same results.

Yields of citraconic anhydride over all hydrotalcites were stabile after the first 60 minutes of the reaction. Some samples from each hydrotalcite were hydrolyzed; citraconate yields were increased after hydrolysis by 15-20% as with SA3177. Catalyst coking over hydrotalcites was substantial and is discussed in detail in the Catalyst Deactivation Section (Section 6.8).

6.5.5. Aluminum Phosphates

Aluminum phosphate ($AlPO_x$) catalyst samples with P/Al molar ratios of 0.5, 1.0, and 1.5 were prepared in our laboratory by the method described in Section 3.1.1 and studied for the reaction of dimethyl succinate with Formalin to form citraconic anhydride at the base case conditions. The acid site densities on the $AlPO_x$ surface increase with P/Al ratio before decreasing considerably at P/Al = 1.5.

Yields of citraconic anhydride, conversions of dimethyl succinate, selectivities of citraconic anhydride from dimethyl succinate, and yields of carbon dioxide evolved from the reaction over $AlPO_x$ (P/Al = 0.5 and 1.0) are given in Table 6.3. Results from $AlPO_x$ with P/Al = 1.5 are not presented in Table 6.3, because it was completely inactive for the desired reaction.

A smaller amount of $AlPO_x$ (1.9 g) was taken into the reactor bed than with aluminas, due to the lower densities of $AlPO_x$. Hence, higher weight hourly space velocities (WSHV) were achieved at the base case conditions. Conversions of dimethyl succinate over $AlPO_x$ with P/Al = 1.0 were always 15-20% higher than the conversions

over $AlPO_x$ with P/Al = 0.5. Yields of citraconic anhydride over $AlPO_x$ with P/Al = 1.0 were always 4-6% higher than the yields of citraconic anhydride over $AlPO_x$ with P/Al = 0.5. Selectivities for citraconic anhydride formation were very low over $AlPO_x$ with P/Al molar ratio of 0.5 and 1.0.

Table 6.3. Results from AlPOs with P/Al molar ratio of 0.5 and 1.0.

Elapsed Time (min)	Yield of citraconic anhydride (%)		Conversion of succinates (%)		Yield of CO_2 (%)		Selectivity (%)	
	P/Al=0.5	P/Al=1	P/Al=0.5	P/Al=1	P/Al=0.5	P/Al=1	P/Al=.5	P/A=1
30	13	9	65	80	30	25	19	12
60	15	20	41	59	4	4	36	35
90	13	16	37	54	7	9	36	29
120	11	20	31	46	3	3	37	44
150	9	16	33	57	2	9	28	27
180	9	14	37	57	3	3	25	25
210	11	17	28	46	3	3	39	37
240	10	15	25	50	3	3	38	31
270	9	13	33	50	6	6	27	27
300	10	15	25	47	3	3	41	32

[1]Reaction conditions: Temperature = 380 °C; Pressure = 60 psi; feed = dimethyl succinate + Formalin (1 to 2 molar ratio of DMS to formaldehyde); liquid feed flow rate = 0.15 ml/min; outlet gas flow rate = 27 ml(STP)/min; pre-heat temperature = 250 °C.

Yields of carbon dioxide were comparatively low to account for lower selectivities due to higher dimethyl succinate conversions. Catalyst weight gain was 1.5 g after five hours of the reaction of dimethyl succinate and Formalin over $AlPO_4$ with P/Al = 1.0. $AlPO_x$, particularly with P/Al = 1.0, facilitate cracking of reactants because of their higher acidic site concentration.

$AlPO_x$ with P/Al = 1.5 was not active for the reaction. Lower conversions of dimethyl succinate over $AlPO_x$ (P/Al = 1.5) were observed with no citraconic anhydride yields and trivial carbon dioxide yields. De-esterification reaction products, succinic acid and monomethyl succinate, accounted for dimethyl succinate conversion over $AlPO_x$ (P/Al = 1.5).

6.5.6. Carbon

In the early part of this study, the reaction of diethyl succinate and Formalin was performed over 0.5 mmol/g ceric sulfate supported on activated carbon (surface area 650 m^2/g; supplied by Cameron-Yakima, Inc.). Citraconic anhydride was not formed over ceric sulfate supported on activated carbon, but 84% conversion of diethyl succinate and 15% yield of monomethyl succinate were observed at the base case conditions. The yield of carbon dioxide evolved from the cracking in the reactor was high (i.e. 50%) and, hence, the catalyst weight gain was significant, 0.77 g, after 1.5 hours of the reaction.

6.5.7. Beads

As discussed in Section 5.2.2.1, significant activity over glass beads was found for the reaction of succinic anhydride and trioxane, where 13% yield of citraconic

anhydride at 78% conversion of succinic anhydride was observed at the base case conditions. The unexpected activity over glass beads from succinic anhydride feed was attributed to coke (carbon) produced by the cracking of succinic anhydride at elevated temperatures. It was essential to conduct a control run of dimethyl succinate and Formalin over glass beads at the base case conditions. No citraconic anhydride was formed from dimethyl succinate and Formalin over glass beads. However, 15% conversion of dimethyl succinate was observed with 7% and 5% yields of monomethyl succinate and succinic acid, respectively. A small amount of carbon dioxide (0.7% yield) was also obtained from the reaction over glass beads.

No de-esterification of dimethyl succinate was seen from dimethyl succinate only in the feed over glass beads (Section 4.5.1), because of the absence of water in the system. For dimethyl succinate and Formalin feed over glass beads, there was a sufficient amount of water present for de-esterification of dimethyl succinate and, hence, some yields of monomethyl succinate and succinic acid were observed.

6.6. Process Optimization over SA3177

More detailed study for optimization of reaction conditions was conducted to maximize citraconic anhydride yields. These studies involved changing feed compositions, temperature, liquid feed and gas flow rate, catalyst particle size, and reactor size to determine the region where both desired product yields were high and the catalyst was stable over time.

6.6.1. Formcel as a Source of Formaldehyde

Yields of de-esterification products monomethyl succinate and succinic acid were significantly higher from dimethyl succinate and Formalin feed than from dimethyl succinate and trioxane because Formalin is a water solution of formaldehyde facilitating hydrolysis of esters. The desired reaction might be affected negatively by competing against the de-esterification reaction. The water present also dilutes the reactants and, thus, decreases WHSV (kg succinate/kg catalyst * hr).

Formcel, blends of 55 wt% formaldehyde, 35 wt% methanol, and 10 wt% water, was also used as a water-scarce formaldehyde source with dimethyl succinate at the base case conditions. Formcel has several advantages over Formalin. First, Formcel has higher formaldehyde content than Formalin, so reactants are more concentrated in the reactor. Second, de-esterification of esters is curtailed because of the higher methanol and lower water content present in Formcel.

Yields of citraconic anhydride, conversions of dimethyl succinate, selectivities of citraconic anhydride from dimethyl succinate, yields of monomethyl succinate, and yields of carbon dioxide evolved from the reaction of dimethyl succinate and Formcel over SA3177 are given and compared with other sources of formaldehyde in Figure 6.1, Figure 6.2, Figure 6.3, Figure 6.4, and Figure 6.5 respectively.

A maximum of 30% yield of citraconic anhydride was obtained from Formcel and dimethyl succinate, which is 4% higher from the maximum yield of citraconic anhydride from Formalin and dimethyl succinate. However, citraconic anhydride yields from both formaldehyde sources were almost identical after 2.5 hours of reaction. The conversion of dimethyl succinate from Formcel and dimethyl succinate feed was very high in the

beginning of the reaction, but decreased sharply over time. After one hour of the reaction, conversions of dimethyl succinate from Formcel and dimethyl succinate were always 10-15% less than the conversions from Formalin and dimethyl succinate. Higher conversions of dimethyl succinate from Formcel in the beginning of the reaction were also reflected in higher yields of carbon dioxide. Yields of carbon dioxide also followed dimethyl succinate conversion trends after one hour of reaction. Monomethyl succinate yields from Formcel and dimethyl succinate were significantly lower, as expected, than the yields from Formalin and dimethyl succinate. Succinic acid yields were also lower from Formcel and dimethyl succinate feed. De-esterification reactions of dimethyl succinate in Formcel were still occurring because they are favorable at the higher reaction temperature in presence of the acidic catalyst. Higher yields of citraconic anhydride in the beginning and lower conversions of dimethyl succinate later from the reaction of Formcel and dimethyl succinate over SA3177 resulted in the better selectivity to citraconic anhydride as compared to Formalin and dimethyl succinate feed.

The gain in the catalyst weight due to coking was higher (1.5 g) with Formcel and dimethyl succinate feed than the catalyst weight gain of 1.0 g from Formalin and dimethyl succinate feed after the five hours reaction. Poor mass balances were obtained with Formcel, likely because of the loss of excess methanol present in Formcel in the form of dimethyl ether. Excess water present in Formalin steam-cleans the catalyst during the reaction. Yields of citraconic anhydride and conversion of dimethyl succinate were not stabile with Formcel and dimethyl succinate to the extent of the yields of citraconic anhydride and conversions of dimethyl succinate from Formalin and dimethyl succinate feed.

6.6.2. Carbon Dioxide as a Carrier Gas

Reaction of dimethyl succinate and Formalin over SA3177 was also carried out with carbon dioxide as a carrier gas instead of helium. There were two reasons behind the using of carbon dioxide as a carrier for the formation of citraconic anhydride. The first was to reduce the coking material deposited on the catalyst by *in-situ* oxidation by carbon dioxide. The second was to see the effect of a carrier gas other than helium on the reaction behavior.

Results from carbon dioxide as a carrier gas were identical to the results from helium as a carrier gas. Carbon dioxide evolved from the reaction was not measured because carbon dioxide was the carrier gas. Even the catalyst weight gain for a five-hour experiment was almost the same in both experiments. The temperature used in the reaction is likely not high enough to oxidize the carbon deposited on the surface of the catalyst.

6.6.3. Helium Gas Flow Rate

The study to see the effect of varying helium gas flow rate on the reaction of dimethyl succinate and Formalin was not conducted independently. The helium flow rate was changed with liquid feed flow rate to keep the molar concentrations of reactants constant at each liquid flow rate studied. Results from different liquid feed flow rate and gas flow rate are discussed in Section 6.6.4.

6.6.4. Liquid Feed Flow Rate

The condensation reaction of dimethyl succinate and formaldehyde over SA3177 was carried out at different liquid feed flow rates ranging from 0.15 ml/min (9 ml/hr) to 0.45 ml/min (27 ml/hr). The flow rate of helium was also changed in the same proportion as liquid feed flow rate to keep the molar concentrations of reactants constant at each liquid feed flow rate. In the first set of experiments, Formalin was used with dimethyl succinate as a source of formaldehyde. In the other set of experiments, reactions were carried out with Formcel as a formaldehyde source.

The effect of the liquid feed flow rate on citraconic anhydride yield, dimethyl succinate conversion, and carbon dioxide yield from Formcel and dimethyl succinate feed may be seen in Figure 6.13, Figure 6.14, and Figure 6.15, respectively. Figure 6.16 and Figure 6.17 present the yield of citraconic anhydride and conversion of dimethyl succinate, respectively, at the two different liquid feed flow rates when Formalin was used as a formaldehyde source.

Results from both Formcel and Formalin follow similar trends as evident from the figures. Conversion of dimethyl succinate was significantly different at two lower liquid feed flow rates studied (9 ml/hr and 18 ml/hr), which is expected according to simple reaction kinetics. The conversion of dimethyl succinate at the lower liquid feed flow rate (9 ml/hr) was always 10-11% more than the conversion at the liquid feed flow rate of 18 ml/hr. However, the conversion of dimethyl succinate was not affected much by increasing the liquid feed flow rate from 18 ml/hr to 27 ml/hr. Yields of citraconic anhydride and carbon dioxide at different liquid feed flow rates followed the dimethyl succinate conversion trends. Yields of citraconic anhydride at 9 ml/hr were ~5% and

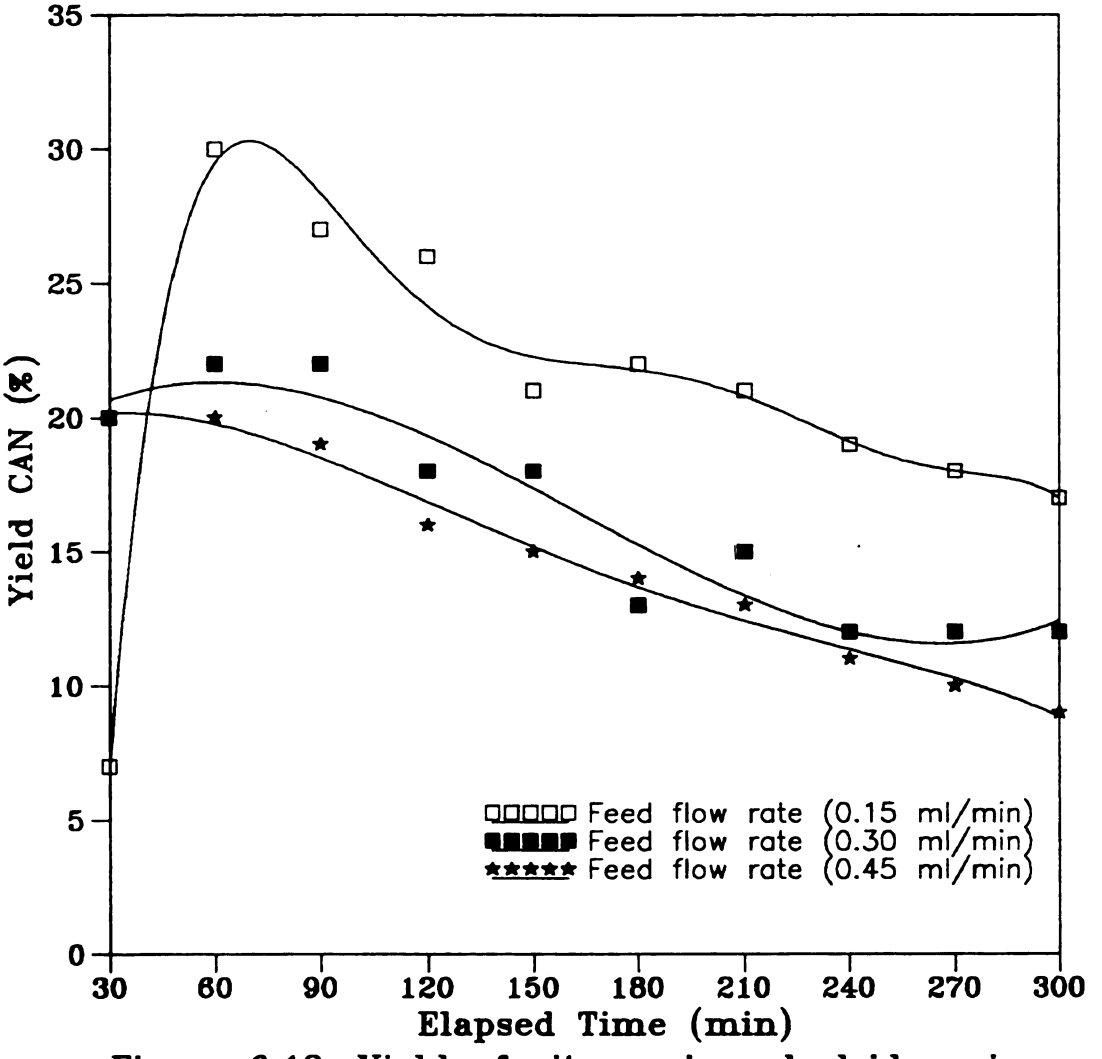

Figure 6.13. Yield of citraconic anhydride using Formcel at different feed flow rate

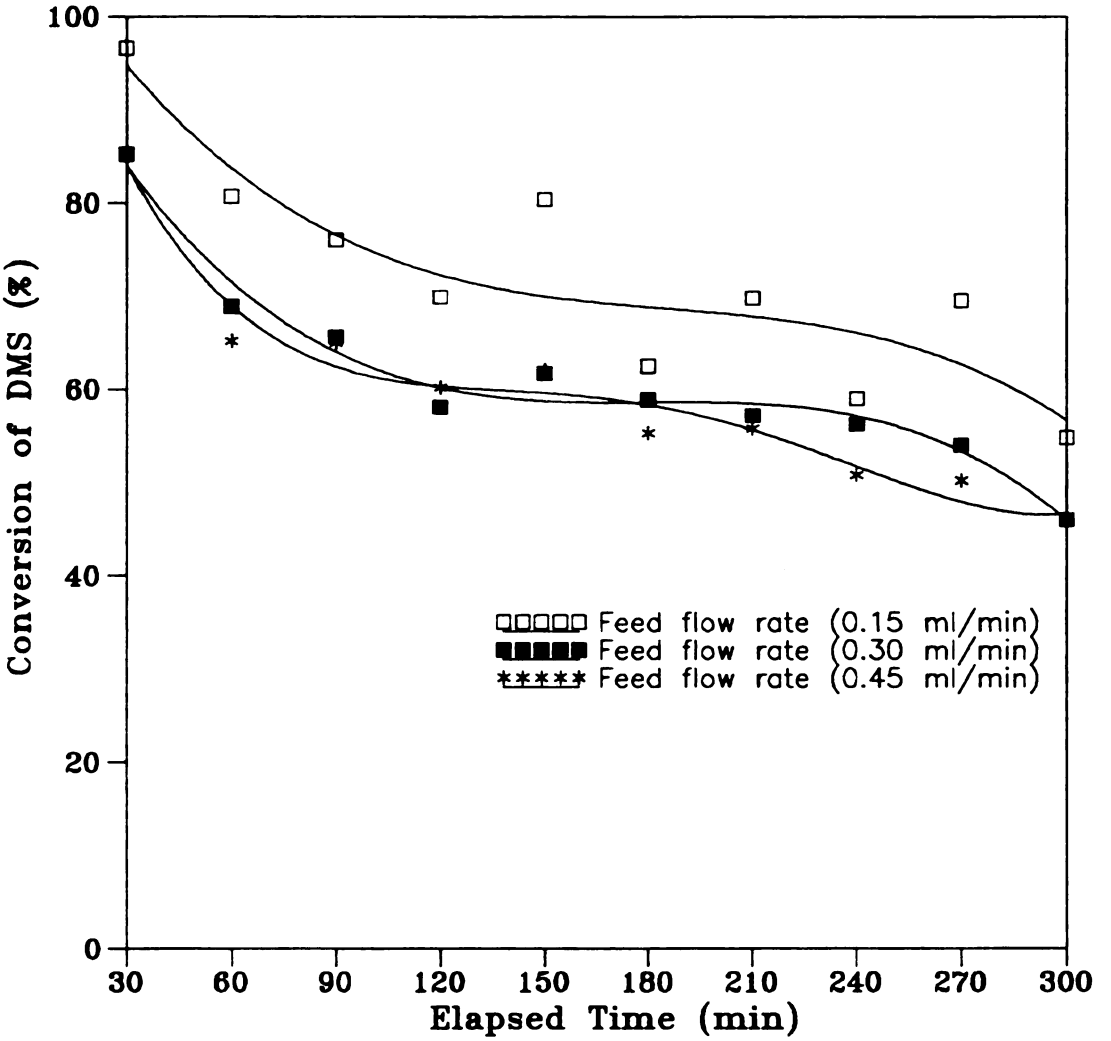

Figure 6.14. Conversion of DMS using Formcel at different feed flow rate

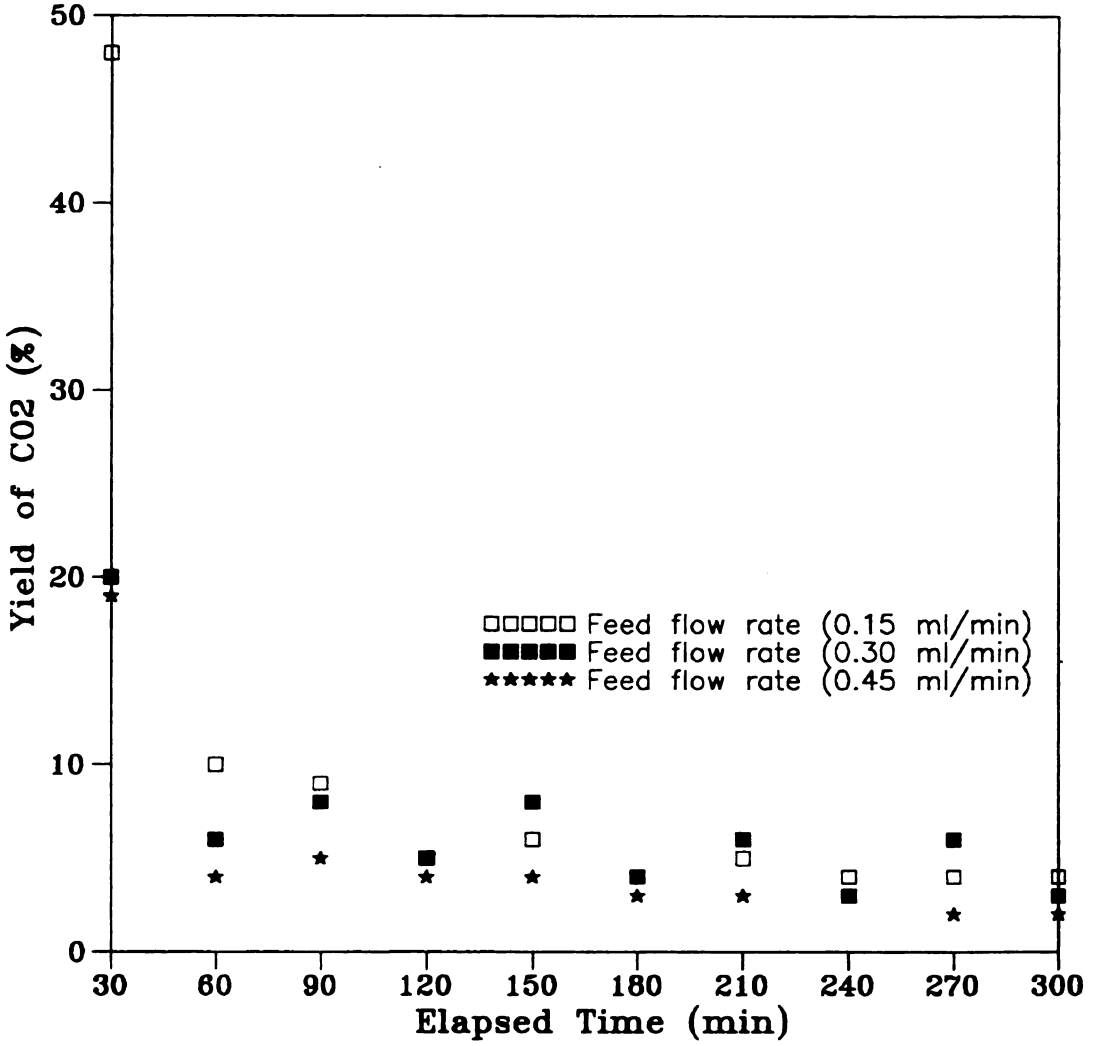

Figure 6.15. Effect of liquid flow rate on yield of CO_2 (Formcel)

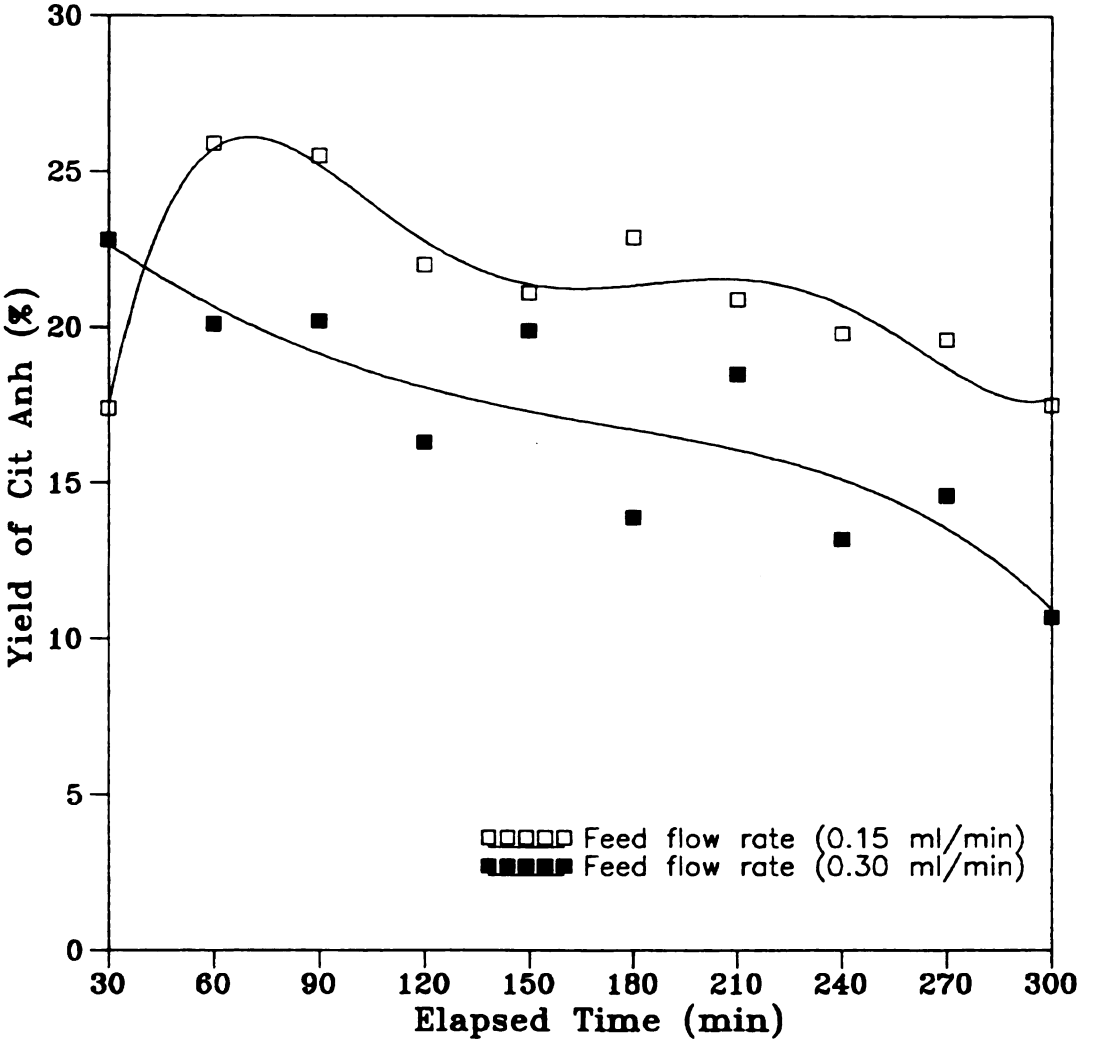

Figure 6.16. Yield of citraconic anhydride using Formalin at different flow rate

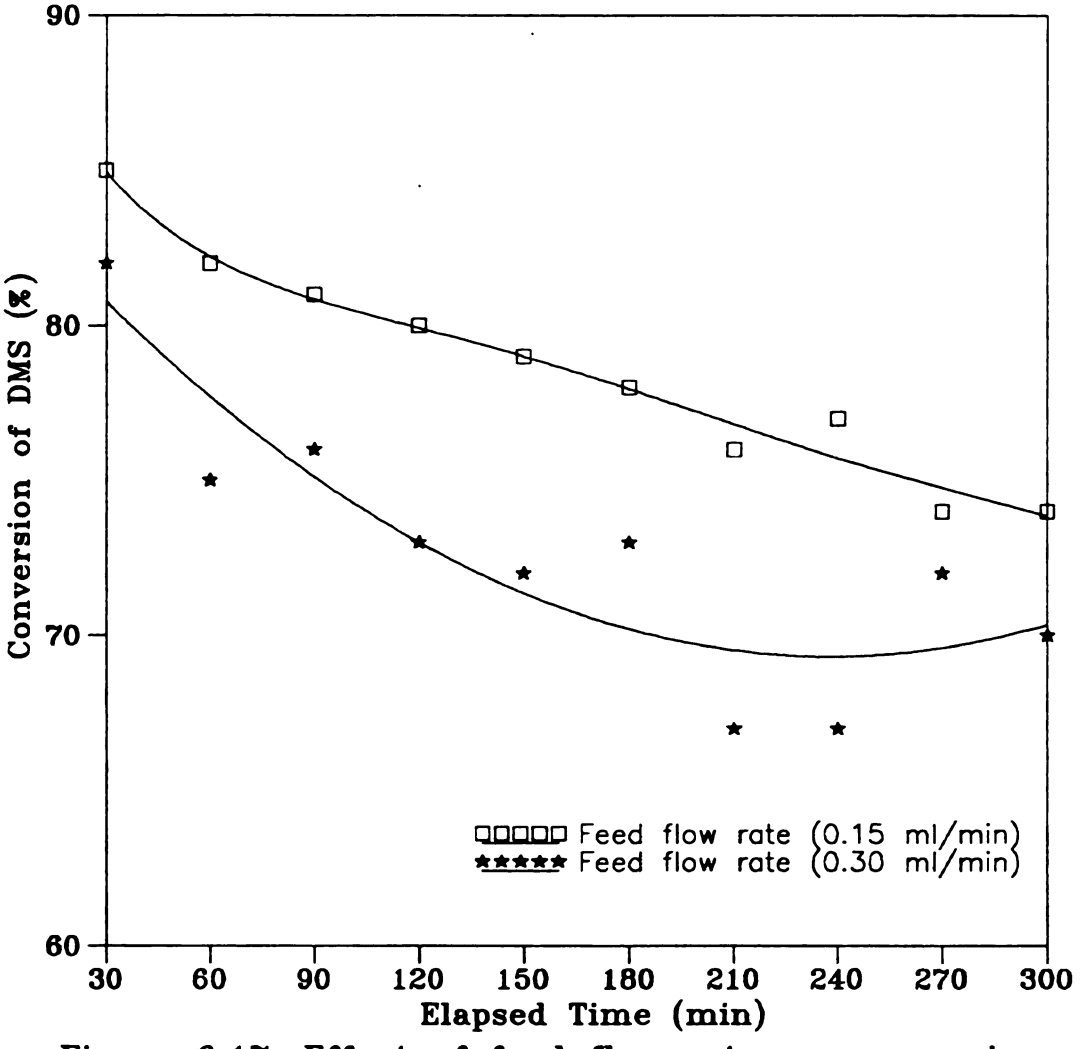

Figure 6.17. Effect of feed flow rate on conversion of DMS (Formalin)

~7% higher than the yields at the flow rates of 18 ml/hr and 27 ml/hr, respectively. Yields of monomethyl succinate and succinic anhydride were not affected by changing the liquid flow rates. The selectivity of citraconic anhydride formation from dimethyl succinate was not affected much by different liquid feed flow rates because yields of citraconic anhydride and conversions of dimethyl succinate were changed in same proportion by changing the liquid flow rate.

6.6.5. Feed Molar Ratio

The effect of molar ratio of formaldehyde to dimethyl succinate in the feed was also comprehensively studied for the formation of citraconic anhydride from dimethyl succinate and formaldehyde. Several different molar ratios of formaldehyde to dimethyl succinate (4:1, 2:1, 1:1, and 0.5:1) were studied for the reaction. Reaction conditions were same as the base case except a liquid feed flow rate of 0.30 ml/min and a gas flow rate of 55 ml(STP)/min was used. The molar concentration of dimethyl succinate, hence WSHV (kg DMS/kg*hr), was kept constant for each run with different feed molar ratio but the same liquid and gas flow rates; and this was done by diluting the feed mixture as needed with a mixture of methanol and water. The relative molar concentration of methanol and water was kept the same as their relative molar concentration in Formcel.

Effect of feed molar ratio on yields of citraconic anhydride, conversions of dimethyl succinate, selectivities of citraconic anhydride from dimethyl succinate, yields of monomethyl succinate, and yields of carbon dioxide are given in Figure 6.18, Figure 6.19, Figure 6.20, Figure 6.21, and Figure 6.22 respectively.

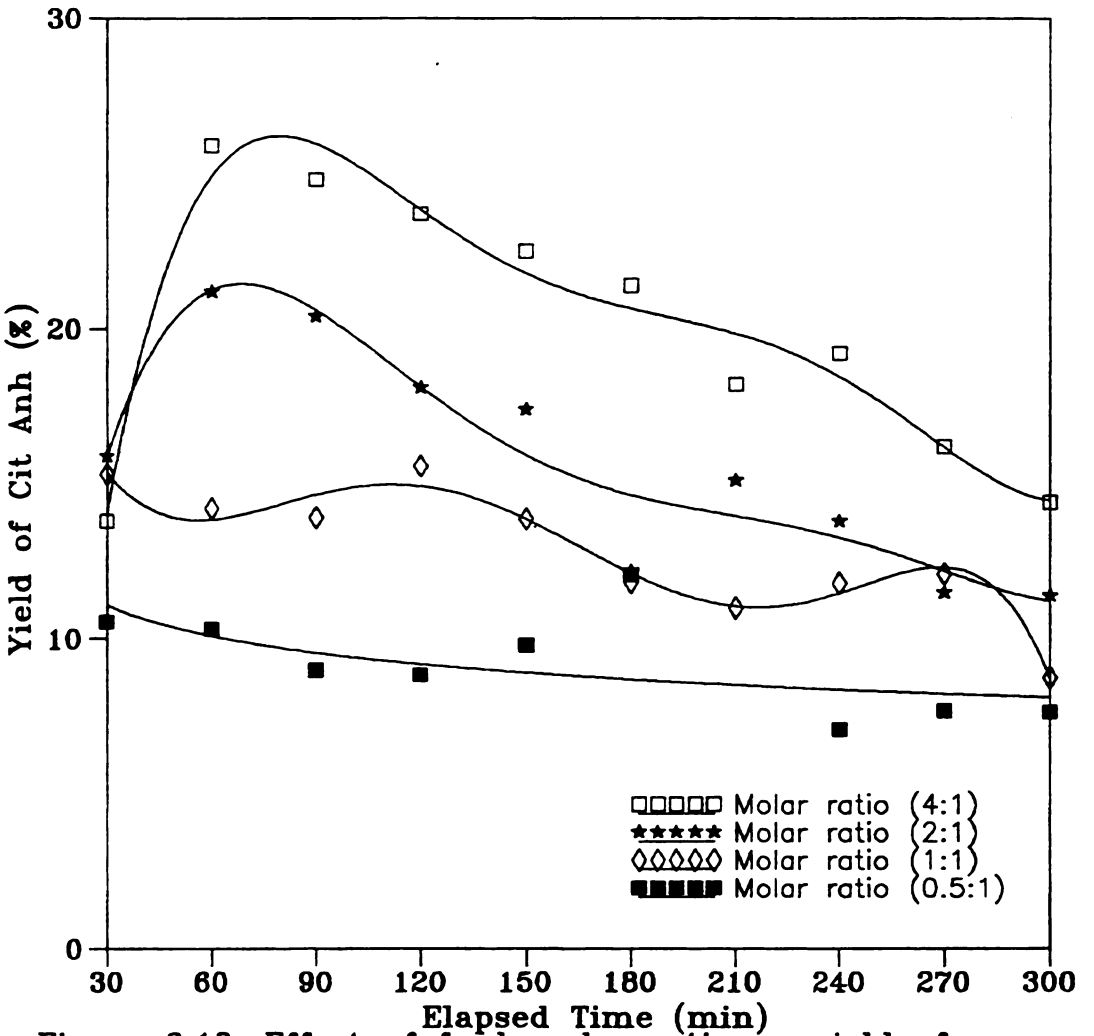

Figure 6.18. Effect of feed molar ratio on yield of citraconic anhydride

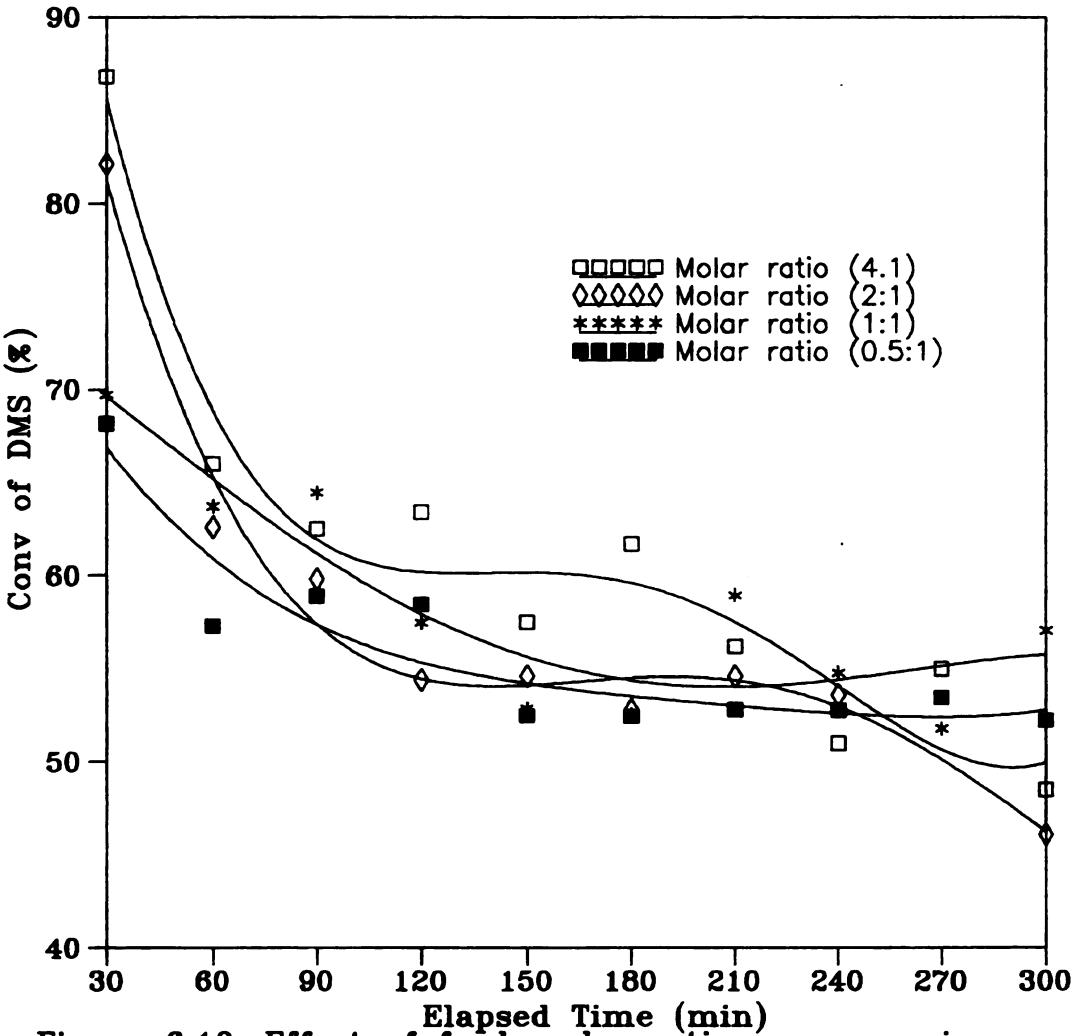

Figure 6.19. Effect of feed molar ratio on conversion of dimethyl succinate

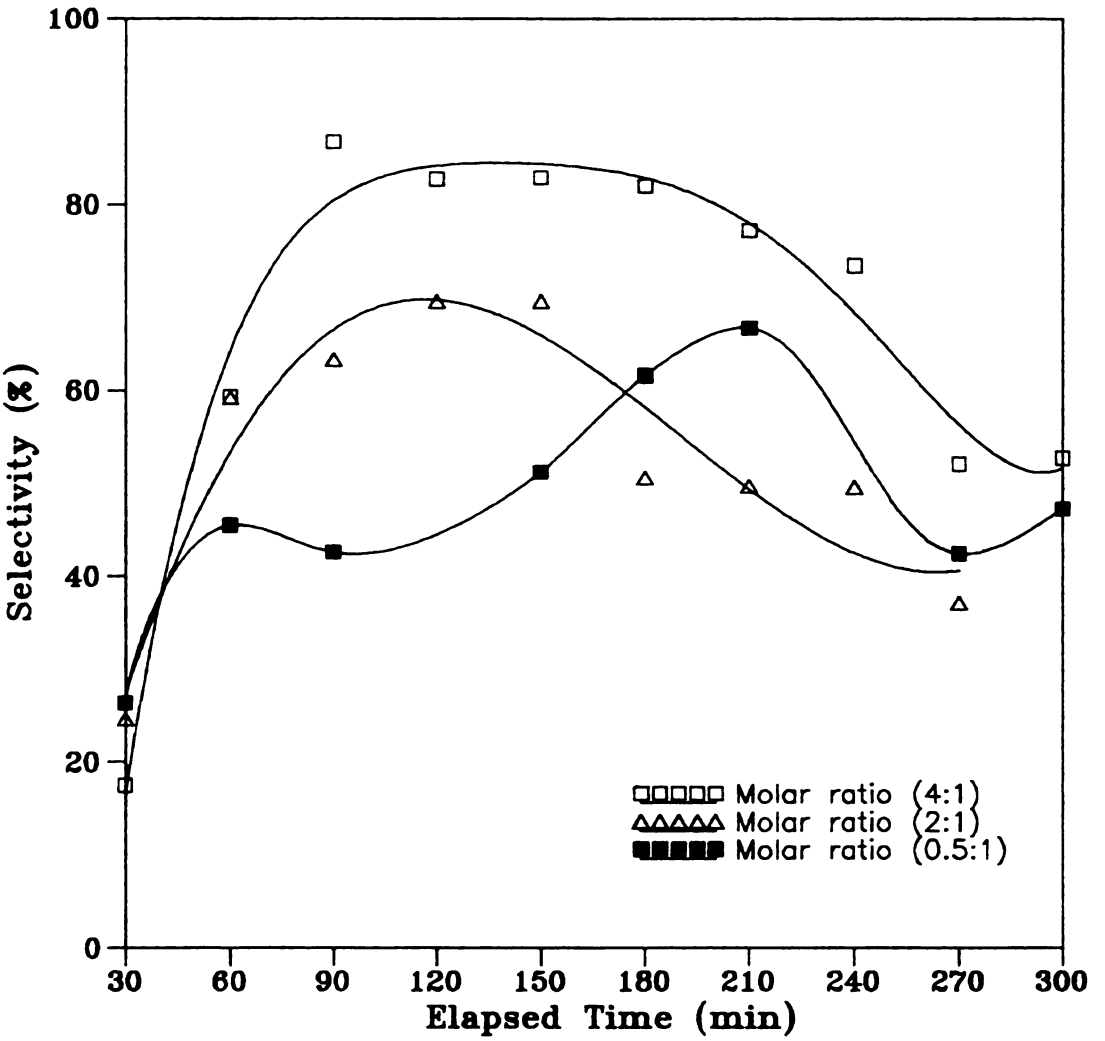

Figure 6.20. Effect of feed molar ratio on selectivity

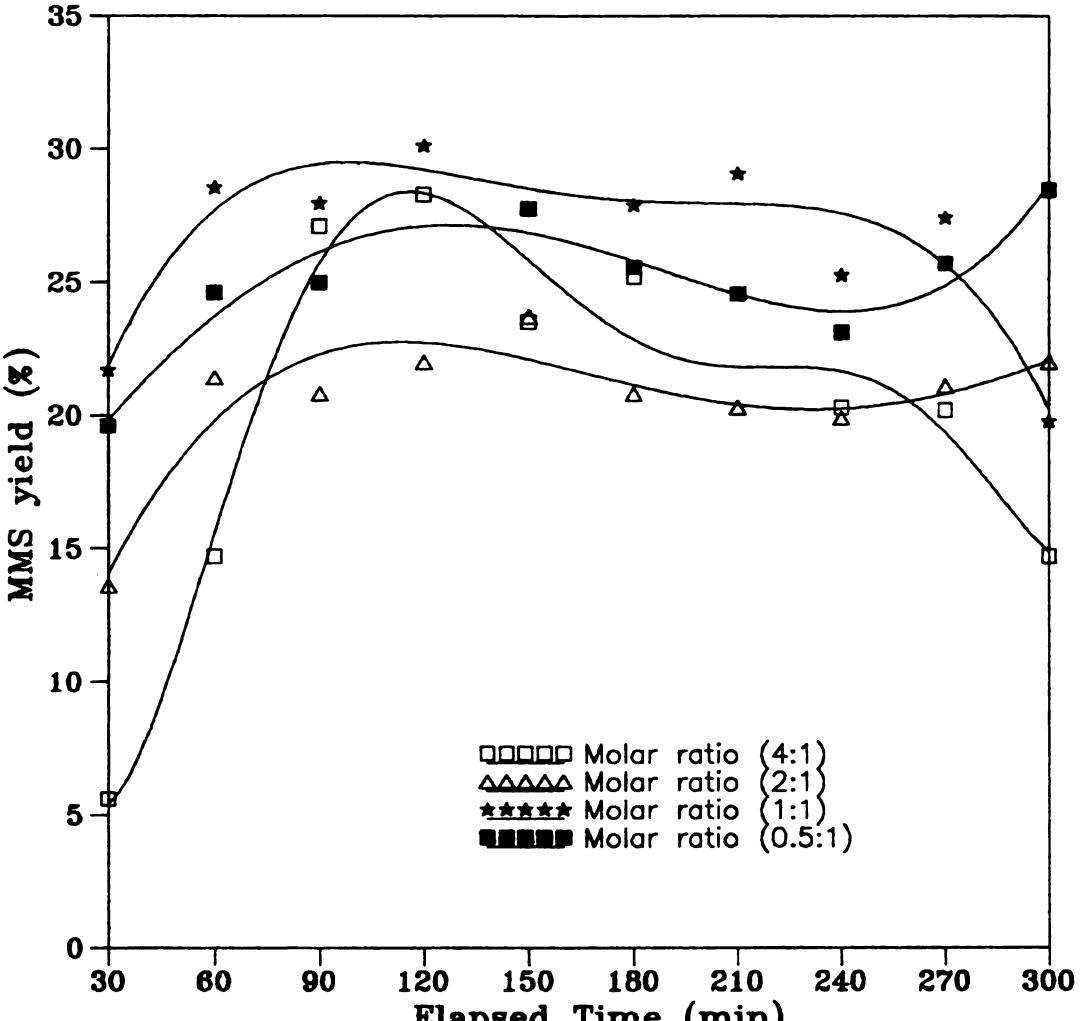

Figure 6.21. Effect of feed molar ratio on MMS yield

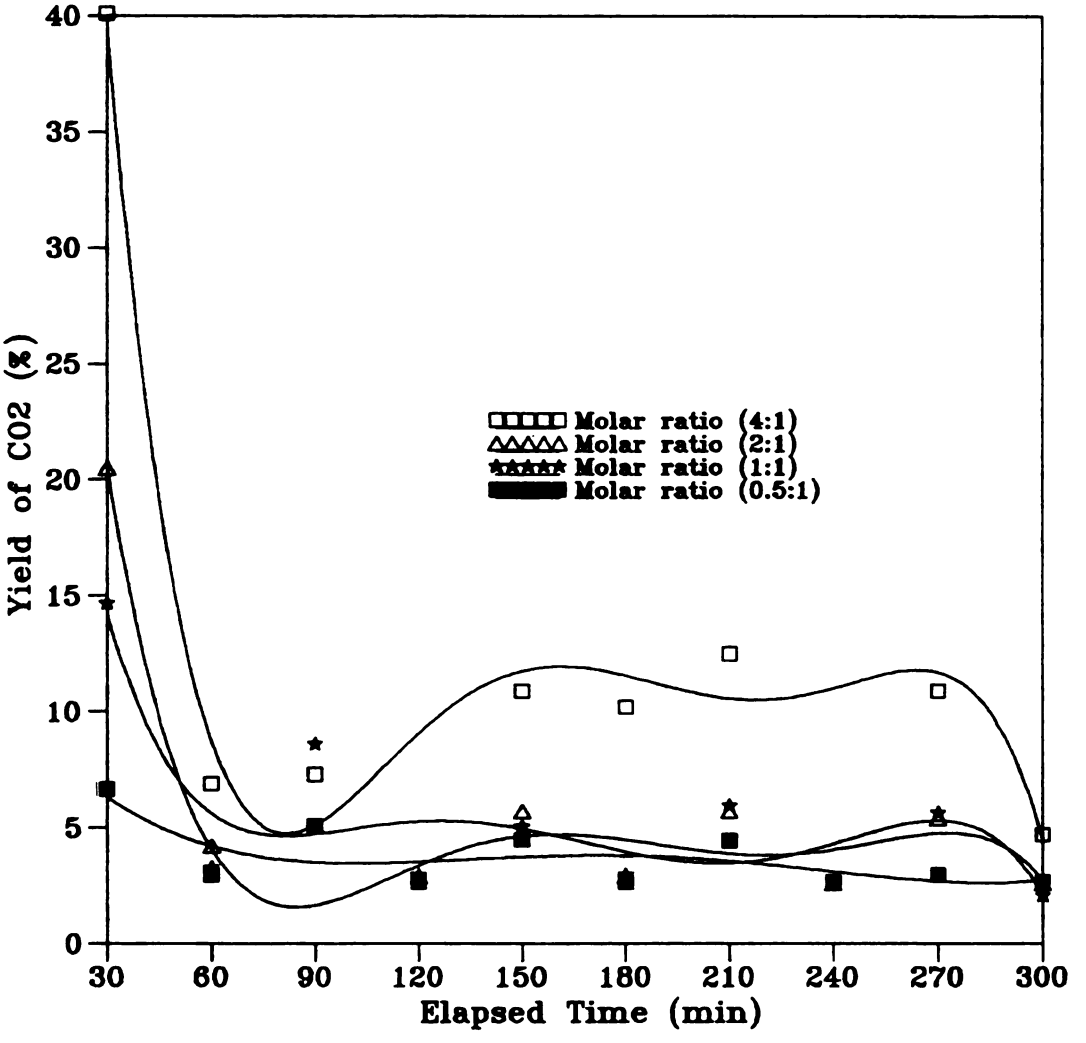

Figure 6.22. Effect of feed molar ratio on yield of CO_2

Yield of citraconic anhydride was increased with increasing feed molar ratio of formaldehyde to dimethyl succinate. A maximum 26% yield of citraconic anhydride at 66% conversion of dimethyl succinate was achieved from 4 to 1 molar ratio of formaldehyde to dimethyl succinate, whereas feed with lean in formaldehyde gave 11% yield of citraconic anhydride at 57% conversion of dimethyl succinate. The difference in conversion of dimethyl succinate from different feed molar ratio was not as pronounced as in the yield of citraconic anhydride. Thus, the selectivity of citraconic anhydride from dimethyl succinate increased with increasing the feed molar ratio of formaldehyde to dimethyl succinate. Yield of carbon dioxide from the reaction increased slightly with increasing the feed molar ratio of formaldehyde to dimethyl succinate. Yield of monomethyl succinate decreased with increasing the feed molar ratio, because the water content of feed, responsible for de-esterification of dimethyl succinate, decreased with increasing the feed molar ratio.

Product samples from each feed molar ratio studied were hydrolyzed to check the overall yields of citraconates. The catalyst weight gain after the completion of the reaction decreased with decreasing the molar ratio, because the feed lean in formaldehyde contained more water, which tends to clean the coke deposited on the catalyst surface.

6.6.6. Effect of Temperature

The effect of temperature on the formation of citraconic anhydride from dimethyl succinate and Formalin over SA3177 was also studied. Reactions were performed at 350 °C and 380 °C, keeping all other reaction conditions unchanged. The effect of

temperature on citraconic anhydride yield (unhydrolyzed results), dimethyl succinate conversion, carbon dioxide yield, and selectivity is shown in Table 6.4.

Table 6.4. Effect of temperature on results[1]

Elapsed Time (min)	Yield of citraconic anhydride (%)		Conversion of DMS (%)		Yield of CO_2 (%)		Selectivity (%)	
	350 °C	380 °C	350 °C	380 °C	350 °C	380 °C	350 °C	380 °C
30	12	18	50	46	24	22	23	61
60	15	26	30	42	10	8	52	61
90	17	26	21	43	8	10	78	51
120	16	22	21	37	8	6	77	59
150	15	21	21	40	6	6	75	52
180	15	23	19	35	7	4	76	63
210	13	20	20	40	5	5	67	50
240	12	20	15	33	5	6	79	59
270	13	20	15	33	5	5	87	58
300	12	18	15	27	4	5	82	58

[1]Reaction conditions: Pressure = 60 psi; feed = dimethyl succinate + Formalin (1 to 2 molar ratio of DMS to formaldehyde); liquid feed flow rate = 0.15 ml/min; outlet gas flow rate = 27 ml(STP)/min; pre-heat temperature = 200 °C.

Higher yields of citraconic anhydride were achieved at 380 °C. The conversion of dimethyl succinate increased with increasing temperature. It is noteworthy that selectivity to citraconic anhydride was highest at 350 °C. At higher temperature,

succinates cracked into carbon monoxide and carbon dioxide, resulting in high conversion of succinates and lower selectivity.

6.6.7. Particle size

A smaller size (60/100 mesh) of catalyst particles was also utilized for the condensation of dimethyl succinate and formaldehyde to observe the mass transfer effects. Identical results were observed from 60/100 mesh size and 30/60 mesh size catalyst particles, suggesting that the condensation reaction is not mass transfer limited.

6.6.8. Longer Reactor Catalyst Bed

The condensation reaction of dimethyl succinate and Formalin was also conducted with a longer reactor catalyst bed to see the effects of catalyst bed length or weight hourly space velocity (WHSV) on the desired results. Table 6.5 gives the summary of a series of experiments, which were carried out to see the effects of catalyst bed length on the results.

Effects of catalyst bed length on yields of citraconic anhydride, conversions of dimethyl succinate, selectivities of citraconic anhydride from dimethyl succinate, and yields of carbon dioxide from the reaction of dimethyl succinate and Formalin over SA3177 are given in Figure 6.23, Figure 6.24, Figure 6.25, and Figure 6.26, respectively. Yield of citraconic anhydride, yield of carbon dioxide evolved from the reaction, and conversion of dimethyl succinate increased with increasing the catalyst bed length, keeping other reaction conditions unchanged. The conversion of dimethyl succinate was not changed with changing catalyst bed length if the WSHV was kept constant by

Table 6.5. Summary of experiments conducted to see WHSV effects[1]

Experiment	Weight of catalyst used (g)	Liquid flow rate (ml/min)	WHSV[2]
Shorter reactor (FR = 0.15 ml/min)	5.2	0.15	0.90
Longer reactor (FR = 0.15 ml/min)	11.0	0.15	0.45
Longer reactor (FR = 0.30 ml/min)	11.2	0.30	0.90
Longer reactor (FR = 0.30 ml/min)[3]	11.3	0.30	0.90

[1]Reaction conditions: Temperature = 350 °C; Pressure = 60 psi; feed = dimethyl succinate + Formalin (1 to 2 molar ratio of DMS to formaldehyde); outlet gas flow rate = 27 ml(STP)/min; pre-heat temperature = 200 °C.
[2]Weight Hourly Space Velocity (WHSV) = kg succinate/(kg catalyst * hr).
[3]This was a repeat of previous experiment to check reproducibility.

adjusting the liquid flow rate, which shows that the reactor exhibits predictable behavior regarding WHSV. However, the yield of citraconic anhydride decreased with increasing bed length at constant WSHV, which suggests that the extra length of catalyst bed led to cracking of citraconic anhydride. Better selectivity for citraconic anhydride formation was observed with a shorter reactor catalyst bed or at lower WSHV. Yields of monomethyl succinate followed the dimethyl succinate conversion trends with the catalyst bed length and WSHV.

6.6.9. Hydrolysis

Hydrolysis of the reaction products from the reaction of dimethyl succinate and Formalin was carried out to convert all citraconates to citraconic acid and succinates to succinic acid. Four product samples out of total ten samples collected from the each run were usually hydrolyzed using the method described in Section 2.8. Table 6.6 shows

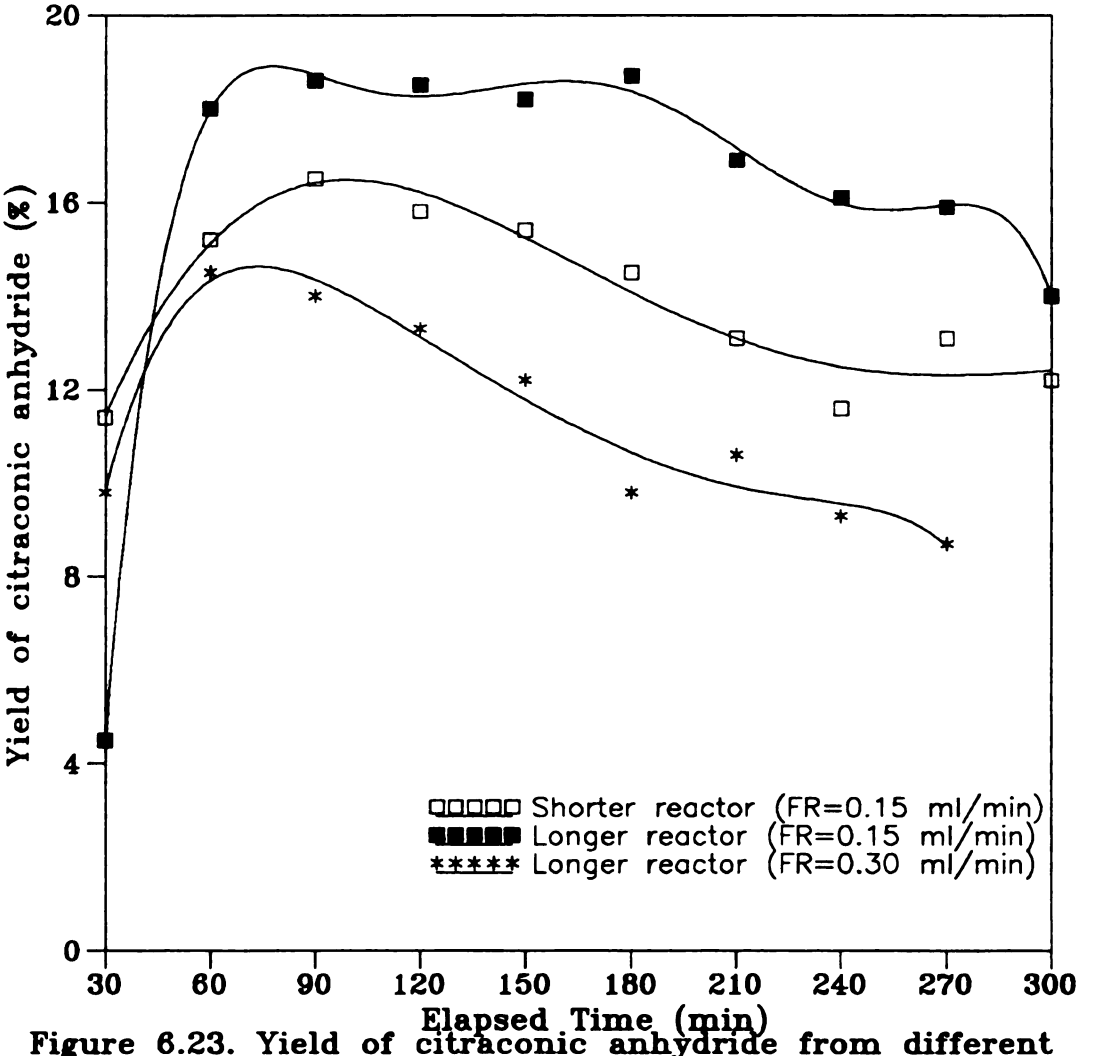

Figure 6.23. Yield of citraconic anhydride from different size catalyst beds

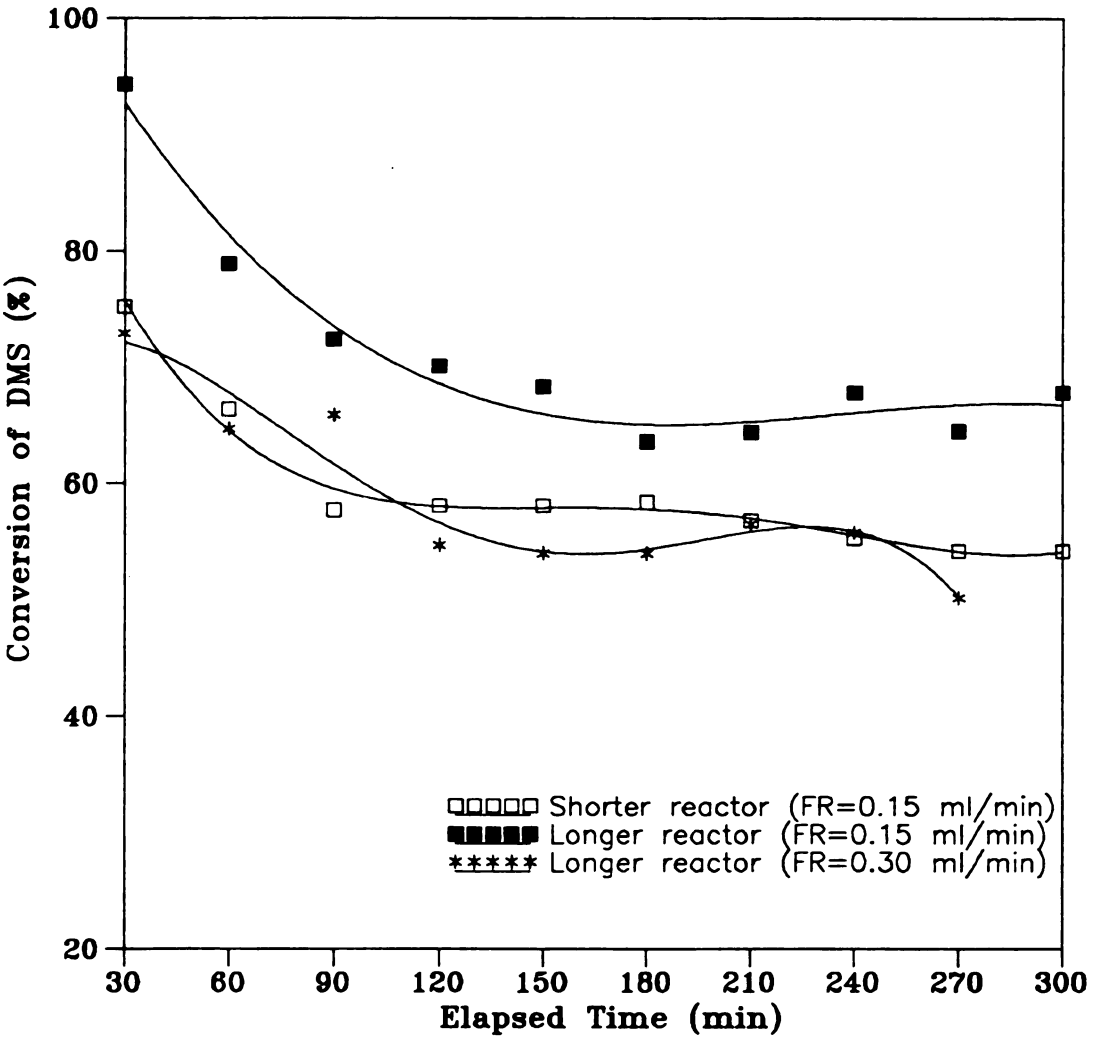

Figure 6.24. Conversion of dimethyl succinate from different size of catalyst beds

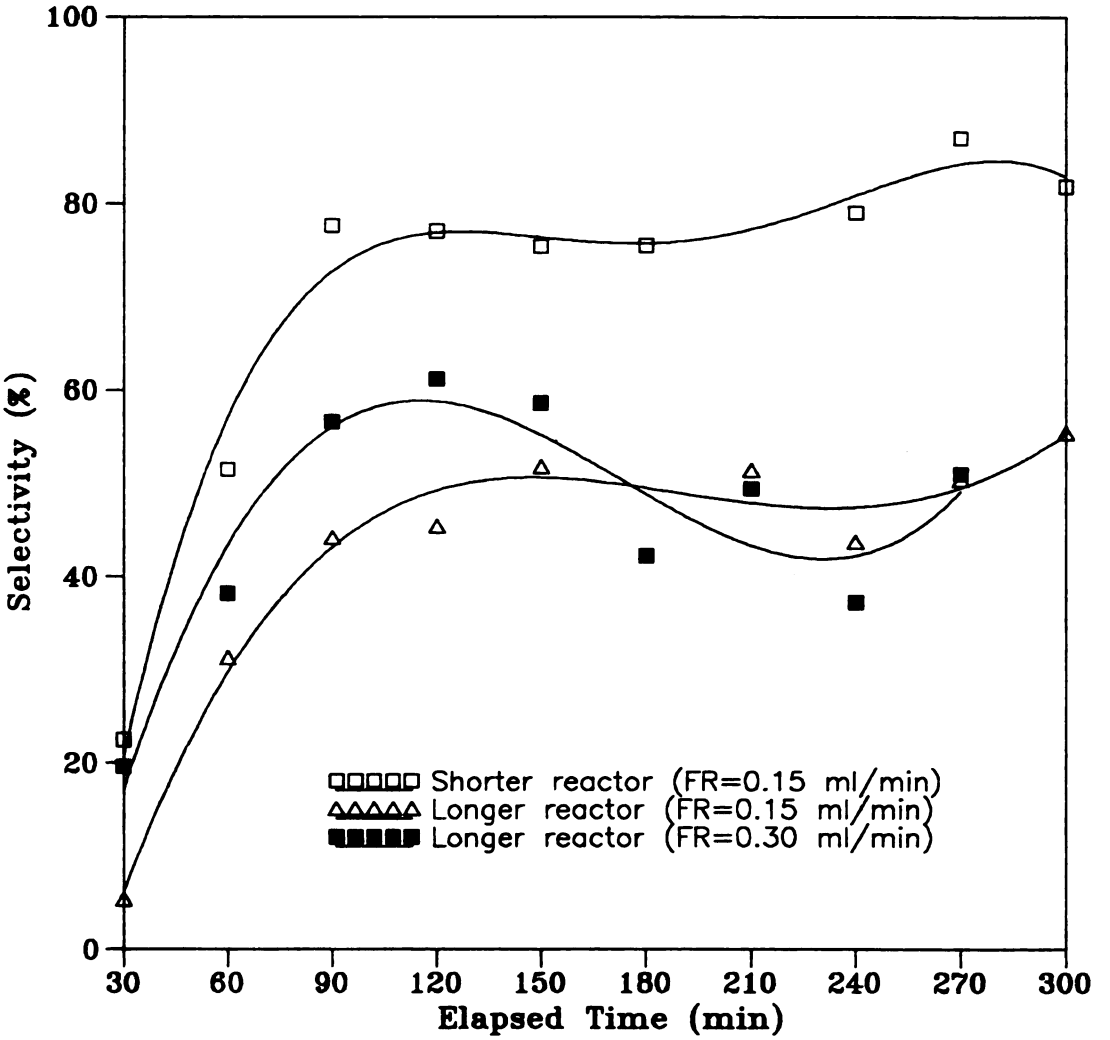

Figure 6.25. Selectivity from different size of catalyst beds

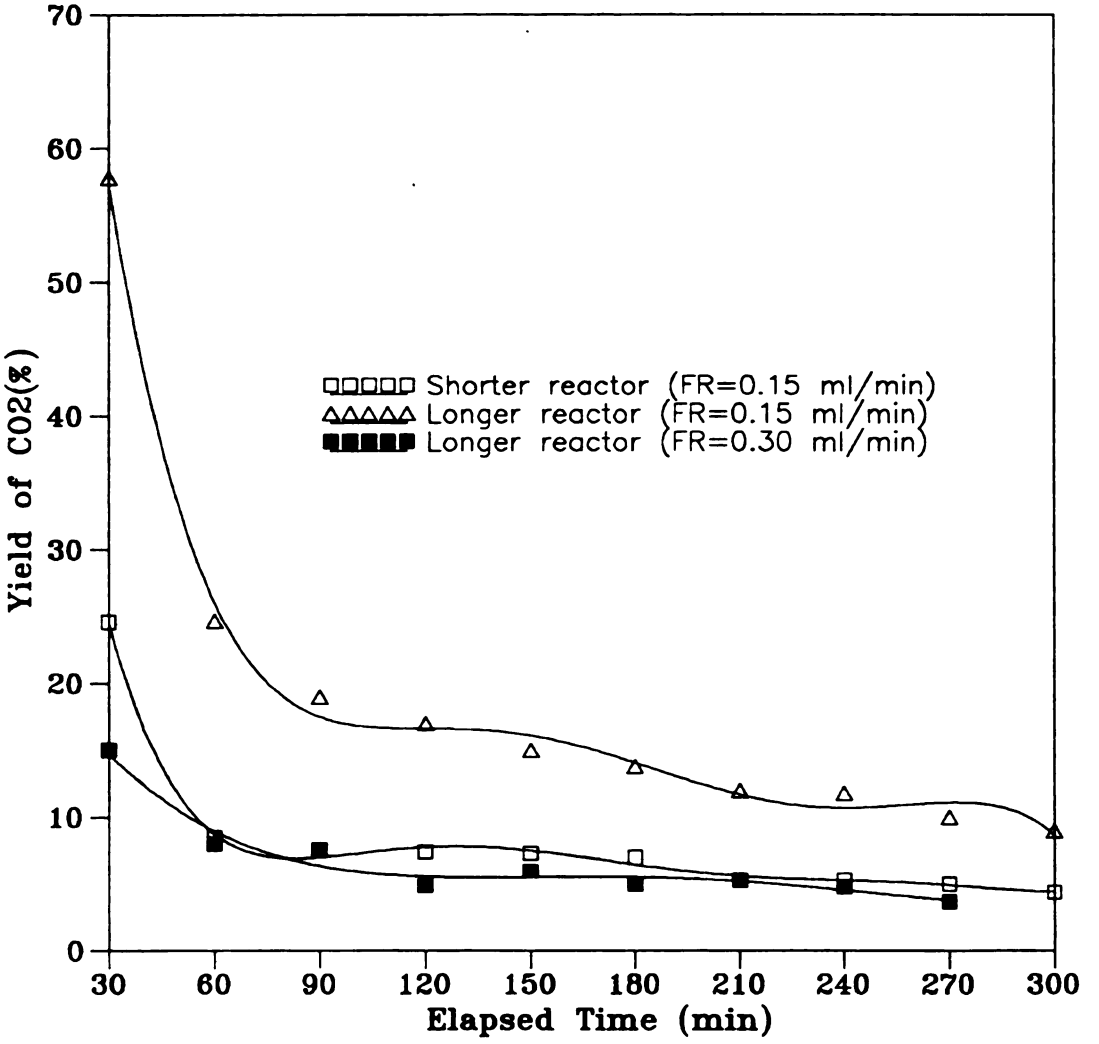

Figure 6.26. Yield of carbon dioxide from different size of catalyst beds

results where all yields, conversions, and selectivities are based on hydrolyzed results. The yield of citraconates after hydrolysis usually increased by 20% over the unhydrolyzed yields.

Table 6.6. Results before and after hydrolysis of product[1]

Elapsed Time (min)	Yield of citraconates (%)		Conv of Succinates (%)		Selectivity[2] (%)
	Before	After	Before	After	
60	26	26	42	55	48
90	26	29	45	42	70
180	23	26	37	46	57
240	20	25	30	42	60

[1]Reaction conditions: Temperature = 380 °C; pressure = 60 psi; feed = dimethyl succinate and Formalin (1 to 2 molar ratio of DMS to formaldehyde); liquid feed flow rate = 0.15 ml/min; outlet gas flow rate = 27 ml(STP)/min; pre-heat temperature = 200 °C.
[2]Selectivity is based on hydrolyzed products.

6.7. Catalyst Deactivation Studies

Catalyst deactivation was much slower with dimethyl succinate and Formalin and, hence, the conversion of dimethyl succinate and yield of citraconic anhydride decreased very little over time. The catalyst weight gain was much less pronounced from dimethyl succinate and Formalin feed, because the water present reacts with the coke deposited to clean the catalyst during the reaction. The catalyst weight gain of 0.9 g was observed after five hours of reaction from dimethyl succinate and Formalin feed, whereas the catalyst gain was 1.5 g after five hours of the reaction from dimethyl succinate and trioxane feed. In early stages of the reaction, catalyst activity was not very extensive for

the reaction of Formalin and dimethyl succinate, unlike the reaction of dimethyl succinate and trioxane where excessive cracking of succinates and very low yield of citraconic anhydride were observed in the beginning of the reaction.

Coking was observed from dimethyl succinate and Formalin feed over all catalyst materials used except glass beads. The rate of catalyst activity decay depends upon the coke deposited on the catalyst material during reaction from the cracking of reactants or products. Coking results in the catalyst weight gain over time. The rate of the cracking reaction depends upon surface properties such as surface area, surface acidic site concentration, and type of acidity and reaction conditions such as temperature, feed flow rate, and feed material. Thus, the catalyst weight gain is directly related to the surface properties of the catalyst material if reaction conditions are unchanged. Table 6.7 gives the catalyst weight gain over different catalyst materials used for the reaction of Formalin and dimethyl succinate.

It was obvious from control experiments that coking involved the reactants, succinate and formaldehyde, and the product, citraconic anhydride.

6.8. Catalyst Regeneration

The catalyst loses its activity upon its prolonged exposure to the reactants for the formation of citraconic anhydride. To prove that catalyst activity can be recovered by catalyst regeneration is very crucial for this process to be commercially viable. It has already been shown that the regenerated catalyst was as good as the fresh catalyst for the reaction (see Section 4.12). It was decided to confirm these results described in Section 4.12 with Formalin and dimethyl succinate at optimal reaction

Table 6.7. Catalyst weight gain from different catalyst materials[1]

Catalyst	Wt. before expt (g)	Wt. after expt (g)	Wt. gain (g)	Wt. gain (%)[2]	Reaction Time (hr)
Beads	13.00	13.02	0.02	0	2
SA3177	5.26	6.20	0.94	18	5
SA3177[3a]	5.32	6.20	0.88	17	5
SA3177[3b]	5.30	6.50	1.20	22	5
SA3177[3c]	5.24	6.45	1.21	23	5
SA3177[3d]	5.50	7.08	1.58	29	5
SA3177[3e]	5.20	5.95	0.75	14	5
SA3177[3f]	11.00	13.54	2.54	23	5
98 Al + 2 Mg	6.74	7.89	1.15	17	5
96 Al + 4 Mg	5.03	6.34	1.31	26	5
94 Al + 6 Mg	4.50	5.66	1.16	26	5
88 Al + 12 Mg	4.85	7.00	2.15	44	5
Alumina(AlH)	6.30	7.88	1.58	25	2.5
AlPO (P/Al=1)	1.90	3.40	1.50	79	5
AlPO(P/Al=0.5)	2.15	3.28	1.13	53	5

[1]Catalyst weight gains are given at the base case conditions, otherwise specified.
[2]Wt. gain (%) = (wt. after expt – wt. before expt)*100/wt. before expt.
[3a]CO_2 as a carrier gas; [3b]0.15 mmol KH_2PO_4/g supported SA3177; [3c]Liquid feed flow rate = 0.30 ml/min; [3d]Formcel is used as a formaldehyde source; [3e]T = 350 °C; [3f]Longer catalyst bed used.

conditions for the process. The catalyst regeneration process illustrated in Section 4.12 was followed here to regenerate the catalyst upon deactivation. Reactions of Formalin and dimethyl succinate over fresh and regenerated catalyst were conducted at identical conditions. Yields of citraconic anhydride and conversion of succinates were identical for both fresh and regenerated catalysts (Table 6.8). This suggests that coke residual on catalyst surface decreases the activity of catalysts and also indicates that other means of deactivation are less probable.

Table 6.8. Yield of citraconic anhydride before and after the regeneration of catalyst[1]

Elapsed Time (min)	Yield of Citraconic Anhydride (%)		Yield of CO_2 (%)		Conversion of DMS (%)	
	Before	After	Before	After	Before	After
30	8	8	11	12	77	74
60	12	13	5	5	57	62
90	11	11	8	8	59	63
120	12	11	4	3	54	60
150	10	9	6	6	58	59
180	9	10	3	2	55	53
210	12	10	5	5	47	50

[1]Reaction conditions: Temperature = 380 °C; pressure = 60 psi; feed = dimethyl succinate + Formalin (1 to 2 molar ratio of DMS to formaldehyde); liquid feed flow rate = 0.20 ml/min; outlet gas flow rate = 27 ml(STP)/min; pre-heat temperature = 200 °C.

6.9. Summary

The reaction of dimethyl succinate and formaldehyde in the vapor phase over various catalysts was performed at the base case conditions. Commercially available formaldehyde solutions such as Formalin and Formcel were used as a source of formaldehyde for the reaction. Optimization of reaction conditions for the reaction of dimethyl succinate and Formalin over SA3177 was conducted to maximize citraconic anhydride yields. These studies involved changing feed compositions, temperature, liquid feed and gas flow rate, catalyst particle size, and reactor catalyst bed size to determine the region where both desired product yields were high and the catalyst was stable over time.

Dimethyl succinate and Formalin were proven to be a good feed material combination for the reaction, as decent yields of citraconate were obtained with very good selectivities of citraconates and the catalyst activity was also stable for a longer time. After hydrolysis of raw products, a maximum 29% yield of citraconates at 42% conversion of succinates were observed from the reaction of dimethyl succinate and Formalin over SA3177 at the base case conditions. Dimethyl succinate is not prone to cracking at elevated temperature as is succinic anhydride and, hence, is a more stable compound at the reaction conditions. Formalin is also proven to be advantageous for the desired reaction. First, the decay in catalyst activity was much slower with Formalin as yields of citraconic anhydride and conversion of dimethyl succinate only dropped off very slowly over time for reaction times out to five hours. Second, the gain in the catalyst weight due to coking was much less with Formalin, likely because the water present cleans the catalyst during the reaction. Excessive water present in Formalin also

causes problem: the excessive water makes the feed dilute and also facilitates de-esterification reactions of dimethyl succinate.

Formcel with dimethyl succinate gave higher yield of citraconates (34% after hydrolysis) compared to Formalin and dimethyl succinate feed. But the rate of catalyst decay was faster with Formcel than Formalin because Formcel contains less water to react with the coke formed. Mass balances from Formcel and dimethyl succinate were also poor due to loss of excessive methanol present in Formcel as dimethyl ether.

Several other catalyst materials were also tested for the reaction of dimethyl succinate and trioxane. It was confirmed that a mildly acidic support in nature like SA3177, without any salts added, showed significant activity for the formation of citraconates from succinates. Higher surface area or highly acidic supports were found to be very active for cracking reaction of dimethyl succinate. Also, the coke-forming tendency is directly related to the acidity of supports. The results observed with hydrotalcites are in accord with those of other catalysts regarding the surface acidity or basicity properties required for an active catalyst.

The condensation reaction of dimethyl succinate with Formalin over intermediate surface area alumina is not mass transfer limited. Higher formaldehyde to dimethyl succinate molar ratio gave better yields and selectivities of citraconic anhydride. Carbon dioxide as a carrier gas did not make any significant difference in yields or in the catalyst activities. Yield of citraconic anhydride decreased with increasing liquid feed flow rate, but selectivity remained unchanged. Yield of citraconic anhydride increased with increasing the reaction temperature, but selectivity lowered due to more cracking of dimethyl succinate at elevated temperatures. Citraconic anhydride yields were increased

with increasing the catalyst bed length, but selectivities decreased. The regenerated catalyst upon deactivation reproduced the fresh catalyst results.

CHAPTER 7

REACTOR MODELING

7.1. Pressure Drop calculation

The feed flow rates from a typical experiment are given in Table 7.1. The total liquid flow rate to the reactor is 9.0 ml/hr.

Table 7.1. Flow rates at the reactor inlet

Species	Volumetric flow rate (ml/hr)	Mass flow rate (g/hr)	Molar flow rate (mol/hr)
DMS	4.0	4.47	0.0306
Formalin	5.0	5.40	
Formaldehyde		2.00	0.0666
Water		2.81	0.1560
Methanol		0.59	0.0186
Helium	3300 @ 298°C	0.27	0.0663
Total	9.0 (liquid)	10.13	0.3380

Total vapor flow rate = 0.3380 mol/hr

= 3622 cm^3/hr @ reaction conditions(T=380°C and P=5 atm)

Reactor tube diameter (D) = 1.12 cm

Superficial vapor velocity at the inlet of the reactor (v)

$$v = \left(\frac{3622\,cm^3}{hr}\right) \times \left(\frac{hr}{3600\,sec}\right) \div \left(3.14 \times (1.12\,cm/2)^2\right)$$

v = 1.03 cm/sec

Density of feed at reaction conditions (ρ)

= (4.47 g/hr + 5.4 g/hr + 4*0.0663 g/hr)/(3622 cm^3/hr)

ρ = 0.0028 g/cm^3

The viscosity of the feed at reaction conditions (μ) is taken as an average of water and helium,

μ = 0.026 cp (air's viscosity @ 380 °C and 1 atm)

μ = 2.6 x 10^{-3} g/(cm.sec)

Bed porosity (ε) = 0.7

Particle size (D_p) = 0.038 cm (30/60 mesh size)

Ergun's pressure drop equation (77);

$$\frac{\Delta P}{\Delta L} = \left(\frac{\rho v}{\rho D_p}\right)\left(\frac{1-\varepsilon}{\varepsilon^3}\right)\left[\left(\frac{150(1-\varepsilon)\mu}{D_p}\right) + 1.75\rho v\right] \qquad (I)$$

Substituting values from above in equation (I), we have

$\Delta P/\Delta L$ = 7 $g/cm^2.sec^2$

$\Delta P/\Delta L = 70$ Pa/m

Catalyst bed length = 8 cm = 0.08 m, then

$\Delta P = 6$ Pa = 5.8×10^{-5} atm = 0.0009 psi

This is an extremely small number; thus for typical WSHV we do not expect pressure drop to be a limiting factor.

Reynolds number for the packed bed (Re_p)

$$Re_p = \frac{D_p \rho v}{(1-\varepsilon)\mu} \qquad \text{(II)}$$

$Re_p = 0.42$

Similarly, Reynolds number for the reactor tube (Re_{tube})

$Re_{tube} = 12$

7.2. Mass Transfer Calculations

7.2.1. Calculation of Observable Rate

Assume flow through reactor is steady state and constant volume.

The rate equation for DMS is given by

$$\frac{dF_{DMS}}{dV_R} = -(1-\varepsilon_B)(R_{obs,\,DMS}) \qquad \text{(III)}$$

Where,

$F_{DMS} = C_{DMS} \times V$ (IV)

where,

C_{DMS} = DMS concentration at any position in the reactor

V = volumetric flow rate @ reaction conditions (5 atm and 380 °C)

is give

X_{DM}

catal

k

$= 3622\ cm^3/hr$

$= 1.01\ cm^3/sec$

V_R = reactor catalyst bed volume

ε_b = bed porosity = 0.7

Assume the reaction is first order in DMS, then the rate of equation (observable) is given by

$$R_{obs.\,DMS} = \eta k C_{DMS} \qquad \text{(V)}$$

η = effectiveness factor (~constant)

k = first order rate constant

Combining equation (III), (IV), and (V) and then rearranging,

$$\frac{dC_{DMS}}{C_{DMS}} = -(1-\varepsilon_B)\eta k d\left[\frac{V_R}{V}\right] \qquad \text{(VI)}$$

Integrating equation (VI) from the reactor inlet to outlet,

$$\ln\left(\frac{C_{DMS}(out)}{C_{DMS}(in)}\right) = -(1-\varepsilon_B)\eta k\left(\frac{V_R}{V}\right) \qquad \text{(VII)}$$

substituting $(C_{DMS}(out)/C_{DMS}(in)) = (1 - X_{DMS})$, where X_{DMS} is conversion of X_{DMS}, and $k' = k\eta$ in equation (VII),

$$\ln(1 - X_{DMS}) = -(1-\varepsilon_B)k'\left(\frac{V_R}{V}\right) \qquad \text{(VIII)}$$

Solving equation (VIII) for k' when $X_{DMS} = 0.8$ (80% conversion of DMS) and catalyst bed volume is 8 cm^3,

$k' = 0.675\ cm^3/(cm^3\ of\ cat.sec)$ (IX)

DMS inlet concentration

$C_{DMS}(in) = (n_{DMS}/n_{Total})P/RT$

(n_{DMS} and n_{Total} from Table 7.1, P = 5 atm, T = 653 K, and R = 82.06 cm^3.atm/(mol.K))

$C_{DMS}(in)$ = 8.5 x 10^{-6} mol/cm^3 (X)

Solving $R_{obs,DMS}$ at inlet of the reactor using values equation (IX), (X), and (V),

$R_{obs,DMS}(in)$ = 5.7 x 10^{-6} mol/(cm^3 of cat.sec) (XI)

7.2.2. Diffusivity Estimation

The diffusivity of a binary gas pair of A (DMS) and B (H_2O) molecules is given by (77),

$$D_{AB} = \frac{1.8583\times10^{-3} T^{3/2}}{P\sigma^2_{AB}\Omega_{D,AB}}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)^{1/2} \quad \text{(XII)}$$

D_{AB} = Diffusivity in cm^2/sec

T = 653 K

P = 5 atm

M_A = 146 and M_B = 18

σ_{AB} = average collision diameter based on the Lennard-Jones potential

$\Omega_{D\text{-}AB}$ = collision integral based on the Lennard-Jones potential

= 1.0 (assume not much interactions between DMS and water)

$\sigma_{AB} = (\sigma_A + \sigma_B)/2$ (XIII)

σ_B = 3.6 A (from (78)) (XIV)

σ_A is estimated from molar volumes,

$\sigma_A = 1.18V_p^{1/3}$ (from (78)) (XV)

V_p = (# of C atoms in A)*V_p(C) + (# of O_2 in A)*V_p(O) + (# of H_2 atoms in A)*V_p(H) (XVI)

Substituting molar volumes from (78) in equation (XVI)

V_p = 6*14.8 + 4*9.1 + 10*3.7

V_p = 162.2 cm^3/mol (XVII)

From equations (XV) and (XVII),

σ_A = 6.4 A (XVIII)

From equation (XIII), (XIV), and (XVIII),

σ_{AB} = 5.0 A

Now, substituting values in equation (XII)

D_{AB} = 5.7 x 10^{-2} cm^2/sec

Effective diffusivity ($D_{e,AB}$),

$D_{e,AB}$ = (ϕ_p^2) D_{AB} (XIX)

ϕ_p = particle porosity ~ 0.4 (low)

$D_{e,DMS}$ = 9.1 x 10^{-3} cm^2/sec

7.2.3. Calculation for Observable Modulus

Observable modulus is give by

$$\eta\phi^2 = \frac{R_{obs,\,DMS}(in)L^2}{D_{e,\,DMS}C_{DMS}(in)} \quad \text{(XX)}$$

L = particle size = 0.038 cm (30/60 mesh size)

Substituting values from previous sections into equation (XX), we obtain

$\eta\varphi^2$ = 0.107

The small value of the observable modulus suggests that the reaction is not significantly mass transfer limited. Uncertainties in this calculation arise from $D_{e,DMS}$, and $R_{obs,DMS}$. The calculated modulus is calculated at the extreme conditions at the inlet of the reactor; the value given above is a upper limit for modulus.

7.3. Residence Time and WSHV Calculation

Residence time (τ, sec) for fixed-bed reactor is given by,

$$\tau = \left(V_R - \frac{W_B}{\rho_{cat}} \right) \div V \qquad \text{(XXIII)}$$

V_R = Reactor volume = 8 cm^3

W_B = weight of the catalyst bed = 5.2 g

ρ_{cat} = density of the catalyst without pores = 2.31 g/cm^3

V = Total vapor flow to the reactor (from Section 7.1)

= 3622 cm^3/hr = 1.01 cm^3/sec

Substituting values of V_R, W_B, ρ_{cat}, and V in equation (XXIII),

τ = 5.7 sec

The Weight Hourly Space Velocity (WHSV) is the ratio of the mass flow rate of DMS to the mass of the catalyst used (W_B). The mass flow rate of DMS to the reactor is 4.47 g/hr (Table 7.1), hence

WSHV = (4.47 g of DMS/hr)/(5.2 g of catalyst)

WSHV = 0.86 g of DMs/(g of cat*hr)

7.4. Kinetic Modeling

A kinetic model for the formation of citraconic anhydride from dimethyl succinate and formaldehyde over γ-alumina (SA3177) has been developed. An analysis gives the observable modulus $\eta\phi^2$ (Section 7.2.3) of less than 0.10 for γ-alumina (SA3177) at all reaction conditions with the diffusitivity of 9.1 x 10^{-6} cm^2/sec (Section 7.2.2), indicating negligible mass transport limitations within the support material. Thus, the intrinsic kinetic rate constants can be obtained from the experimental data. The reactions included in the kinetic model are listed in Figure 7.1.

7.4.1. Calculation of Rate Constants from Control Experiments

7.4.1.1. Citraconic Anhydride Cracking Reaction

Carbon dioxide was the only product formed from citraconic anhydride at the base case conditions. It is assumed that the cracking reaction of citraconic anhydride (Reaction 2 in Figure 7.1) is a first order reaction; the rate expression is given by:

$$\frac{dC_c}{d\tau} = -k_7 C_c \qquad \text{(I)}$$

Solving differential equation (I) will give:

$$C_c = C_{c0} e^{-k_7 \tau} \qquad \text{(II)}$$

Or $X_c = 1 - e^{-k_7 \tau}$ (III)

where,

C_c (moles/l) = concentration of citraconic anhydride at the time τ,

C_{c0} (moles/l) = concentration of citraconic anhydride at τ = 0,

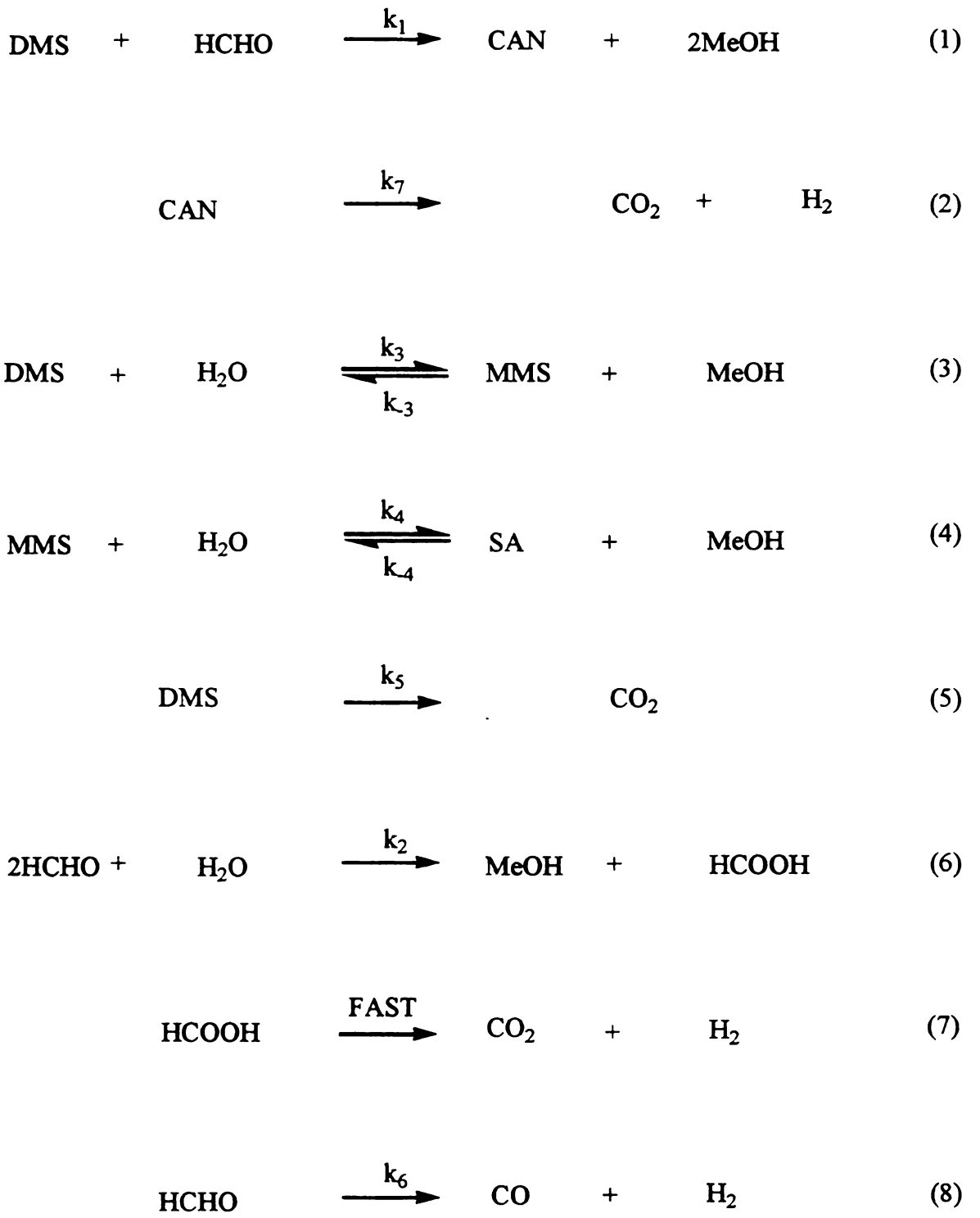

Figure 7.1. List of reactions included in the kinetic model (DMS = dimethyl succinate, MMS = monomethyl succinate, SA = succinic acid, and CAN = citraconic anhydride)

X_c = fractional conversion of citraconic anhydride at the τ

k_7 (sec^{-1}) = first order rate constant for the cracking reaction

τ (sec) = residence time

At the steady state, τ = 10.7 sec and X_c = 0.20; solving equation (III) for k_7,

$$k_7 = 0.021\,\text{sec}^{-1} \qquad \text{(IV)}$$

7.4.1.2. Dimethyl Succinate Cracking Reaction

The rate expression for the cracking reaction of dimethyl succinate (Reaction 5 in Figure 7.1) is given by:

$$\frac{dC_d}{d\tau} = -k_5 C_d \qquad \text{(V)}$$

Solving differential equation (V) will give:

$$C_d = C_{d0} e^{-k_5 \tau} \qquad \text{(VI)}$$

Or $$X_d = 1 - e^{-k_5 \tau} \qquad \text{(VII)}$$

where,

C_d (moles/l) = concentration of dimethyl succinate at the time τ,

C_{d0} (moles/l) = concentration of dimethyl succinate at τ = 0,

X_d = fractional conversion of dimethyl succinate at the τ

k_5 (sec^{-1}) = first order rate constant for the cracking reaction

At the steady state, τ = 18 sec and X_d = 0.07; solving equation (VII) for k_5,

$$k_5 = 0.004\,\text{sec}^{-1} \qquad \text{(VIII)}$$

7.4.1.3. Formaldehyde Reactions

Formaldehyde undergoes the Cannizzaro reaction in the presence of basic sites and forms methanol and formic acid; formic acid further decomposes to carbon dioxide at elevated temperatures (Reaction 6 and 7 in Figure 7.1). Formaldehyde itself also decomposes at elevated temperatures to give carbon monoxide (Reaction 8 in Figure 7.1). It was assumed that the Cannizzaro reaction and the decomposition reaction are second and first order reactions with respect to formaldehyde, respectively. The rate equation is given by:

$$-\frac{dC_f}{d\tau} = 2k_2 C_f^{\,2} C_w + k_6 C_f \qquad \text{(IX)}$$

where,

C_f (moles/l) = concentration of formaldehyde at time τ,

C_w (moles/l) = concentration of water, which is assumed constant because it is present in excess

k_2 ($l^2 moles^{-2} sec^{-1}$) = third order rate constant for the Cannizzaro reaction

k_6 (sec^{-1}) = first order rate constant for the decomposition reaction

Complete conversion (100%) of formaldehyde was obtained when Formalin itself was passed over γ-alumina (SA3177). The catalyst activity was not changed over the five-hour reaction time because the water present in Formalin oxidized any coke formed from the cracking of formaldehyde. However, a significant amount of the unreacted formaldehyde is recovered in the product from the reaction of dimethyl succinate and formaldehyde. Data from the reaction of dimethyl succinate and formaldehyde were therefore used to calculate the rate constants for the formaldehyde reactions, instead of the control run of the formaldehyde. It was assumed that the only source of carbon

monoxide is the decomposition of formaldehyde. The concentration of formaldehyde was also adjusted by subtracting the concentration of citraconic anhydride formed in the reaction to account for formaldehyde consumption in the primary reaction.

The rate constants, k_2 and k_6, were adjusted simultaneously until the difference in the predicted and experimental values of concentrations of formaldehyde and carbon monoxide were minimized. This was accomplished using the software Polymath. The calculated values of rate constants are

$$k_2 = 40\,l^2 mol^{-2} sec^{-1} \quad \text{(X)}$$

$$k_6 = 0.014\,sec^{-1} \quad \text{(XI)}$$

7.4.2. Equilibrium Calculations

The rate equations for succinates (Reaction 3 and 4 in Figure 7.1) are given by:

$$\text{DMS: } -\frac{dC_d}{d\tau} = k_3 C_d C_w - k_{-3} C_m C_{oh} \quad \text{(XII)}$$

$$\text{MMS: } \frac{dC_m}{d\tau} = k_3 C_d C_w - k_{-3} C_m C_{oh} - k_4 C_m C_w + k_{-4} C_{sa} C_{oh} \quad \text{(XIII)}$$

$$\text{SA: } \frac{dC_{sa}}{d\tau} = k_4 C_m C_w - k_{-4} C_{sa} C_{oh} \quad \text{(XIV)}$$

$$K_{e1} = \frac{C_{me} C_{ohe}}{C_{de} C_{we}} = \frac{k_3}{k_{-3}} \quad \text{(XV)}$$

$$K_{e2} = \frac{C_{sae} C_{ohe}}{C_{me} C_{we}} = \frac{k_4}{k_{-4}} \quad \text{(XVI)}$$

We also know that

$$C_{d0} = C_d + C_m + C_{sa} \quad \text{(XVII)}$$

$$C_{oh} = C_{oh0} + C_m + 2C_{sa} \quad \text{(XVIII)}$$

$$C_w = C_{w0} - C_m - 2C_{sa} \qquad \text{(XIX)}$$

where,

C_d (moles/l) = concentration of DMS at the time τ,

C_m (moles/l) = concentration of MMS at the time τ,

C_{sa} (moles/l) = Concentration of succinic acid at the time τ,

C_w (moles/l) = Concentration of water at the time τ,

C_{oh} (moles/l) = Concentration of methanol at the time τ,

k_3, k_{-3}, k_4, and k_{-4} ($lmol^{-1}sec^{-1}$) = second order rate constants,

K_{e1} = equilibrium constant for the Reaction 3 in Figure 7.1,

K_{e2} = equilibrium constant for the Reaction 4 in Figure 7.1.

Subscript 'e' represents the concentration of the particular species at the equilibrium and subscript '0' denotes the concentration at $\tau = 0$.

By simplifying above equations we get

$$-\frac{dC_d}{d\tau} = k_3[C_d(C_{w0} - C_{d0} + C_d - C_{sa}) - (C_{d0} - C_d - C_{sa})(C_{oh0} + C_{d0} - C_d + C_{sa})/K_{e1})] \qquad \text{(XX)}$$

$$\frac{dC_{sa}}{d\tau} = k_4[C_m(C_{w0} - C_{d0} + C_d - C_{sa}) - C_{sa}(C_{oh0} + C_{d0} - C_d + C_{sa})/K_{e2})] \qquad \text{(XXI)}$$

$$C_m = C_{d0} - C_d - C_{sa} \qquad \text{(XXII)}$$

It was observed from several different runs of dimethyl succinate and formaldehyde that Reaction 3 and Reaction 4 in Figure 7.1 are equilibrium reactions. The equilibrium constants, K_{e1} and K_{e2}, were calculated by using the reactor outlet concentrations; the values are:

$$K_{e1} = 0.192 \qquad \text{(XXIII)}$$

$$K_{e1} = 0.075 \qquad \text{(XXIV)}$$

The rate constants, k_3 and k_4, were adjusted simultaneously in equations XXII, XXIII, and XXIV until the difference in the predicted and experimental values of concentrations of dimethyl succinate, monomethyl succinate, and succinic acid are minimized. This was accomplished using the software Polymath. The calculated values of rate constants are

$$k_3 = 3.98\ \text{lmol}^{-1}\text{sec}^{-1} \qquad \text{(XXV)}$$

$$k_4 = 3.05\ \text{lmol}^{-1}\text{sec}^{-1} \qquad \text{(XXVI)}$$

7.4.3. Presentation of Equations

The one-dimensional molar balances in an integral, tubular reactor are given below for all species involved in the reactor system:

Citraconic anhydride: $\dfrac{dC_c}{d\tau} = k_1 C_d C_f - k_7 C_c$ (XXVII)

DMS: $-\dfrac{dC_d}{d\tau} = k_1 C_d C_f + k_3 C_d C_w - k_{-3} C_m C_{oh} + k_5 C_d$ (XXVIII)

MMS: $\dfrac{dC_m}{d\tau} = k_3 C_d C_w - k_{-3} C_m C_{oh} - k_4 C_m C_w + k_{-4} C_{sa} C_{oh}$ (XXIX)

SA: $\dfrac{dC_{sa}}{d\tau} = k_4 C_m C_w - k_{-4} C_{sa} C_{oh}$ (XXX)

Formaldehyde: $-\dfrac{dC_f}{d\tau} = k_1 C_d C_f + 2k_2 C_f^2 C_w + k_6 C_f$ (XXXI)

MeOH:

$$\frac{dC_{oh}}{d\tau} = k_1 C_d C_f / 2 + k_3 C_d C_w - k_{-3} C_m C_{oh} - k_4 C_m C_w + k_{-4} C_{sa} C_{oh} + k_2 C_f^2 C_w \qquad \text{(XXXII)}$$

Water: $$-\frac{dC_w}{d\tau} = k_2 C_f{}^2 C_w + k_3 C_d C_w - k_{-3} C_m C_{oh} - k_4 C_m C_w + k_{-4} C_{ca} C_{oh} \quad \text{(XXXIII)}$$

CO: $$\frac{dCco}{d\tau} = k_6 C_f \quad \text{(XXXIV)}$$

CO2: $$\frac{dCco_2}{d\tau} = k_5 C_d + K_6 C_f + k_7 C_c \quad \text{(XXXV)}$$

where

k_1 ($lmol^{-1}sec^{-1}$) = first order rate constant for the desired reactions

Other variables are defined and calculated in the previous sections. The rate constant k_1 was adjusted until the difference in the predicted and experimental values of concentrations of all species in the reaction system were minimized. This was accomplished using the software Polymath. The calculated value of rate constant k_1 is

$$k_1 = 4.1\, lmol^{-1}sec^{-1} \quad \text{(XXXVI)}$$

7.4.4. Results

The predicted values of concentrations of species present in the product stream of the reactor are compared with the experimental concentrations at different conditions in Table 7.2. The concentrations of each species in the last 2.5 hours of the reaction are averaged and then used for the model.

The concentrations of product species predicted from kinetic model developed here are plotted against the residence time in Figure 7.2. The concentration of citraconic anhydride reaches maximum at τ = 18 sec before it starts declining because of the secondary cracking reaction. It is obvious from Figure 7.2 that the concentrations of

Table 7.2. Comparison of predicted and experimental values of concentrations

Condition	FR = 0.15 ml/min (60/100 mesh size)		FR = 0.15 ml/min (30/60 mesh size)		FR = 0.23 ml/min		FR = 0.30 ml/min	
RT (t, sec)	5.9		6		3.6		2.9	
	Expt.	predicted	Expt.	predicted	Expt.	predicted	Expt.	predicted
CAN (10^{-3} mol/l)	1.74	1.72	2.04	1.81	1.67	1.50	1.26	1.32
DMS (10^{-3} mol/l)	2.84	3.19	3.63	3.50	2.59	4.10	2.67	4.38
HCHO (10^{-3} mol/l)	9.68	11.03	11.50	10.51	11.00	12.01	13.68	13.22
MMS (10^{-3} mol/l)	2.18	3.12	3.05	3.37	2.61	2.54	2.67	2.28
SA (10^{-3} mol/l)	0.66	1.06	0.95	1.12	1.20	0.57	1.06	0.50
MeOH (10^{-3} mol/l)	10.92	12.41	9.71	12.00	8.16	10.01	10.41	9.61
CO (10^{-3} mol/l)	1.26	1.12	0.92	1.09	0.51	0.70	0.44	0.61
CO2 (10^{-3} mol/l)	2.02	1.39	1.04	1.38	0.58	0.86	0.57	0.73

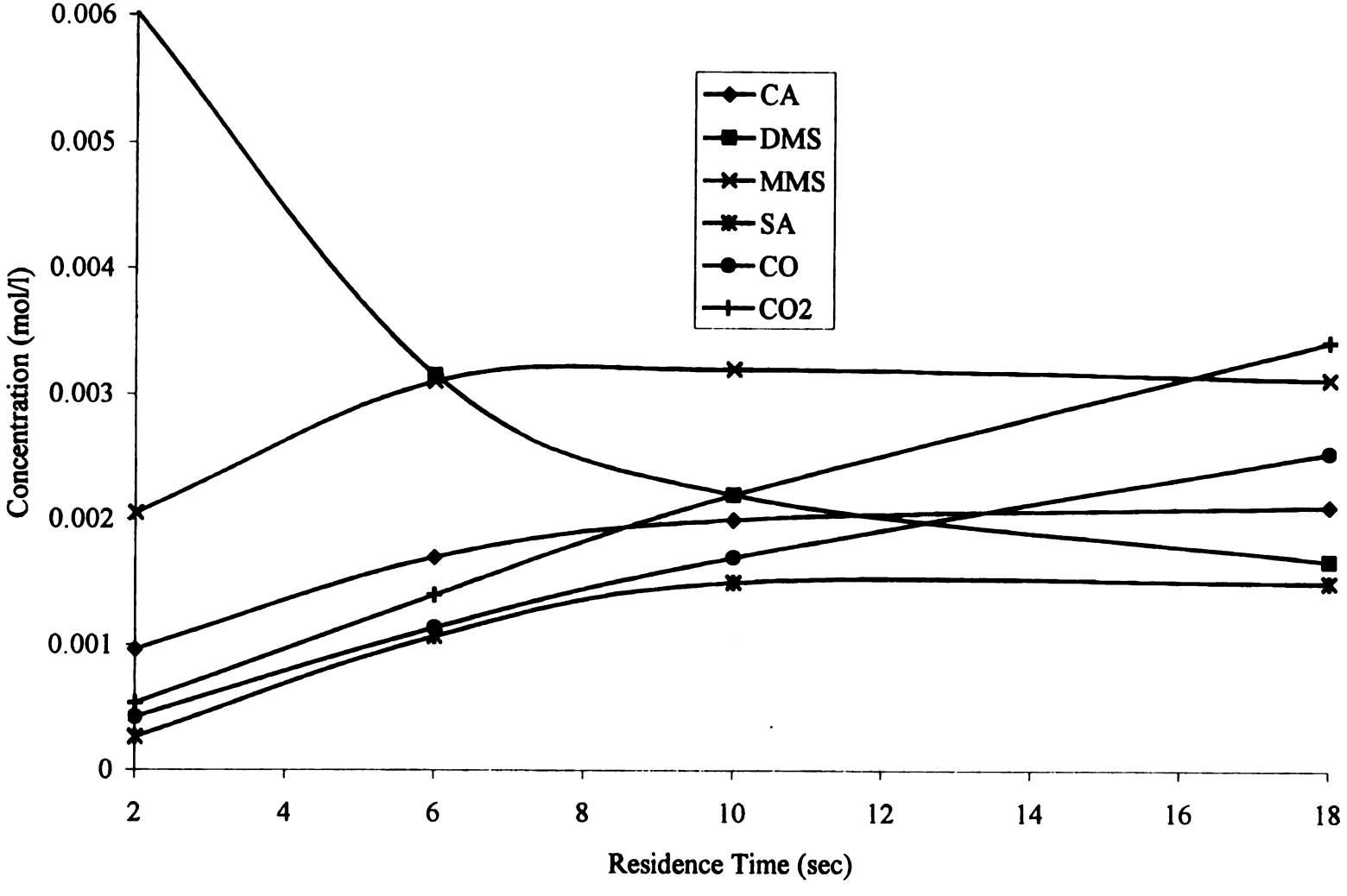

Figure 7.2. Concentration vs residence time

succinates and citraconic anhydride do not change much after τ = 6-7 sec. The predicted concentration of formaldehyde is not shown in Figure 7.3, because its relatively higher concentration at small residence times makes other concentration profiles indistinct in the graph. However, the concentration of formaldehyde decreases with the increasing residence time.

7.5. Molecular Modeling

Data from PM3 and *ab initio* calculations at the STO-3G, 3-21G, and 6-31G* levels performed for the reactants, possible intermediates, and products are presented in Table 7.3. Figure 7.3 displays the reaction scheme for the formation of citraconic anhydride from dimethyl succinate and formaldehyde, which also includes the possible intermediates. In the reaction scheme, the most of the intermediates are stabilized by intramolecular hydrogen bonding. Based on the PM3 and *ab initio* calculations, the energy variations for each step of the mechanism has been evaluated and are presented in Table 7.4.

The experimental gas phase enthalpy for the formation of citraconic anhydride from dimethyl succinate and formaldehyde was evaluated from the literature data to be ΔH_r = +15.1 Kcal/mol (Please see below for calculation)***. The overall reaction enthalpy from ab-initio method and PM3 model was also calculated to be endothermic, with a range of 7.6 kcal/mol (PM3) to 23.8 kcal/mol (RHF/3-21(*)), in quantitative agreement with the experimental value. Considering the crudeness of the method employed enthalpy of citraconic anhydride formation from the *ab initio* or PM3 model is in rather good agreement with the experimental value.

Table 7.3. Ab initio and PM3 data for reactants, intermediates, and products involved in the mechanism of the formation of citraconic anhydride

Species	*Ab initio* energy (hartrees)			PM3
	STO-3G	3-21G	6-31G*	(kcal/mol)
Dimethyl succinate	-525.636008	-529.545829	-532.516166	-177.99
Intermediate I	-638.046617	-642.806772	-646.400651	-219.55
Intermediate II	-524.488637	-528.378357	-531.346548	-169.10
Monomethyl itaconate	-524.415785	-528.366884	-531.334238	-161.08
Itaconic anhydride	-410.855760	-413.931921	-416.267792	-104.35
Citraconic anhydride	-410.863932	-413.933579	-416.275307	-100.68
Methanol	-113.549193	-114.398092	-115.035418	-51.88
Formaldehyde	-112.354347	-113.221820	-113.866331	-34.08

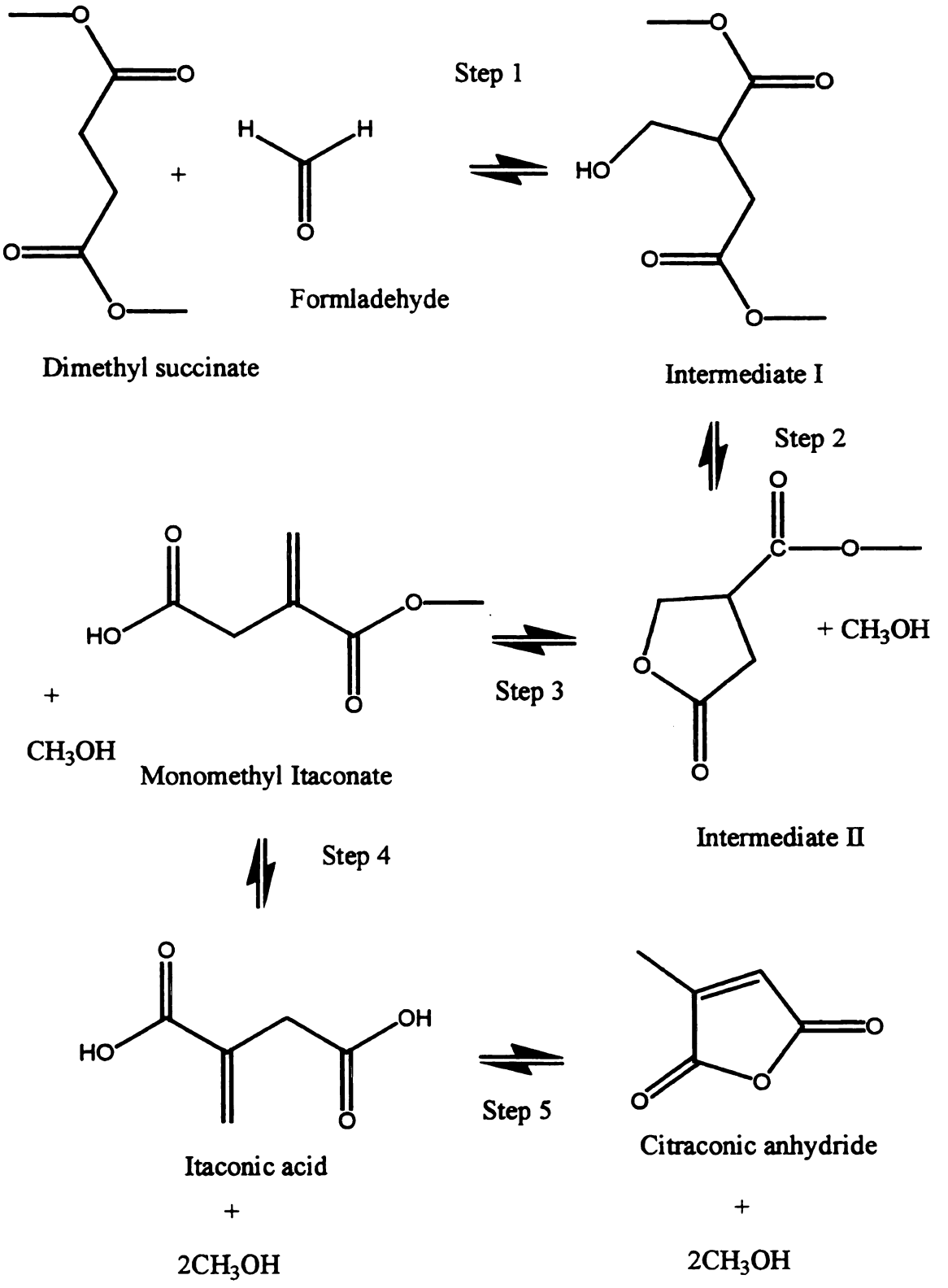

Figure 7.3. Reaction scheme for the formation of citraconic anhydride from dimethyl succinate and formaldehyde including the possible intermediates

Table 7.4. Relative energies calculated in gas phase from PM3 and ab initio methods at each step of the mechanism, normalized to the energy of the starting materials

Step	STO-3G (kcal/mol)	RHF/3-21G (kcal/mol)	RHF/6-31G* (kcal/mol)	PM3 (kcal/mol)
Feed	0	0	0	0
1	-35.3	-24.5	-11.4	-7.5
2	-29.8	-5.5	0.3	-8.9
3	15.9	1.7	8.1	-0.9
4	22.7	24.8	27.5	4.0
5	17.6	23.8	22.8	7.6

***Estimated enthalpy (gas phase @25 C): ΔH_f (Cit an) + $2\Delta H_f$ (EtOH) – ΔH_f (DES)- ΔH_f (CH_2O)

ΔH_f (Cit an) = ΔH_f (Maleic anhydride) + ΔH_f (2-methyl propenoic acid) –ΔH_f (propenoic acid)

where

ΔH_f (Maleic anhydride) (gas) = -398.3 kJ/mol

ΔH_f (2-methyl propenoic acid) (gas) = -367.3 kJ/mol

ΔH_f (propenoic acid) (gas) = -330.7 kJ/mol

ΔH_f (EtOH) (gas) = -234.4 kJ/mol

ΔH_f (DES) (gas) = -851.0 kJ/mol

ΔH_f (CH_2O) (gas) = -115.9 kJ/mol

CHAPTER 8

PROCESS DEVELOPMENT

8.1. Introduction

Several catalysts and reagents have been identified from which citraconic anhydride can be formed. We have also optimized the reaction conditions to maximize the yield and selectivity of the desired product. We have characterized the catalyst deactivation and regeneration procedure, so that the catalyst can be used in a continuous process. The isomerization of citraconic anhydride to itaconic acid has also been performed successfully in our laboratory. Finally, we have also developed a separation protocol to recover a refined grade (99.4%+) product of itaconic acid. An integrated process for production of itaconic acid from succinates is thus approached.

8.2. Process Specifications

Basis: Production rate = 20 MM lb/yr of itaconic acid.

Product purity > 99.4%.

Raw materials: succinic acid ($0.25/lb), methanol ($0.04/lb), and Formalin (37.5 wt% formaldehyde) ($0.09/lb).

Feed to the reactor: 2 to 1 molar ratio of formaldehyde (Formalin) to dimethyl succinate.

Reactions: DMS + Formaldehyde => Citraconic Anhydride

Citraconic anhydride + Water => Citraconic acid

Citraconic acid => Itaconic acid.

Reaction conditions: reactor temperature = 380 °C and pressure = 1 atm.

Catalyst: γ-alumina.

Design parameters: (1) in reactor, 30% yield of citraconic anhydride at 43% per pass conversion of succinates and thus 70% selectivity to citraconic anhydride from succinate. 70% overall conversion of DMS.

(2) 80% recovery of itaconic acid from citraconic anhydride isomerization/ purification.

(3) 50% conversion of formaldehyde.

(4) WHSV = 0.90 kg succinate/(kg catalyst * hr)

Constraints: (1) Unreacted succinate and formaldehyde are recycled.

(2) MeOH should be mostly recovered and then recycled.

8.3. Feed costs Calculation

⇒ Itaconic acid (IA) production rate

$= 20 \times 10^6$ lb IA /yr

$= 1.54 \times 10^5$ lbmol IA/yr

⇒ Citraconic anhydride (CAN) production rate

$= (1.54 \times 10^5/0.8)$ lbmol CAN/yr

(80% recovery of IA from CAN isomerization/purification)

$= 1.92 \times 10^5$ lbmol CAN/yr

$\Rightarrow$ DMS feed rate

$= (1.92 \times 10^5/0.7)$ lbmol DMS/yr

(Overall reactor yield with complete succinate conversion is 70%)

$= 2.75 \times 10^5$ lbmol DMS/yr

$= 4.01 \times 10^7$ lb DMS/yr

$\Rightarrow$ Succinic acid feed rate

$= 2.75 \times 10^6$ lbmol SA/yr

$= 3.24 \times 10^7$ lb SA/yr

$\Rightarrow$ Methanol feed rate

$= 2 \times 2.75 \times 10^6$ lbmol MeOH/yr

$= 5.50 \times 10^6$ lbmol MeOH/yr

$= 1.76 \times 10^7$ lb MeOH/yr

$\Rightarrow$ Formaldehyde feed rate

$= 2 \times 2.75 \times 10^6 \times 0.50$ lbmol formaldehyde/yr

(Formaldehyde to DMS is 2:1, but 50% conversion of formaldehyde)

$= 2.75 \times 10^6$ lbmol formaldehyde/yr

$\Rightarrow$ Formalin feed rate

$= (2.75 \times 10^6 \times 30/0.375)$ lb Formalin/yr $= 2.12 \times 10^7$ lb Formalin/yr

(Formalin contains 37.5 wt% formaldehyde)

$\Rightarrow$ Succinic acid cost ($/lb itaconic acid produced)

$= \$0.25/\text{lbSA} \times [(3.24 \times 10^7 \text{ lb SA/yr})/(2.0 \times 10^7 \text{ lb IA/yr})]$

= \$0.40/lb IA

⇒ Formaldehyde cost (\$/lb itaconic acid produced)

= \$0.09/lb Formalin x [(2.12 x 10^7 lb Formalin/yr)/(2.0 x 10^7 lb IA/yr)]

= \$0.10/lb IA

⇒ Feedstock costs (\$/lb itaconic acid produced)

= Succinic acid cost + Formaldehyde cost

(Methanol required for esterification of succinic acid is mostly recovered)

= \$0.50/lb IA

8.4. Process Concept for Itaconic Acid Production

A schematic of a process concept for conversion of succinate to itaconic acid is given in Figure 8.1. The primary components of the proposed process are discussed individually in the following sections in detail.

8.4.1. Esterification Reactor

The esterification of succinic acid with methanol takes place in the esterification reactor. Section 1.3 discusses about the esterification of succinic acid in detail. We have also studied ester formation of succinic acid in our laboratory via standard esterification techniques. A reactive distillation column can be used for the esterification reaction (77). By using the distillation column, it is possible to get high reaction conversion and separation simultaneously.

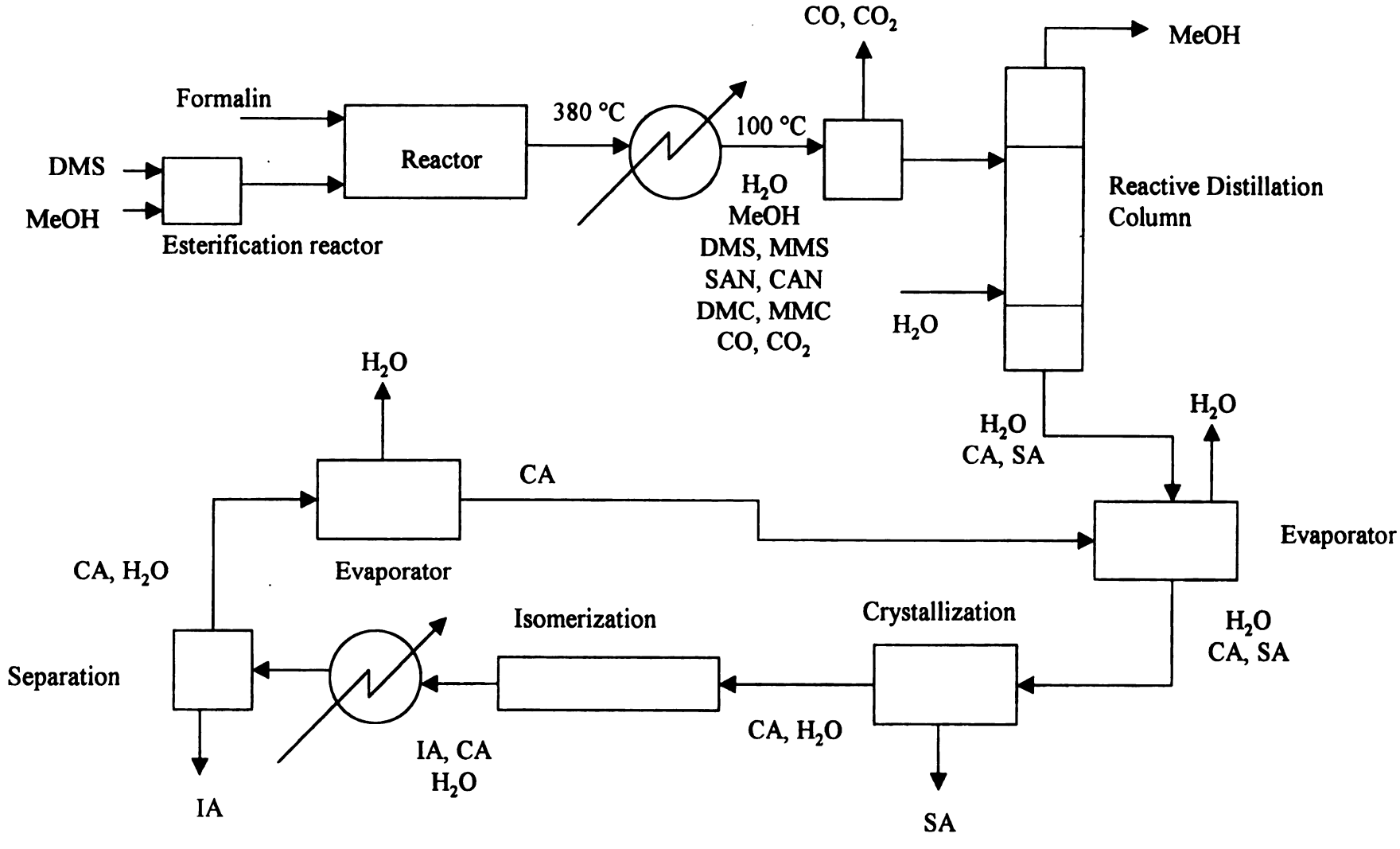

Figure 8.1. A schematic of a process concept for conversion of DMS to IA

8.4.2. Reactor

The reactor is the heart of the process where the reaction of dimethyl succinate and formaldehyde takes place. A continuous fixed-bed reactor can be employed for the reaction, as employed in this work. The catalyst bed volume may be estimated by scaling up on the basis of laboratory data. Required catalyst weight would be 12,500 kg to produce 20 MM lb itaconic acid/yr from succinates (Assumptions: plant operates for 8150 hr/yr, 43% dimethyl succinate conversion per pass, and WHSV = 0.90 kg succinate/(kg catalyst*hr)) and hence the catalyst volume would be 19 KL (catalyst density = 0.67 kg/L. Required catalyst for this process, γ-alumina, is very cheap ($9/kg) and no catalyst pretreatment is needed for the reaction.

To overcome the catalyst deactivation problem, moving bed reactors or several parallel fixed-bed reactors may be used.

8.2.3. Flash Drum

A flash drum (gas-liquid separator) may be used to discard CO, CO_2, and other gaseous products from the reactor. The reactor effluent at 380 °C should be cooled to 40 °C before it enters to the flash drum. The heat from the reactor effluent may be used for pre-heating the feed.

8.2.4. Distillation Column I

An initial distillation column is needed to recover and recycle unreacted formaldehyde back to the reactor. Apparent azeotrope at atmospheric and higher pressures has been reported on distillation of aqueous formaldehyde solution (64). So,

one can take advantage of the azeotropic property to distill formaldehyde away from the reaction products at 60 psi.

Formaldehyde may be fed as a limiting reactant to avoid the distillation step. Unreacted formaldehyde may be distilled along with methanol after hydrolysis of products as discussed in next section.

8.3.4. Reactive Distillation Column

The raw product exiting the reactor is a mixture of citraconic anhydride, citraconic acid, monomethyl citraconate, dimethyl citraconate, succinic anhydride, succinic acid, monomethyl succinate, and dimethyl succinate. It is essential for the separation of citraconates from succinates to hydrolyze the product mix to recover all species as the free acid. In this work, hydrolysis was carried out in aqueous H_2SO_4 solution to clearly evaluate product yields and selectivity. In large-scale process, hydrolysis of product mix can be carried out by using the reactive distillation technique. In this technique, ion-exchange resin such as Amberylist can be used in the distillation column to catalyze the hydrolysis of esters and the resulting methanol can be removed on the top of the column simultaneously. Methanol may be recycled back for the esterification of succinic acid.

8.3.5. Succinic Acid Crystallizer

An evaporator may be used before the succinic acid crystallizer to remove the excessive water resulting from hydrolysis of the product mix.

Large difference in solubilities of succinic acid (70 g/l @ 25 °C) and citraconic acid (2500 g/l @ 25°C) in water is advantageous in separation of succinic acid and itaconic acid using crystallization. The saturated solution of succinic acid from the evaporator at 100 °C is cooled down to 15 °C and, thus, substantial amount of succinic acid will crystallize. The crystallized succinic acid will be pure because of high solubility of citraconic acid in water and it may be recycled back to the esterification reactor.

The succinic acid crystallization from the solution of succinic acid and citraconic acid in water was performed in our laboratory. The composition of solution was designed on the basis of expected succinate to convert conversions and selectivities from the reactor. The crystallization of the simulated solution at 13 °C gave crystals that were 97% succinic acid by weight and 70% of succinic acid of total acid taken was crystallized. After washing these succinic acid crystals with cold water, crystals were 99.9 wt% succinic acid.

8.3.6. Isomerization Reactor

Citraconic acid is converted to itaconic acid in the isomerization reactor. The isomerization reaction of citraconic acid to itaconic acid has been reported in literature. The isomerization was also studied comprehensively in our laboratory. Reactions were done at various temperatures, citraconic acid concentrations, and pHs to understand the effects each had on the isomerization of citraconic acid. The best results were obtained at 170 °C after three hours of isomerization reaction; 61% yield of itaconic acid at 87% selectivity was observed. Byproducts of isomerization reaction were citramalic acid (9%

yield) and mesaconic acid (trace). In a separate experiment, it has been shown that citramalic acid can be converted to citraconic acid by feeding citramalic acid solution in our fixed-bed reactor over SA3177 alumina at 250 °C. The conversion of citramalic acid to citraconic acid was complete. The citraconic acid composition and pH have a negligible effect on itaconic acid yields.

Thus, the isomerization of citraconic acid to itaconic acid is a simple thermal arrangement and can be carried out in stirred reactor at 170 °C. A continuous stirred tank type reactor will be used for the isomerization reaction.

8.3.7. Itaconic Acid Crystallizer

Excessive water from the isomerization reactor effluent is evaporated. After cooling the saturated solution of itaconic acid from the evaporator to 25 °C, itaconic acid crystals will be formed preferably. The itaconic acid crystallizer operates at 25 °C, which is higher a temperature than the succinic acid crystallizer to avoid cocrystallization of succinic acid with itaconic acid. These itaconic acid crystals may be further purified by recrystallization in ethanol to get the desired purity of 99.5%+. The liquid stream from the itaconic acid crystallizer, containing citraconic acid, and smaller amounts of itaconic acids, is passed through a high temperature reactor to convert itaconic acid and citramalic acid back to citraconic acid and then recycled to the evaporator just after the reactive distillation column.

The itaconic acid crystallizations were also performed and were designed to simulate the composition of the process stream exiting the isomerization reactor. The crystallization at 25 °C gave crystal purity of 98.5 wt% itaconic acid after being washed

with cold water at 81% recovery of itaconic acid from the simulated solution. The 99.5 wt% purity of itaconic acid was achieved after ethanol crystallization of crystals obtained from the first crystallization.

CHAPTER 9

SUMMARY AND RECOMMENDATIONS

9.1. Summary

A novel process and catalysts to produce itaconic acid via condensation of succinic acid or its derivatives and formaldehyde were comprehensively studied. Itaconic acid is a valuable monomer in the formulation of polymers because of its unique chemical properties, which derive primarily from the conjugation of its two-carboxyl groups and its methylene group. Itaconic acid is primarily used as copolymer for improved fiber toughness, improvement of the emulsion stabilization, and performance characteristics such as adhesion to substrates. Itaconic acid polymer can be used as super absorbing polymers (SAP), because of its excellent water absorbing capacity (2-3 times more than acrylic polymers).

The primary goal of this study was to form the intermediate citraconic anhydride from the vapor phase condensation of succinates with formaldehyde using a fixed bed reactor. The subsequent process steps for separation of citraconic acid from unreacted succinates and conversion of citraconic acid to itaconic acid have been studied. The process developed is highly selective toward the desired products at potentially lower cost. A number of succinate and formaldehyde substrates were studied for the reaction.

Catalyst screening to find an optimal catalyst for the reaction was also done extensively. Finally, the reaction conditions were optimized to get the best yields and selectivities of citraconic anhydride.

The nature of sites on the support played an important role in the formation of citraconates in the vapor phase reaction. Neither highly acidic (e.g. zeolites) nor basic (e.g. alumina-magnesia mixed oxides) sites on the support favored the reaction. The highly acidic supports were found to be very active for cracking succinates into carbon dioxide, but not for condensation to citraconic anhydride. The basic supports gave little citraconic anhydride but catalyzed the Cannizzaro reaction of formaldehyde to methanol and formic acid, thus preventing formaldehyde from participating in the desired condensation.

In contrast, γ-alumina, a mildly acidic support, without any salt added showed significant activity for the formation of citraconates from succinates. Results from different feedstocks over γ-alumina at the base case (standard) conditions are summarized in Table 9.1 (after hydrolysis). The product from the reactor was hydrolyzed to recover all species as the free acid for better product analysis.

Table 9.1. Summary of Results from Different Feedstocks over γ-Alumina

S.N.	Feedstock	Yield of citraconates (%)	Conv of succinates (%)	Selectivity (%)
1	DMS + trioxane	35	48	73
2	SAN + trioxane	44	67	66
3	MMS + trioxane	26	40	78
4	DMS + Formalin	29	42	70
5	DMS + Formcel	34	56	61

The decay in catalyst activity was much slower with Formalin. Yields of citraconic anhydride and conversion of DMS dropped off very slowly over time for

reaction times out to five hours. Coking on the catalyst was also much less with Formalin, likely because the water present steam-cleaned the catalyst during the reaction. Also, coke forming tendency is directly related to surface properties such as surface area, acidic site density, and type of acidity and to reaction conditions such as temperature and feed material. Coking involves both the succinate species and formaldehyde. For all alumina supports, heavy cracking of succinates to carbon dioxide accompanied the early stages of reaction, inductive of initial high support acidity which is deactivated by coking after exposure to succinates. Citraconic anhydride yield stabilizes following acid site deactivation.

Upon deactivation, the alumina catalyst was regenerated by exposure to air at 500 °C for five hours. The yields of citraconic anhydride were identical before and after the regeneration process, which demonstrated the robust nature of the oxide catalysts and their ability to be regenerated.

Yield of citraconic anhydride increased with increasing reaction temperature, but selectivity lowered due to more cracking of dimethyl succinate at elevated temperatures. Citraconic anhydride yields were highest at 380 °C. Higher formaldehyde to dimethyl succinate molar ratios gave better yields and selectivities of citraconic anhydride. The yield of citraconic anhydride decreased with increasing liquid feed flow rate, but selectivity remained unchanged. Citraconic anhydride yields were increased with increasing catalyst bed length, but the selectivities decreased. The condensation reaction of dimethyl succinate with Formalin over intermediate surface area alumina is not mass transfer limited.

The subsequent process steps for separation of citraconic acid from unreacted succinates and isomerization of citraconic acid to itaconic acid have also been studied. A maximum 99.5% of purity of itaconic acid was observed.

Finally, a process concept for itaconic acid production from succinates and formaldehyde is proposed. Values from our optimal run were used to calculate the feedstock costs. The calculated feedcost is $0.50/lb itaconic acid produced (base case results) for a 20-MM lb itaconic acid/yr capacity plant.

9.2. Recommendations

Although we have tried our best to do a complete study for the formation of itaconic acid or citraconic anhydride from succinates, there are some other issues, which may be useful for commercialization of this process, that are discussed here.

Moving bed reactors may be used to overcome the catalyst deactivation problem. In the moving bed, a fresh catalyst is introduced continuously at the bed entrance and the spent catalyst is withdrawn continuously at the exit. Hence, while a nonuniform catalyst activity profile exists within the bed all times, it is invariant and the time-averaging effect seen in fixed-bed operation does not exist here.

Two parallel reactors may also be used to check the rapid catalyst deactivation problem. Regeneration can be performed in one reactor by flowing air or water at higher temperature. Other reactor will be used for the desired reaction. The moving bed or parallel reactor system will not add much in the process economics because alumina is very cheap ($9/lb) material and can be easily regenerated upon deactivation.

Ultimate goal of this work was to develop chemical pathways to value-added chemicals from "fermentation-derived" succinic acid. We carried out our studies using reagent-grade feedstocks. Reaction studies should be conducted with actual "fermentation-derived" succinates to see the possible effects of "extrinsic" deactivating agents such as biogenic residues present in the fermentation broth such as proteins, carbohydrates, and minerals on catalyst performance.

A small amount of O_2 may be fed to the reactor along with an inert gas for *in-situ* oxidation of coke formed on the catalyst. The adverse effects of O_2 on reactants or products in the presence of γ-alumina are unknown.

Promoters such as piperidine may be used, which could form a complex with formaldehyde and thus enhance its activity and concentration in the reaction medium. Some other reagents, which can halt the Cannizzaro reaction in order to spare formaldehyde for the desired reaction, may be used. The esterification and de-esterification reactions also compete against the desired reaction.

The best yield of citraconic anhydride was obtained from succinic anhydride and trioxane. Very small internal diameter tubing is used in the laboratory and it is hard to keep a uniform temperature around this tubing from the feed source to the collection traps. Any cold surface on the tubing or a relative large particle of coke can disrupt the experiment in the laboratory scale reactor. On a commercial scale, larger pipe sizes are used and a uniform heating around pipes is easy thing to do, so the properties of succinic anhydride should pose less of a problem.

An anhydride stabilizer may be used to stabilize succinic anhydride and citraconic anhydride against the deteriorative effects of elevated temperature. A patent from

Texaco, Inc. (12) reports that the acid anhydrides are stabilized against the deteriorative effects of heat by addition of a boron-oxygen compound such as boric acid, boric anhydride, tributyl borate, or borax.

Some other sources of succinates may be tried for the reaction. N-butyl succinimide is a liquid at room temperature and it can be fed easily with Formalin or any other source of formaldehyde. Succinimides might be more stable than succinates at the reaction conditions. Resulting citraconimide or itaconimide can be hydrolyzed easily to citraconic acid or itaconic acid. Citraconimide or itaconimide itself finds applications as a useful copolymer in polymer industry.

Anhydrous formaldehyde may be used to avoid the feeding and handling of 52% water present in Formalin. Trioxane, a source of anhydrous formaldehyde, is not commercially available compound. Formaldehyde required for the reaction can be generated just before the reactor by the methanol oxidation. Methanol oxidation is an exothermic reaction, so the resulting heat may be used for feed pre-heating or reactor heating.

In-situ reactions may be studied using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). DRIFTS studies of reactions in-situ may provide mechanistic insights of citraconic anhydride formation from succinates and formaldehyde. Once the reaction intermediates on the catalyst surface are identified, then their presence can be related to the catalyst performance easily. In other words, a correlation of the nature of the adsorbed species to the acid-base properties of the support can be made. DRIFTS method analyses infrared radiation reflected from a solid sample. In-situ reactions may be carried out using an infrared transmittance cell in which gas

phase reactants are passed over a crushed KBr-catalyst mixture and DRIFTS spectra can be collected as the reaction proceeds. Several examples and designs for this type of reactor are presented in literature.

APPENDICES

Appendix A

1. To find the concentration of an unknown compound in GC or HPLC using the internal standard method:

$$C_i\,(g/ml) = \frac{(Area)_i}{(Area)_{IS}} * C_{IS} * (RF)_i$$

where,

Ci = concentration of compound i;

CIS = concentration of internal standard (g/l),

$(Area)_i$ = peak area of compound 'i'

$(Area)_{IS}$ = peak area of internal standard

RF_i = Response Factor of compound 'i' compare to internal standard.

2. GC Operating Parameters

Column	SPB1 from Supelco
Column type	Intermediate Capillary
Initial column temperature	40 °C
Initial column hold time	5 min
Program 1 final column temperature	135 °C
Program 1 column rate in	10 °C/min
Program 1 column hold time	5 min
Program 2 final column temperature	200 °C
Program 2 column rate in	15 °C/min
Program 2 column hold time	0 min

Injector temperature	250 °C
Initial auxiliary temperature	150 °C
Initial auxiliary hold time	0 min
Temperature program auxiliary?	NO
Detector	B
FID B initial attenuation	8
FID B initial range	11
FID B auto zero on	YES
End time	23.83 min
Hydrogen flow rate	30 ml/min
Helium flow rate	30 ml/min
Air flow rate	300 ml/min

3. Water 410 refractometer parameters

Sensitivity (SENS)	32
Column temperature (EXT1)	40 °C
Internal oven temperature (INT)	off
Time constant (TC)	3 sec
Scale factor	20

4. Data Module (HPLC) parameters

Time (TT) = 35 Function (TF) = ER Value (TV) = 1

Method number (MN) = 2

Number of levels (NV) = 0

Chart speed = 0.5 cm/min

PT EVAL ~ 2500 to 5500

Attenuation (AT) = 1024

Appendix B

Summary of results

1 KH2PO4 CPG-3000 means 1mmol loading of KH2PO4 on CPG3000
In DMS + TO (1:4) , molar ratio is between DMS and Formaldehyde, not between DMS and Trioxane (TO)
In temperature cell, 350-500(30) means rxn is carried out in that temp range with 30 C temp ramp
In conversion or yield cell, temp for best yield is given in bracket.
C means catalyst gain or loss, + means gain after the rxn.

Run#	cat, support loading	Feed	Temp	Pres	Conv%	Yield%	C	Comments
1	CPG-3000	DMS + TO(1:4)	335-350	365	-	-	=	Reactor outlet plugged after 3 samples, not much rxn
2	CPG-3000	DMS	330-370(20)	300	-	-	+	No rxn
3	1 KH2PO4 CPG-3000	DMS	350-450(25)	400				
4	1 KH2PO4 CPG-3000	DMS + TO(1:4.6)	350-500(30)	490	44	.25(500	+	First successful rxn, Two unknown peaks in HPLC
5	1 KH2PO4 CPG-3000	DMS + TO(1:4.6)	400	290	-	-	=	Reactor outlet plugged rightaway because of Trioxane
6	1 KH2PO4 CPG-3000	DMS + TO(1:4.6)	400	290	-	-	=	Reactor outlet plugged rightaway
7	1 KH2PO4 CPG-3000	DMS + TO(1:4)	400-430	300	40	.2(430)	=	Two samples collected, solid white stuff in tubing after sample trap
8	1 KH2PO4 CPG-3000	DMS	400-500(25)	480	49(500)	-	+	Losing some DMS at high temp
9	1 KH2PO4 CPG-3000	TO + Methanol	350-500	490	-	-	-	Losing 50% of feed, TO not analyzed
10	1 KH2PO4 CPG-3000	DES	350-500(30)	400	69(500)	-	+	
11	2 KH2PO4 CPG-3000	DES+TO(1:5)	350	400	-	-	=	Unsuccessful run, outlet blocked
15	CPG-3000	-.	350-450(50)	325	-	-	=	No feed, only helium was flown through to see DMSO vaporization in trap
16	CPG-3000	DES	350-500(50)	350	74(500)	-	=	Prod collected in DMSO
17	CPG-3000	DES	280-380(25)	350	32(380)	-	=	
18	CPG-3000	DES	305-430(25)	350	40(430)	-	=	Outlet gas was flown through liq N2 to trap CO2 or CO(nothing trapped)
19	2 KH2PO4 CPG-3000	DES + TO(1:4)	350-470(30)	370	55(470)	0.8	+	
20	2 KH2PO4 CPG-3000	DES + TO(1:4)	350-440(30)	375			+	
21	2 KH2PO4 CPG-500	DES + TO(1:4)	350-440(30)	375			+	
22	2 KH2PO4 CPG-500	DES + TO(1:4)	350-440(30)	375	70	.8(440)	+	Try high surfacearea CPG next time
23	2 KH2PO4 CPG-75	DES + TO(1:4)	350-410(30)	375	48	.4(440)	+	CPG is not good support, Bye CPG
24	1 Li2CO3 SA3132	DES + TO(1:4)	350-440(30)	375	-	-	+	No conversion of DES and no CA yield
25	1 Li2CO3 SA3132	DES + TO(1:4)	380	280	-	-	+	No conversion of DES and no CA yield

26	.25 Ce3Sulfate SA3132	DES + TO(1:4.6)	380	300	25	5.4	+	products collected in DMSO
27	.25 Ce3Sulfate SA3132	DES + TO(1:1.5)	380	300	42	4.5	+	yield slightly decreased with decreasing molar ratio of feed
28	SA3132	DES + TO(1:2)	320-410(30)	300	31	3.2(410	+	Yield of CA increases with temp but also decreases with time
29	SA3132	DES	350-410(30)	350	10	-	-	Not much conversion of DES observed
30	SA3132	DES + CA(4:1)	350-410(30)	350	20	-	+	No conversion of CA @ low temp, but ~30% conv @ 410
31	0.53 CeSulfate SA3132	DES + TO(1:2)	380-410(30)	350	62(410)	3.8	-	Highest yield so far
32	0.53 CeSulfate SA3132	DES +TO(2:1)	380-410(30)	350	58	3.6(410	-	Large unknown peak @21 in UV
33	0.53 CeSulfate SA3132	DES + TO(1:4)	380-440(30)	350	55	4.8(410	=	high CO & CO2, low CA and bad mass balance at high temp
34	0.39 CeSulfate SA3132	DES + TO(1:2)	380-410(30)	60	50	5.6(380	-	First rxn in new lab with new setup(eldex pump & valco valve in outlet), outlet clogged in beginning
35	0.39 CeSulfate SA3132	DES + TO(1:2)	380-440(30)	60	50	6.9(380	=	large unknown peak @21 in UV, Feed treated with CaSO4 and cat calcined
36	0.5 LaCl3 SA3132	DES + TO(1:2)	380-410(30)	60	26	1(380)	=	Feed treated with CaSO4, high CO2 during first collection
37	0.5 CeSulfate SA3132	DES + TO(1:2)	350-380(30)	60	-	-	-	short circuited heating tape could not collect samples
38	0.5 CeSulfate SA3132	DES + TO(1:2)	410-470(30)	60	50	7(410)	+	Unknown peak area decreased and MEC peak area increased after 5 days, large peak of DEC in esterified product
39	0.5 CeSulfate SA3132	DES + TO(2:1)	410	60	52	7.8	+	15.5% yield on the basis of formaldehyde(limiting reactant),low CO2
40	0.5 CeSulfate SA3132	DES	410	60	-	-	-	outlet was blocked by SA, could not collect sample nicely
41	0.5 CeSulfate Zeolite-x	DES + TO(1:2)	410	60	84	6.7	+	Only water in first sample
42	0.5 CeSulfate Zeolite-x	DES + TO(1:2)	410	60	-	-	+	to confirm water in first sample
43	0.5 CeSulfate Zeolite-x	DES + TO(1:2)	350	60	-	-	+	rxn carried out at low temp to see activity of Zeolite, but lot of CO2(>50%)
44	Zeolite-x	DES	350	60	-	-	+	More than 50% CO2 with only DES and only Zeolite, Zeolite too active
45	2 KH2PO4 SA3132	DES + TO(1:2)	380	60	10	0.4	+	KH2PO4 not suitable for this rxn
46	0.5 CeSulfate SA3132	DES + TO(1:2)	380	60	53	7.8	-	Rxn carried out to see reproducibility of results
47	0.5 CeSulfate SA3132	DES + form(1:3)	380	60	50	5.2	-	Two pumps to feed DES & formalin, feed preheated from now on
48	0.5 CeSulfate SA3132	DES + form(1:2)	380	60	51	6.7	=	Sod sulfite used to collect any formaldehyde (0.30%) in outlet
49	NdCl3 LaCl3 Zeolite-x	DES + form(1:2)	380	60	-	-	+	Ion exchanged cat, first sample water, second two phase, high CO2
50	0.5 CeSulfate Carbon	DES + form(1:2)	380	60	-	0	+	Activated carbon not active for this rxn
51	0.5 CeSulfate SA3177	DES + form(1:2)	410	60	64	16.8	+	MMC peak area increases with time
52	0.5 CeSulfate SA3177	DES + form(1:2)	410	60	87	17.2	+	Same cat(R51) used after regeneration (flowing air at 410 C for 6 hrs)
53	0.5 CeSulfate SA3177	DMS + form(1:1.3)	410	60	75	22.5	+	7% yield of MMC,CO2 decreases as product yield increases, High selectivity
54	0.5 CeSulfate SA3177	DMS + form(1:1.3)	380	60	74	9.3	+	yield of CA decreases with the temp
55	0.75 CeSulfate SA3177	DMS + form(1:1.3)	380	60	87	12.2	+	Yield increases with the loading
56	SA3177	DMS + form(1:1.3)	380	60	80	27	+	7.3% yield of MMC, low CO2
57	SA6175	DMS + form(1:1.3)	380	60	-	-	=	Could not complete the experiment
58	SA6175	DMS + form(1:1.3)	380	60	92	15.5	+	> 50% co2 observed and yield increases as conversion decreases with time.

59	SA6173	DMS + form (1:1.3)	380	60	94	15.3	+	>50% CO2 observed in a couple of collections.
60	25:75 :: Al : Mg	DMS + form(1:1.3)	380	60	83	0.65	+	preferentially catalyses the cannizaro's reaction of form to MeOH
61	SA3177	DMS + form(1:4)	380	60	55	19.5	+	Reactor temp accidentally went up 1200, prods analyzed only by RI, to confirm the yield
62	SA3177	Formalin	380	60	-	-	+	100% conversion of formaldehyde observed
63	SA3177	Formalin	380	60	-	-	+	Previous experiment's result confirmed
64	SA3177	DMS	380	60	48	-	+	
65	SA3177	DMS + TO (1:2)	380	60	49	20.5	+	Yield goes upto 35% after hydrolysing the product, MMC & DMC confirmed
66	SA3177	DMS + TO (1:2)	410	60	89	14	+	Yield decreases, conv increases, and CO2 increases with temp
67	SA3177	DMS + TO (1:2)	350	60	33	16	+	Low yield, but high selectivity
68	Zirconia	DMS + TO (1:2)	380	60	33	3.7	+	Zirconia is not sufficient active for the rxn
69	Fe2O3	DMS + TO (1:2)	380	60	35	0	+	High yield of CO2 with no CA
70	SA6173	DMS + TO (1:2)	380	60	45	18	+	Lot of CO2 in beginning, selectivity increases with time
71	SA3177	DMS + TO (1:2)	380	60	55	19	+	Yield goes upto 30% after hydrolysing the product
72	TiO2	DMS + TO (1:2)	380	60	72	0	+	No citraconates
73	Alumina(lab)	DMS + TO (1:2)	380	60	56	18	+	Alumina prepared in lab also gives similar results to alundum
74	SA6173	DMS + TO (1:2)	350	60	-	-	+	Experiment could not completed
75	SA6173	DMS + TO (1:2)	350	60	36	15.5	+	Low yield, but high selectivity
76	SA3177	DMS + TO (1:2)	380	400	53	20	+	Low CO2 observed, but same catalyst wt gain after the rxn
77	SA6175	DMS + TO (1:2)	380	60	71	16.3	+	Lot of CO2 in beginning, selectivity increases with time
78	SA3177	DMS + TO (2:1)	380	60	48	12	+	24% yield of CA based on formaldehyde
79	SA3177	DMS + TO (1:2)	380	400	50	18.5	+	Run76 results confirmed, almost same results as at low P
80	AlPO	DMS + TO (1:2)	380	60	52	17.3	+	AlPO was prepared in lab, now AlPO can compete with Alndm
81	85%ZrO2+15%Al2O3	DMS + TO (1:2)	380	60	34	6	+	Run68(prprd in lab) results confirmed with this MieChem ZrO2
82	TiO2	DMS + TO (1:2)	380	60	71	0	+	Run72(prprd in lab) results confirmed with this Degusa titania
83	Fe2O3	DMS + TO (1:2)	380	60	40	0	+	Run69(prprd in lab) results confirmed with this Aldrich Fe2O3
84	90:10 :: Al : Mg	DMS + TO(1:2)	380	60	80	1	+	Nothing much different from high content of Mg(Run60)
85	85%ZrO2+15%Al2O3	DMS	380	60	20	-	+	No significant reaction with only DMS
86	glass beads	DMS	380	60	0	0	=	No reaction observed
87	KOH on SA3177	DMS + TO(1:2)	380	60	40	0	+	.0.28 mmol KOH (more than acid sites) killed reaction completely
88	AlPO	DMS + TO(1:2)	380	60	50	15	+	AlPO prepared differently (from R80), but almost same result
89	K2CO3 on SA3177	DMS + TO(1:2)	380	60	70	0	+	High conv in beginning, but decreasing sharply; no CA
90	Zeolite-x	DMS + TO(1:2)	300	60	60	0	+	Convs (93, 60, 26, 16, 11)% after 30 mins, NO CA
91	SA3177	DMS + TO(1:2)	380	60	43	32	+	Extended run; results after hydrolysis, catalyst stable for 6 hrs

92	SA3177	SAn + TO(1:5)	380	60	-	-	+	First rxn with SAN, pumped 30 ml in 20 min (pumps stupidity(not mine))
93	SA3177	SAn + TO(1:5)	380	60	80	34	+	First successful run with SAN, but with struggle; not bad yield
94	SA3177	SAn + TO(1:5)	380	60	70	40	+	Cat deactivates faster with SAN; Paraformaldehyde a problem
95	SA3177	SAn + TO(1:2)	380	60	75	43	+	Not bad results, but cat dies soon and some other known problmes
96	SA3177	SAn + TO(1:2)	380	60	86	18	+	Some leakage in feed, obviously high conv and low yield
97	SA3177	SAn + TO(1:2)	380	60	73	42	+	Outlet gas flow rate increased 55 from 27 ml/min; 2 samples collected
98	SA3177	SAn + TO(1:2)	380	60	60	42	+	Feed rate 10 from 6ml/hr; 4 samples; nice results in beginning, but...
99	SA3177	SAn + TO(1:2)	380	60	-	-	+	High preheat 340 from ~200 C; reaction stopped because of plugging
100	SA3177	SAn + TO(1:2)	380	60	68	33	+	6 samples, 12% yield in 6th sample
101	glass beads	SAn + TO(1:2)	380	60	74	14	+	Lot of CO2; no MMS; unreacted TO and formaldehyde
102	glass beads	SAn + TO(1:2)	380	60	78	14	+	Results from R101 confirmed
103	Empty Reactor	SAn + TO(1:2)	380	60	0	0	=	No reaction means it is not a thermal rxn
104	Fe2O3	SAn + TO(1:2)	380	60	100	0	+	To see results from an inactive cat (our point of view)
105	Fe2O3	SAn + TO(1:2)	380	60	100	0	+	Results from R104 confirmed
106	SA3177	SAn + TO(1:2)	350	80	37	30	+	Very good results if we can reproduce; Yields(41, 30, 30 7, 19)%
107	SA3177	SAn + TO(1:2)	320	80	80	20	+	Preheat here and R106 200 C; At low rxn T feed cracks more bcos not vaporized
108	SA3177	SAn + TO(1:2)	350	80	60	30	+	Outlet gas flow rate 82 from 55 ml/min; same yield, but more conv
109	SA3177	SAn + TO(1:2)	350	80	71	37	+	Feed rate 6 from 10ml/min; higher yield and higher conv
110	SA3177	SAn + TO(1:2)	350	80	85	20	+	Feed rate 10 from 6ml/hr; Gas rate 55ml/min; Longer reactor but furnace not long
113	SA3177	CAN	350	80	24	-	+	80% of CAN recovered; no other products (only CO2 and CAN)
114	SA3177	CAN	350	80	30	-	+	Product collection system new, but results same
115	SA3177	CAN	350	80	20	-	+	He and top of the furnace not heated, but same results
116	SA3177	SAn + TO(1:2)	350	80	76	39	+	Wanted to repeat R106, but high yield - high conv - low sel, 3 samples
117	SA3177	MMS+methanol	350	60	0	-	+	Methanol as a solvent from now; no rxn here; no cat deactivation
118	SA3177	MMS+TO(1:2)+me	350	60	40	31	+	Good sel; 32% DMS; Results after hydrolysis; low cat wt gain
119	SA3177	MMS+TO(1:2)+me	350	-	29	21	+	No He; lot of DMS
120	SA3177	MMS+TO(1:2)+me	350	-	29	22	+	No He; 45% DMS; good sel
121	SA3177	MMS+TO(1:2)+me	380	60	42	32	+	Results almost same as at 350 C;
122	SA3177	TO + methanol	350	60	100	-	+	Product gas only; I thought MTG process but Dr J says DME; ok he is right
123	SA3177	methanol	350	60	100	-	+	Not much in the trap, No cannizaro here so only water in trap
124	0.15 KH2PO4 SA3177	MMS+TO(1:2)+me	350	60	85	5	+	Loading equivalent to acid sites, presence of base kills rxn
125	CPG-75	MMS+TO(1:2)+me	350 & 400	60	90	0	+	No citraconates, but lot of DMS, No more CPGs from now
126	SA6175	MMS+TO(1:2)+me	350	60	30	18	+	Results after hydrolysis; not great--similar to SA3177

127	98 Al + 2 Mg	DMS + Form (1:2)	380	60	73	19	+	Lot of CO2, lot of methanol, 25% CA & 42% conv after hydrolysis
128	SA3177	DMS + Form (1:2)	380	60	80	26	+	Standard experiment, our optimal conditions
129	SA3177	DMS + Form (1:2)	380	60	77	26	+	CO2 as a carrier; Same result as with helium as a carrier gas
130	96 Al + 4 Mg	DMS + Form (1:2)	380	60	73	17	+	Hydrotalcites (HT) very reactive in beginning, bad MB in first 2-3 samples
131	99 Al + 1 Mg	DMS + Form (1:2)	380	60	75	20	+	Increasing Mg in HT increases methanol
132	99.5 Al + 0.5 Mg	DMS + Form (1:2)	380	60	89	23	+	CA conversion increases with decreasing Mg in HT
133	Alumina(lab)	DMS + Form (1:2)	380	60	81	23	+	Increasing Mg in HT increases CO2 also
134	Beads	DMS + Form (1:2)	380	60	15	0	+	Some MMS and SA in beginning, no CA like R101 & 102
135	0.015 KH2PO4 SA3177	DMS + Form (1:2)	380	60	81	26	+	Loading equivalent to (acid sites/10), 33% CA at 43% conc after hydrolysis
136	94 Al + 6 Mg	DMS + Form (1:2)	380	60	63	17	+	Conv of DMS decreases with increasing Mg in HT
137	88 Al + 12 Mg	DMS + Form (1:2)	380	60	61	12	+	End of HT runs, see HT comparison tables
138	SA3177	DMS + Form (1:2)	380	60	76	24	+	High He flow (double); FR=0.23ml/min; conv & Yield lower
139	SA3177	DMS + Form (1:2)	380	60	-	-	+	Same as R140, but some human error
140	SA3177	DMS + Form (1:2)	380	60	74	21	+	FR=0.3 ml/min; increased preheat to 250 to vaporize feed complete
141	SA3177	DMS+Formcel(1:2)	380	60	81	35	+	FR=0.15ml/min; bad MB because we lose MeOH in DME, good result
142	SA3177	DMS+Formcel(1:2)	380	60	66	22	+	FR=0.3 ml/min; conv & yield down; more cat wt gain than formalin
143	SA3177	DMS+Formcel(1:2)	380	60	65	20	+	FR=0.45 ml/min; didn't change much from above;
144	SA3177	DMS+Formcel(1:2)	380	60	59	9	+	Same as R143, same cat, no regen; checked temp 3 diff points above reactor
145	SA3177	DMS+Formcel(1:2)	380	60	-	-	+	
146	SA3177	DMS+Formcel(1:4)	380	60	66	26	+	Inlet DMS molar fraction = 0.086 (const) in R146 to R149
147	SA3177	DMS + Form (1:2)	380	60	62	21	+	
148	SA3177	DMS + Form (1:1)	380	60	57	15	+	Conversion decreases (not much) with decreasing formaldehyde
149	SA3177	DMS + Form (1:0.5)	380	60	52	10	+	Yield decreases with decreasing formaldehyde
150	AlPO; P/Al = 1	DMS + Form (1:2)	380	60	81	20	+	Not much methanol yield; high form conv;
151	AlPO; P/Al = 0.5	DMS + Form (1:2)	380	60	71	15	+	High cat wt gain in those AlPO run compare to wt taken initially
152	AlPO; P/Al = 1.5	DMS + Form (1:2)	380	60	49	0	+	No CA when P/Al = 1.5; Not moch CO2; not much form conv
153	SA3177	DMS + Form (1:2)	350	60	57	17	+	Good sel at low temp, though low yield of CA
154	SA3177	DMS + Form (1:2)	350	60	72	19	+	Longer Reactor; FR=0.15ml/min; not much diff from above
155	SA3177	DMS + Form (1:2)	350	60	65	14	+	Longer Reactor; FR=0.30ml/min; follows R153 results
156	SA3177	DMS + Form (1:2)	350	60	62	15	+	Same as R155; to see reproducibility=> excellent
157	SA3177	Itaconic + water	350	60	96	46	+	IA converts into CA at rxn conditions, ~100% conv, very dil IA in feed
158	Empty Reactor	Formalin	350	60	0	-	=	No loss of material; 100% recovery of form
159	SA3177	Formalin	200	60	52	-	+	Lot of CO2, negligible CO; methanol 31%

160	AlPO	Formalin	200	60	61	-	+	Not much CO2, more CO, 28% methanol
161	SA3177 (acid treated)	DMS + Form (1:2)	380	60		3	+	High yield of SA, fresh cat blackish;
162	66% Mg + 34% Al	Formalin	200	60	42	-	+	Lot of CO2, negligible CO; methanol 31%
163	SA3177	DMS + Form (1:0.5)	380	60	56	13	+	High conv of form (see R164); not good sel
164	SA3177	DMS + Form (1:0.5)	380	60	61	13	+	Cat regenerated from R163; cat activity preserves
165	SA3177	DMS + Form (1:2)	380	60	74	22	+	Mesh size 60/100; does not matter; not MT limited
166	SA3177	Formalin	380	20	100	-	+	Lot of CO in product

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