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CATALYTIC UPGRADING OF LACTIC ACID OVER SUPPORTED SALT CATALYSTS

presented by

Garry Clyde Gunter

has been accepted towards fulfillment of the requirements for

Ph.D. degree in <u>Chemical Engineering</u>

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CATALYTIC UPGRADING OF LACTIC ACID OVER SUPPORTED SALT CATALYSTS

By

Garry Clyde Gunter

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemical Engineering

1994

ABSTRACT

CATALYTIC UPGRADING OF LACTIC ACID OVER SUPPORTED SALT CATALYSTS

By

Garry Gunter

Liquid phase conversion of lactic acid over zeolites was performed in a batch reactor at 240-260°C and 590-960 psig for residence times of 2-3 hours. Products include acetaldehyde and ethanol at 30-42% selectivities, and lesser amounts of propanoic acid, acetic acid and acrylic acid. Conversions are 3.7-5.3% at 240°C based on lactic acid fed.

Lactic acid conversion over supported and neat sodium phosphate catalysts was performed in a packed bed reactor at 1.4-10 atmospheres, 280-350°C and contact times of 0.4-5.0 seconds. Five major reaction pathways were observed: 1) decarboxylation to acetaldehyde, 2) decarbonylation to acetaldehyde, 3) dehydration to acrylic acid, 4) reduction to propanoic acid and 5) condensation to 2,3-pentanedione. Minor products include ethanol, acetic acid, acetone and acetol. The high-value flavoring ingredient, 2,3pentanedione, has never been previously observed as a product of lactic acid condensation.

Production of acrylic acid is favored at 350°C and 0.4 seconds residence time. 2,3-Pentanedione formation is

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Sentaredione States. favored at 280°C and 4.0 seconds residence time. Basic phosphate salts favor acrylic acid and 2,3-pentanedione. Relatively acidic salts produce more acetaldehyde and propanoic acid.

A catalyst survey compared various supported sodium salt catalysts including tetraborate, carbonate, nitrate, silicate, phosphate, sulfate, chlorate, arsenate, bromate and molybdate. Very basic salts produce higher selectivities to 2,3-pentanedione, acidic salts produce more propanoic acid and moderately basic salts produce more acetaldehyde. Group V salts (nitrate, phosphate and arsenate) produce 2,3pentanedione selectivities up to 64%. Conversion increases with increasing size of the central atom of the catalyst salt.

A mixture of condensed sodium phosphate salts is present on the surface of supported phosphate salt catalysts and was analyzed using MAS-³¹P-NMR.

Chemical species adsorbed on model catalyst surfaces were studied using transmission FTIR. The more basic sodium phosphate salts alter the equilibrium between the gas phase and the surface reactants to produce a greater surface reactant concentration. This leads to greater conversion and better product selectivity.

Proposed reaction mechanisms to acrylic acid and 2,3pentanedione both involve formation of cyclic transition states. Copyright by Garry Clyde Gunter 1994

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Gunter, who

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I dedicate this work to my parents, Clyde and Geneva Gunter, who provided a strong foundation for development in my youth.

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Chapter 1. Introduction

1.1. Background

Lactic acid holds great potential as a feedstock in the chemical process industry. Lactic acid is produced by fermentation of corn starch hydrolysate. Increased demand for biodegradable polymers manufactured from lactic acid monomers has led to improved technology for production of lactic acid from starch hydrolysate at high yield and low cost. These developments enhance the prospects for use of lactic acid as a renewable-resource feedstock for production of traditionally petroleum derived chemicals. Lactic acid may be converted to several valuable products using inorganic catalysis. These products include acrylic acid, 2,3-pentanedione, propanoic acid, acetol and acetaldehyde.

Acrylic acid is the starting material for the production of acrylic and acrylate polymers, and is currently produced from petroleum by oxidation of propylene. One of the keys to the production of polymers from renewable resources is the conversion of lactic acid to acrylic acid. Lactic acid may be converted to the condensation product 2,3-pentanedione with greater than 50% selectivity over inorganic salt catalysts.

We have attempted to determine catalysts and conditions which favor the various product pathways and to achieve high

product yi attempted . lactic aci of surface using both 1.2. Litera 1.2.1. Lact ^{1.2.1.1.} Ma The ma the J.S. (1 preparation as producti 113 18 a r ias Ruch po lactic acid sich as eth already ext Presen produced by Via lactori by-product prepared t product yields using inorganic salt catalysts. We have also attempted to understand the chemistry of the conversion of lactic acid. We have gained insight into mechanistic aspects of surface reactions by determination of surface species using both NMR and FTIR.

1.2. Literature Review

1.2.1. Lactic Acid

1.2.1.1. Manufacture

The market for lactic acid is about 50 million lb/yr in the U.S. (1,2). Its uses include pharmaceutical preparations, leather and textiles, food additives, as well as production of inks, solvents, lacquers and plastics (3). This is a rather small market at present, but lactic acid has much potential. Its possible uses include production of lactic acid polymers, acrylic polymers, and small molecules such as ethanol and propylene glycol for which large markets already exist.

Presently, about 85% of the lactic acid sold is produced by synthesis. The most important synthetic route is via lactonitrile, as shown in Figure 1.1. Lactonitrile is a by-product of acrylonitrile synthesis, but can also be prepared from acetaldehyde and hydrogen cyanide (4).

CHICHO Acetaldehy CH3CH (CH) Lactonitri Figure 1.1 In the exclusivel organisms. routes and recently ar plants to r Plants will cost utiliz improved fe greater that Rentraditio Separation. . Actic acid With a low-).35/12. Xo polymer Bro Will Rake i $\begin{array}{rcl} CH_{3}CHO &+ & HCN &\rightarrow & CH_{3}CH\left(OH\right)CN\\ \mbox{Acetaldehyde} & & Lactonitrile\\ CH_{3}CH\left(OH\right)CN &+ & 2 & H_{2}O &+ & HCl &\rightarrow & CH_{3}CH\left(OH\right)COOH &+ & NH_{4}Cl\\ \mbox{Lactonitrile} & & & Lactic & Acid\\ \mbox{Figure 1.1. Lactic } Acid & Synthesis & via & Lactonitrile \\ \end{array}$

In the past, lactic acid was manufactured almost exclusively from sugar by fermentation using various microorganisms. The present trend is shifting away from synthetic routes and back to fermentation pathways. Plans have been recently announced by DuPont, ConAgra and Cargill to build plants to make lactic acid from corn starch. These new plants will produce higher yields of lactic acid at lower cost utilizing new technology. This technology includes improved fermentation processes with lactic acid yields greater than 95% theoretical and better purification using nontraditional separation techniques such as membrane separation. Current projections predict a tripling of the lactic acid market to greater than 150 million lb/yr in 1995 with a lowering of the price from \$0.60-1.00/lb to \$0.25-0.35/lb. Most of this new market is targeted for lactic acid polymer production, but the lower price of the feedstock will make its use for other products more viable.

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1.2.1.2. Properties

Lactic acid has rather interesting chemistry because it contains both hydroxy and carboxylic acid functional groups. Lactic acid self-esterifies to form lactide and polylactic acid (5). Lactic acid forms esters easily with alcohols. The boiling point of lactic acid is about 190°C at 1 atm pressure, so in many cases the high boiling point of lactic acid derivatives makes separation by distillation difficult because of unwanted side reactions.

1.2.1.3. Primary Conversion Pathways

Several studies have been performed which examine the conversion pathways of lactic acid. Many of these studies have focused on acrylic acid formation since acrylic acid is believed to be one of the keys to production of polymers from renewable resources.

Some of the challenges associated with catalytic conversion of lactic acid include: 1) difficulty in vaporizing lactic acid, 2) coking, cracking and esterification of the high boiling lactic acid, 3) poor selectivity to any one product leading to a complex product mixture, 4) difficulty in shutting down undesirable pathways, 5) sensitivity of product selectivity to contact materials and catalyst supports and 6) problems in developing reliable methods of analysis.

Holmé over sulfa rields of lactic aci Odell to acrylic acetic aci CH.CH(CH)CO Lactic Aci: Eigure 1.2 mese experiment of group .: rajor prod 2-538. Acr 48. Signie obtained . rendratio and lactic Detyg activite ac Catalysts Holmen describes reaction of lactic acid and lactates over sulfate and phosphate catalysts (6). Acrylic acid yields of 68% were obtained at about 400°C using 10% aqueous lactic acid solutions.

Odell, et al., (7) described conversion of lactic acid to acrylic, propanoic, β -hydroxypropanoic, pyruvic and acetic acids, as shown in Figure 1.2.

 $\begin{array}{rcl} CH_{3}CH(OH)COOH & \rightarrow & CH_{2}=CHCOOH \ + & CH_{3}CH_{3}COOH \ + & HOCH_{2}CH_{2}COOH \ + \\ \\ Lactic Acid & Acrylic Acid & Propanoic Acid & \beta-Hydroxypropanoic \\ & & Acid \end{array}$

CH₃CHOCOOH + CH₃COOH Pyruvic Acid Acetic Acid

Figure 1.2. Products of Lactic Acid Conversion Reported by Odell (7)

These reactions were carried out in sealed ampoule experiments in aqueous solution at 220-250°C over catalysts of group VIII metal complexes such as $[PtH(PEt_3)_3]^*$. The major product in all cases was propanoic acid with yields of 2-50%. Acrylic acid was produced at 230°C with a yield of 4%. Significant yields of β -hydroxypropanoic acid (28%) are obtained under the same conditions. This suggests rehydration of acrylic acid to form β -hydroxypropanoic acid and lactic acid.

Dehydration of lactic acid and ammonium lactate to acrylic acid in the vapor phase over aluminum phosphate catalysts is described by Paperizos, *et al.* (8,9). Aluminum

phosphate base such In the bes a reaction time using lactic aci acetaldehy ^{Catalyst} c. conversion Sawic of silica . and then b acid feed reactor, ti of 65% to A they acid in sup Cones (11). l acid ca-^EC, 2) dec dehydratio: are furthe: acid tydrog to form et: dehydratic: terperature

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phosphate catalysts were treated with an aqueous inorganic base such as ammonia to improve selectivity to acrylic acid. In the best case, a 61% yield of acrylic acid is obtained at a reaction temperature of 340°C and 4.2 seconds residence time using ammonium lactate feed. The best yield using lactic acid feed was 43% at 340°C. Propanoic acid, acetaldehyde and gases were the other major products. Catalyst calcination temperature was found to affect both conversion and yield.

Sawicki describes a catalyst prepared by impregnation of silica supports with monobasic sodium phosphate catalyst and then buffering with sodium bicarbonate (10). When lactic acid feed was introduced into a downflow Pyrex-lined reactor, this catalyst gave a yield of 58% and selectivity of 65% to acrylic acid at 350°C.

A thorough study of the reaction pathways of lactic acid in supercritical water was published by Mok, Antal and Jones (11). Three primary reaction pathways are described: 1) acid catalyzed decarbonylation to acetaldehyde, CO and H_2O , 2) decarboxylation to acetaldehyde, CO₂ and H_2 and 3) dehydration to acrylic acid and H_2O . Acetic acid and acetone are further reaction products of acetaldehyde, while acrylic acid hydrogenates to form propanoic acid or decarboxylates to form ethene. Increasing solvent density favors the dehydration pathway. Effects of solvent concentration, temperature, pressure and acid catalysts are described for

each pathw observed b CH_ICH (CH) C . Lactic Ac CH₂CHC Acetaldehy CH:=CHCCC: Aprilie Ac Figure 1.3 112a acid in st Catalysts ^{tar and 36} acid vield reactive s each pathway. Primary reaction pathways of lactic acid observed by Mok, Antal and Jones are shown in Figure 1.3.

 $\rightarrow CH_{3}CHO + CO + H_{2}O$ Acetaldehyde $CH_{3}CH(OH)COOH \rightarrow CH_{3}CHO + CO_{2} + H_{2}$ Lactic Acid
Acetaldehyde $\rightarrow CH_{2}=CHCOOH + H_{2}O$ Acrylic Acid

 $CH_3CHO \rightarrow CH_3COOH + CH_3COCH_3 + CH_4$ Acetaldehyde Acetic Acid Acetone Methane

$$\begin{array}{cccc} CH_2=CHCOOH & \stackrel{+H_2}{\rightarrow} & CH_3CH_2COOH \\ \mbox{Acrylic Acid} & \mbox{Propanoic Acid} \\ & \rightarrow & CH_2=CH_2 & + & CO_2 \\ & & & & & \\ & & & & \\ & & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & & \\ & &$$

Figure 1.3. Lactic Acid Reaction Pathways Observed by Mok, Antal and Jones (11)

Lira and McCrackin studied the dehydration of lactic acid in supercritical water using phosphate, acid and base catalysts (12). They observed 58% acrylic acid yields using homogeneous sodium phosphate catalysts at pressures of 310 bar and 360°C. Aging of the reactor favored higher acrylic acid yields. This was thought to be due to passivation of reactive sites on the reactor walls which cause undesired

side react selective under the pathways w Antal and a role in s Water-Gas CO ^{1.2.1.4}. Ti Reats Tajor reac; ^{values} or ϵ literature ali Major : ^{so only} kin Table 1.1.

Reaction CH (CH (CH) CC CH(CH)CC CH(CH)CC SCH (OH) O · Estimated

side reactions. This passivation is possibly caused by selective dissolution of metals from the alloy reactor walls under the influence of supercritical water. The same basic pathways were observed that had been seen before by Mok, Antal and Jones. The water-gas shift reaction may also play a role in product distribution.

Water-Gas Shift Reaction

 $CO + H_2O \neq CO_2 + H_2$

1.2.1.4. Thermodynamics

Heats of reaction and equilibrium constants for the major reaction pathways were calculated using literature values or estimated from molecular orbital calculations if literature values were not available. As seen in Table 1.1., all major reaction pathways are thermodynamically favorable, so only kinetic limitations exist for product formation.

Reaction	ΔH _{r,298 κ} (kJ/mol)	К
$CH_3CH(OH)COOH \rightarrow CH_3CHO + CO + H_2O$	87	2×10 ⁶
$CH_3CH(OH)COOH \rightarrow CH_3CHO + CO_2 + H_2$	46	7×10 ⁷
$CH_3CH(OH)COOH \rightarrow CH_2=CHCOOH + H_2O$	27	8×10 ³
$2CH_{3}CH(OH)COOH \rightarrow CH_{3}C(O)C(O)C_{2}H_{5} + 2H_{2}O + CO_{2}$	-21.	2×10 ^{8*}

Table 1.1. Heats of Reaction and Equilibrium Constants for Major Reaction Pathways

* Estimated from molecular orbital calculations.

1.2.2. Manu Acryl: and solution paints, pol polymers. about 10% : at about 54 acrylates y acrylate pr 14. EASF and Europe supply in 1 A verj production absorbing r Market has diapers, ad About 500 p the world : Production Clarity and وتنكز يروينيا ويداد Many I activitic act àti the ace the present

1.2.2. Manufacture of Acrylic Acid

Acrylic acid and acrylates are used to prepare emulsion and solution polymers used in coatings, finishes, binders, paints, polishes, adhesives, fibers and specialty acrylic polymers. The market for acrylates has grown at a rate of about 10% for many years and is expected to continue growth at about 5% in the near future. The world production of acrylates was about 2 billion pounds in 1985 (13). U.S. acrylate production in 1987 was about 1.1 billion pounds (14). BASF of Germany operates acrylate plants in the U.S. and Europe and produced about half of the world acrylate supply in 1991 (15).

A very large market for acrylates has been found in production of acrylic fibers for use in polyacrylate superabsorbing polymers (SAP). The exceptional growth of this market has been due largely to the use of SAPs in disposable diapers, adult incontinence and feminine hygiene products. About 500 million pounds of acrylic fibers were produced in the world in 1990, which is about 25% of the world acrylate production (16). Acrylate polymeric products have good clarity and strength and are resistant to chemical and environmental attack (17).

Many processes have been used commercially to produce acrylic acid in the past. Only the propene oxidation route and the acetylene-based Reppe process (BASF) are in use at the present time. All new plants being built are based on

propene ox propene is developed is about 8 of the con process f: oxidative 1.2.3. Rea Interreactions derivative. ^{1.2.3.1}. Py A seri described . acetoxy iso; (18-20). CH³COOCH Methyl a-20 ^{C∺್ಕCOOC}€ Nethyl a-20 ice by a vertical :

propene oxidation. This process is attractive because propene is cheap and very selective catalysts have been developed for the process. The overall yield of acrylic acid is about 80% based on propene (13). Figure 1.4. lists some of the commercial methods of acrylate production. Another process for the production of acrylic acid involves the oxidative carbonylation of ethene over a palladium catalyst.

1.2.3. Reactions Related to Acrylate Production

Interesting work has been published dealing with reactions of lactic acid derivatives to acrylates and derivatives thereof.

1.2.3.1. Pyrolysis of α -Acetoxypropionates

A series of papers in 1935 by Burns, Jones and Ritchie described the pyrolysis of α -acetoxypropionates and α -acetoxyisobutyrates to produce acrylates and methacrylates (18-20).

 $CH_3COOCH(CH_3)COOCH_3 \rightarrow CH_2=CHCOOCH_3 + CH_3COOH$ Methyl α -Acetoxypropionate Methyl Acrylate Acetic Acid

 $CH_3COOC(CH_3)_2COOCH_3 \rightarrow CH_2=C(CH_3)COOCH_3 + CH_3COOH$ Methyl α -Acetoxyisobutyrate Methyl Methacrylate Acetic Acid

The pyrolysis was carried out under nitrogen or CO_2 in a vertical Pyrex glass-lined iron tube packed with quartz

Propene C CH₁=CHC Propen CH2=CHCH2 Acrolein Acetylene 4HC≡CH + Acetylene Acetylene HC≡CH 1 Acetylene Acrylonity CHUECHOE SECHOECHOEC SCIECCITIC Ketene Rou-R(C=C=C) Ketere Ethylene C: ROCHICH staylene cy . • Condensatio CESCOCH Acetic Acid Figure 1.4.

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Propene Oxidation Route

catalyst $CH_2 = CHCH_3$ o, \rightarrow $CH_2 = CHCHO + H_2O$ Propene Acrolein + ½ 0₂ CH,=CHCHO \rightarrow CH,=CHCOOH Acrolein Acrylic Acid Acetylene Route (Reppe) $4HC \equiv CH + Ni(CO)_4 + 4H_2O + 2HC1 \rightarrow 4CH_2 = CHCOOH + H_2 + NiCl_2$ Acetylene Acrylic Acid Acetylene Route (BASF) Ni Catalyst $HC \equiv CH + CO + H_2O \rightarrow$ CH₂=CHCOOH Acrylic Acid Acetylene Acrylonitrile Route $CH_2 = CHC \equiv N + H_2SO_4 + 2H_2O \rightarrow CH_2 = CHCOOH + NH_4HSO_4$ Acrylic Acid Acrylonitrile Ketene Route CH₂O CH₂=CHCOOH $H_2C=C=O$ β -Propiolactone Acrylic Acid Ketene Formaldehyde Ethylene Cyanohydrin Route $HOCH_2CH_2C\equiv N + H_2SO_4 + H_2O \rightarrow CH_2=CHCOOH + NH_4HSO_4$ Ethylene Cyanohydrin Acrylic Acid Condensation of Acetic Acid with Formaldehyde CH₃COOH CH₂O \rightarrow $CH_2 = CHCOOH + H_2O$ Acetic Acid Formaldehyde Acrylic Acid Figure 1.4. Routes for the Production of Acrylic Acid

chips. At were obtain temperatur A nuri researcher. Filachione Eurns, Jor. pyrolysis on the eff. groups on acetoxypro; 3(8) Were Quartz chi: rods, copy. Materials, the format to lower c results we: ^{because} th. higher sel. ^{1.2.3.2}. Pr Vario: Waite (Wiroxyiso: chips. At 470-485°C, yields of 80-83% methyl methacrylate were obtained. This study also addressed the effect of both temperature and ester group on product yields.

A number of papers were published in the 1940s by the researchers Smith, Fisher, Ratchford, Fein, Rehberg, Filachione and Lengel (21-30). Building on the work of Burns, Jones and Ritchie, these papers also dealt with the pyrolysis of lactic acid derivatives to acrylates, focusing on the effects of contact times, contact materials and ester groups on the acrylate yields. For pyrolysis of methyl α acetoxypropionate, the best methyl acrylate yields (of about 90%) were obtained at 550°C and 10 seconds contact time. Quartz chips, aluminum strips, Pyrex, carborundum, carbon rods, copper and iron were found to be good contact materials, while silica gel and alumina led to coking and the formation of gases. Clay was found to be inert and led to lower conversions when used as a contact material. Best results were obtained using methyl ester groups mainly because the thermal stability of the methyl group led to higher selectivity to the desired products.

1.2.3.2. Preparation of Methacrylic Acid

Various preparations of methacrylic acid are discussed by White (31). These include dehydration of α hydroxyisobutyrates using phosphorus trichloride and dehydrohalogenation of α -halo isobutyrates.

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$CH_3C(OH)(CH_3)COOP$	R ·	+ PCl ₃	\rightarrow	CH ₂ =C(C	H ₃) COOR	+	H ₂ O
α-Hydroxyisobutyra	Phosphorus Trichloride		Methacrylate				
CH ₃ CX (CH ₃) COOR	\rightarrow	CH ₂ =C(0	CH ₃) COC)R +	НХ		

α-Halo Isobutyrate Methacrylate Hydrogen Halide

Filachione, Fein, Lengel and Fisher published a paper which discussed pyrolysis of acetoxyisobutyrates to esters of methacrylic acid (32). This was an extension of their work on acetoxypropionates. In this work, the ester groups were a series of lactates with various ester groups attached. The highest yield observed was 85% at 450°C for pyrolysis of the acetoxyisobutyrate of methallyl lactate.

 $CH_3COOC(CH_3)_2COOCH(CH_3)COOCH=CHCH_3$

Acetoxyisobutyrate of Methallyl Lactate

→ CH₂=C(CH₃)COOCH(CH₃)COOCH=CHCH₃ + CH₃COOH Methacrylate of Methallyl Lactate Acetic Acid

Abe, et al., observed a 93% yield of methacrylate at 240°C over aluminosilicate 13X molecular sieve (33). The vaporized feed was a 50% solution of methyl α -hydroxyisobutyrate in methanol.

CH₃C(OH) (CH Methyl a-Hydroxyisch 1.2.3.3. Ox Me Mary s mixed catic selectivity: isobutyric CHICH (CHI) C lsobutyric Watkin at 380-490% bismuch oxy tixed phosp ie. Ag. ...Cr. 75% às desc Ruszala sho ^{Selectiviti} Noresc rixed prosp ^{Se}. MeXp_{3.5}O,

1.2.3.3. Oxydehydrogenation of Isobutyric Acid to Methacrylic Acid

Many studies have been performed on phosphates with mixed cations. These catalysts have been shown to exhibit selectivity to methacrylic acid in oxydehydrogenation of isobutyric acid.

 $CH_{3}CH(CH_{3})COOH + \frac{1}{2}O_{2} \rightarrow CH_{2}=C(CH_{3})COOH + H_{2}O$ Isobutyric Acid Methacrylic Acid

Watkins reported methacrylic acid yields of about 70% at 380-490°C (34,35). The catalyst was a calcined residue of bismuth oxynitrate, iron phosphate and lead phosphate. A mixed phosphate catalyst with a composition of $Fe_{1.0}Ag_{0.15}Cr_{0.1}P_{1.31}O_x$ supported on silica gave yields of about 75% as described by Daniel (36,37). About the same time, Ruszala showed that iron phosphate catalysts can give selectivities up to 80% at 380°C (38).

Moreschini, et al., obtained yields of about 76% on mixed phosphate catalysts with an empirical formula $Fe_{1.5}MeKP_{3.5}O_x$, where Me is Ni, Zr or Al (39). Reaction

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A very interesting kinetic and catalyst screening study of heteropoly acids was published by Haeberle and Emig in 1988 (40). Their results pointed to 10-molybdo-2-vanadophosphoric acid and its cesium salts as catalysts for oxydehydrogenation of isobutyric acid at nearly 80% selectivity at 305°C. Three major pathways were identified which lead to formation of methacrylic acid, acetone and propene as well as CO and CO₂. Pulse reactor experiments showed that higher temperatures favor propene formation while high oxygen partial pressure favors the methacrylic acid pathway.

 $\begin{array}{c} + \frac{1}{2} O_{2} \\ \rightarrow \end{array} CH_{2}=C(CH_{3})COOH + H_{2}O \\ Methacrylic Acid \\ + O_{2} \\ CH_{3}CH(CH_{3})COOH \end{array} \xrightarrow{+ O_{2}} CH_{3}COCH_{3} + CO_{2} + H_{2}O \\ Isobutyric Acid \\ Acetone \\ H^{+} \\ \rightarrow CH_{2}=CHCH_{3} + CO + H_{2}O \\ Propene \end{array}$

1.2.4. Dehydration of Alcohols

1.2.4.1. Mechanism of Acid Catalysis

Dehydration of alcohols to form alkenes occurs via an El mechanism (41). First an acid catalyst donates a proton to the hydroxy group. In the rate determining step, a water

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Secondary

(CH) 2C*CH (CH

Figure 1.5.

molecule leaves to form a carbocation. If possible, the carbocation rearranges via methylene or hydride shifts in order to stabilize the positive charge. The last step involves abstraction of a hydrogen on a carbon adjacent to the carbocation by water to regenerate the acid catalyst and yield the alkene. The stability of the carbocation formed controls the product distribution. The product with the most stable cation will be the major product. This dehydration mechanism is presented in Figure 1.5.

Catalysts for alcohol dehydration include concentrated Brönsted inorganic acids such as sulfuric and phosphoric acid for primary alcohols. Secondary alcohols require less acidic conditions and tertiary alcohols are easier still. They react in dilute inorganic acids.

fast, 80°C $CH_3C(CH_3)_2CH(CH_3)OH + H_3O^+$ $CH_3C(CH_3)_2CH(CH_3)OH_2^+ + H_2O$ ₽Ż 3,3-Dimethyl-2-butanol slow $CH_{3}C(CH_{3})$, $CH(CH_{3})OH_{2}^{+}$ $CH_3C(CH_3)_2C^{+}HCH_3$ **₽**₽ H₂O + ~CH₃ $CH_3C^{+}(CH_3)CH(CH_3)CH_3$ $CH_3C(CH_3)_2C^{+}HCH_3$ secondary tertiary fast

 $(CH_3)_2C^*CH(CH_3)_2 + H_2O \rightarrow (CH_3)_2C=C(CH_3)_2 + CH_2=C(CH_3)CH(CH_3)_2 + H_3O^*$

major

minor

Figure 1.5. Acid Catalyzed Dehydration Mechanism

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1.2.4.2. Dehydration over Zeolite Catalysts

Zeolite catalysts were considered good candidates for dehydration of lactic acid to acrylic acid because Lewis acid catalysts such as zeolites and alumina have been used to catalyze gas phase dehydration of alcohols (42). Zeolites have both Brönsted and Lewis acid sites and are known to catalyze hydrocarbon cracking via carbonium ion intermediates (43-45). Several other considerations suggested zeolite catalysts to be suitable for the conversion of lactic acid: 1) high acidity, 2) high activity, 3) low coke formation and 4) regenerability (45).

Y and ZSM zeolites are both synthetic aluminosilicates. Y zeolite has a Si/Al ratio of about 2.4 and a structure made of sodalite cages connected to form 13Å faujasite supercages. The faujasite structure is entered through a twelve-membered ring about 8Å in diameter (46). ZSM-5 zeolite has a Si/Al ratio of about 3.5 and consists of a building unit of eight five membered rings which are joined at the edges to form chains. These chains link to form sheets and the sheets stack to form a three dimensional structure known as pentasil. The structure is entered through a ten-membered ring about 6.3Å in diameter (45). The topology of zeolite structure is presented in Table 1.2.
Table 1.2. T Zeolite Tr Superstruc+ Number of 7 Pore diamet Approximat. Many y. zeolite cat propanol CC: propene and (47). Methan over HZSM-5 Dehydra reviewed by ! reported over Was observed denydration ²⁴⁰⁻²⁷⁰¹⁰. c of ethanol t l-propanci t s-brobardl s. Wclohexene / Water, activity ove.

Table 1.2. Topology of Y and ZSM-5 Zeolites

Zeolite Type	Y	ZSM-5
Superstructure	Faujasite	Pentasil
Number of Tetrahedra in Ring	12	10
Pore diameter (Å)	8.0	6.3
Approximate Si/Al Ratio	2.4	3.5

Many researchers report dehydration of alcohols using zeolite catalysts. The acid catalyzed dehydration of 2propanol occurs via a carbocation intermediate to form propene and diisopropyl ether at 150°C over H Y zeolite (47). Methanol and ethanol are converted to hydrocarbons over HZSM-5 at 400°C (48).

Dehydration of alcohols using zeolite catalysts was reviewed by Turkevich (49). Dehydration of 2-butanol was reported over Ca A zeolite. Dehydration of ethanol to ethene was observed over metallic cadmium on X zeolite. 2-propanol dehydration over H X, Na Y and Ca A zeolites was seen at 240-270°C. Ca Y zeolite was reported to produce dehydration of ethanol to ethene at 250°C in 100% yield, dehydration of 1-propanol to propene in 90% yield at 275°C, dehydration of 2-propanol at 230°C and dehydration of cyclohexanol to cyclohexene in 100% yield at 170°C.

Water, alcohol and CO_2 are known to reversibly promote activity over faujasite zeolites for a wide variety of

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conditions and reactions (50). Promotion of isooctane cracking by CO_2 over ion-exchanged Y zeolites was studied using IR spectroscopy. The promotion mechanism involves reaction of surface species with CO_2 to convert basic hydroxyl sites to acidic hydroxyl sites and destruction of basic metal hydroxide species which inhibit cracking on the surface of the zeolite catalyst (51,52).

Dehydration of ethanol to ethene has been demonstrated by Cursetji, et al., over high silica zeolites containing iron (53). Yields of 98% were obtained at 350°C. This temperature is much lower than for more familiar catalysts such as alumina. Yields of 98.9% were observed over alumina at 450°C.

Ethene yields of 98.3% were reported by Dao over Zn and Mn ion-exchanged ZSM-5 zeolites at about 400°C (54).

Mao, et al., observed ethene yields greater than 97% over ZSM-5 zeolites for feeds with low ethanol concentrations of less than 19% by volume. The feed also contained other impurities present in fermentation products (55).

1.2.5. α -Diketones

1.2.5.1. Properties and Uses

 α -Diketones find most use in the pharmaceutical, flavor, fragrance and dye industries. Aliphatic diketones are yellow liquids with a penetrating odor at high

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α-Diketo

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^{EC(O)}C(O)CH a-Diketone ^{Eigure} 1.6. concentrations but a sweet, buttery smell when diluted. This is why they find use as butter flavor ingredients. The boiling point of 2,3-pentanedione is 108°C. 2,3-Butanedione and 2,3-pentanedione are both soluble in water but solubility decreases rapidly with increasing molecular weight (56). The market for 2,3-pentanedione is about 5 klb/yr while 2,3-butanedione has a market of about 50 klb/yr (14).

1.2.5.2. Reactions

Tautomerization of α -diketones forms the enol. Selfcondensation of α -diketones forms first the aldol, then quinones. α -Diketones may be reduced to α -ketols and then to α -diols (57). These reactions are shown in Figure 1.6.

RC(O)C(O)CH ₂ R'	\rightarrow	RC(O)C(OH)	=CHR '	
α -Diketone		Enol		
2 CH ₃ C (O) C (O) CH ₃	\rightarrow	CH ₃ C(O)C	(ОН) (С	² H ₃)CH ₂ C(Ο)C(Ο)CH ₃
α -Diketone			Ale	dol
CH ₃ C(O)C(OH)(CH ₃)CH ₂ C	C(O)C(C	$O) CH_3 \rightarrow \Box_{C (CH)}$	3) =CHC	C(O)C(CH ₃)=CHC(O)
Aldol				Quinone
$RC(O)C(O)CH_2R' \rightarrow$	RC (OI	H)C(O)CH ₂ R'	\rightarrow	RC (OH) C (OH) CH_2R'
α -Diketone	α-	-Ketol		α-Diol
Figure 1.6. Reaction	ns of c	-Diketones		

1.2.6. Cata 1.2.6.1. Pr Phosph. orthophosph. menebasic, condense to simplest ch phosphate c. Triphosphatthree phosp: is called to phosphale s crosslinking Tembered rin game common Egize 1.7. A Kal orthophospha sodium phosp MaHP.O.Y. F ^{results} in t quartities c is present i Boot. Maddre terperature.

1.2.6. Catalysts

1.2.6.1. Properties of Phosphate Salts

Phosphate salts exist in several different forms. The orthophosphate salts of sodium, for example, can exist in monobasic, dibasic and tribasic forms. Phosphates may condense to form chains and rings of various sizes. The simplest chain is called pyrophosphate and is made of two phosphate centers joined by a common oxygen atom. Triphosphate contains three phosphate centers. When these three phosphate ligands are joined to form a ring, the salt is called trimetaphosphate. Other stable forms of the phosphate salts include a long chain form with some crosslinking called Maddrell's salt and a rather stable six membered ring called hexametaphosphate or Graham's salt. Some common forms of sodium phosphate salts are presented in Figure 1.7.

Alkali phosphate salts are prepared by heating alkali orthophosphates (58,59). Partial dehydration of monobasic sodium phosphate (NaH₂PO₄) gives disodium pyrophosphate (Na₂HP₂O₇). Further heating to temperatures above 220°C results in the formation of Maddrell's salt. Small quantities of trimetaphosphate are formed also and this form is present in substantial amounts when heated above about 350°C. Maddrell's salt changes from a low to hightemperature form at about 300°C, as shown in Figure 1.8.



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Disodium Pyrophosphate



Tripolyphosphate



Sodium Trimetaphosphate





0 0 0 0 || || || || -0-P-O-P-O-P-O-P-O-| | | | ONa ONa ONa ONa

Maddrell's Salt

Figure 1.7. Sodium Phosphate Salts

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Monosodium Phosphate
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Maddrell's salt changes to trimetaphosphate in increasing amounts as heating continues up to the melting point of 625° C. Quenching of the melt yields formation of the glassy Graham's salt. Other forms of salts exist in the system $Na_2O-P_2O_5-H_2O$, but most of them are not very stable.

An excellent general review of phosphates as catalysts was published by Moffat in 1978 (60). This article describes various reactions catalyzed by phosphates and the effects of promoters such as copper(II) on selectivity. Phosphate structure and preparation as well as surface characterization are discussed. Phosphate catalysts have been used for both dehydration of alcohols to alkenes and oxidation of benzene to phenol.

1.2.6.2. Studies of Phosphate Salts using MAS-³¹P-NMR

Magic Angle Spinning Phosphorus-31 Nuclear Magnetic Resonance (MAS-³¹P-NMR) has been used to characterize phosphate salts. The chemical shifts and anisotropies of several sodium phosphates are listed as reported in the literature in Table 1.4. Chemical shifts reported are relative to 85% H_3PO_4 where $\sigma = -\delta$. The chemical shift, δ , is reported according to IUPAC convention with $\delta > 0$ representing a downfield shift and deshielding.

Andrew, et al., identified three factors which determine the ³¹P chemical shift of sodium triphosphate $(Na_5P_3O_{10})$: 1) the number and electronegativaties of ligands on phosphorus, 2) the bond angles about phosphorus, and 3) the occupation of π -bonding orbitals of phosphorus (61). The observed difference in chemical shift between terminal and central phosphorus in sodium triphosphate is attributed mostly to increased π -bonding to terminal phosphorus atoms. Burlinson, et al., also studied linear sodium triphosphate and determined its chemical shift and shift tensor (62).

Duncan and Douglass studied sodium pyrophosphate (Na₄P₂O₇) and sodium polyphosphate (NaPO₃)_n, (where n≈26) (63). They found that the difference between the principal shielding components σ_{22} and σ_{33} increases with bonding of the phosphate unit. These differences are listed in Table 1.3. This effect is attributed to the change in the π character of the phosphorus bonds.

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Phosphate Unit		$ \sigma_{22} - \sigma_{33} $, ppm
End	0 ₃ -P-O-R**	0-35
Middle	$O_2 - P - (O - R)_2$	135-225
Ring	O ₂ -P-(PO ₃) _n	195-225
Branching	0-P-(0-R) ₃	230-295

Table 1.3. Effect of Phosphate Unit on Difference in Shielding Components σ_{22} and σ_{33}

* from analysis by Duncan and Douglass (63).

** R is a phosphate unit.

A thorough study of sodium phosphates was published by Hayashi and Hayamizu in which NMR results for several ortho-, pyro-, tri-, tetra- and metaphosphates are compared with literature (64). Rothwell, *et al.*, performed an extensive study of calcium phosphates, as well as a mineralized calcium phosphate, specifically human dental enamel (65). Both an upfield chemical shift and increased anisotropy were observed upon protonation of a phosphate species.

Prabhakar, et al., developed a relationship for ortho-, pyro- and metaphosphates in which the chemical shift of phosphorus is correlated with the effective nuclear charge of the cation, the partial charge on the phosphorus and the radius of the cation (66). The chemical shifts of the various forms of phosphates fall into distinct regions. Orthophosphates exhibit the highest chemical shift, metaphosphates have the lowest and pyrophosphates have intermediate shifts.

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Turner, et al., developed a correlation for the chemical shift of ortho-, pyro-, and metaphosphates which depends on five factors: 1) the number of π -bonding electrons, 2) the electronegativity of the next nearest neighbor, 3) the effective nuclear charge of the cation, 4) the radius of the cation and 5) the average deviation from the tetrahedral O-P-O bond angle (67).

Un and Klein studied the orientation and values of the principal components of the chemical shift tensor of several ortho-, pyro- and metaphosphates and found each to be sensitive to different chemical features (68). σ_{11} is coplanar with the shortest bond, σ_{22} is sensitive to the formal charge of the phosphate group and σ_{33} lies along the longest P-O bond and correlates with the P-O bond length and R-O-P-O-R' bond angle. The overall isotropic chemical shift, δ_i , is dominated by π -bonding effects, as reported by several other researchers.

Compound	Chemical Shift, ppm	Chemical	Shift Te	ensor, ppm	Ref.
	δ	σ ₁₁	σ ₂₂	σ_{33}	
Ca ₁₀ (OH) ₂ (PO ₄) ₆	2.8	19	4	-15	(65)
Human Dental Enamel	3.3				(65)
NaH ₂ PO ₄ •H ₂ O	2.3	77.3	-23.1	-61.1	(67)
Na ₂ HPO ₄	6.6	48.9	5.7	-74.5	(67)
Na ₂ HPO ₄ •12H ₂ O	-16.6	69.8	35.5	-55.4	(68)
Na ₃ PO ₄	14.0				(64)
	13.0				(69)
	13.7				(66)
Na ₃ PO ₄ •10H ₂ O	7.7				(64)
Na ₃ PO ₄ •12H ₂ O	7.8				(67)
Na ₄ P ₂ O ₇	2.4	37	37	-80	(63)
	1.2	37	37	-80	(63)
	3.0	40	40	-89	(64)
	2.2	40	40	-89	(64)
	3.2				(66)
	2.1				(66)
	2.7	46	33	-87	(68)
	1.3	50	27	-81	(68)
$Na_{4}P_{2}O_{7} \cdot 10H_{2}O$	-1.4				(64)
	-2.3	38	38	-70	(64)
$Na_{4}P_{2}O_{7} \cdot 12H_{2}O$	-1.7	49	32	-76	(68)
	-2.0	58	26	-78	(68)
$Ja_2H_2P_2O_7$	-13.0	80	24	-65	(68)

Table 1.4. Chemical Shifts and Tensors Reported in Literature

Compound	δ	σ_{11}	σ ₂₂	σ_{33}	Ref.
Na ₅ P ₃ O ₁₀ -I	1.2 ^T				(70)
	-8.0 ^c				(70)
Na ₅ P ₃ O ₁₀ (-II)	5.6 ^T				(61)
	-6.2 ^c				(61)
	5.1 ^T	62	32	-109	(64)
	-5.6°	120	-24	-79	(64)
	4.6	69	24	-107	(68)
	-5.6	117	-20	-80	(68)
Na ₅ P ₃ O ₁₀ -II	4.0 ^T	62	37	-113	(62)
	-5.7°	118	-22	-79	(62)
	4 .6 ^T				(70)
	-6.6 ^c				(70)
Na ₅ P ₄ O ₁₃	1.5 ^T	47	47	-98	(64)
	-16.4 ^c	152	-18	-85	(64)
(NaPO ₃) ₆	-6.0 ^T				(64)
	-19.6 ^c	165	-19	-87	(64)
(NaPO ₃) _n (n≈26)	2.0 ^T	45	45	-95	(63)
	-19.0 ^c	160	-13	-90	(63)
(NaPO ₃) _n	-15.6				(66)
	-18.5				(66)
	-19.9				(66)
	-24.1				(66)
	-26.8				(66)
	1.0 ^T				(64)
	-6.2 ^T				(64)
	-19.9 ^c	165	-20	-85	(64)

Table 1.4. Chemical Shifts and Tensors Reported in Literature (Continued)

1.2.7. Stu Infra characteri frequencie modes in a have been heteropoly (72). Stud IR technia spectrosc CTAT.SK.188 reactors a thin ca Windows w álsk Múst ⁰⁰⁰125. AI.05 With this islder it ret.ected Sarple an ^{gases} may Wile Der

1.2.7. Studies of Reaction Systems using IR Spectroscopy

Infrared spectroscopy (IR) has been used to characterize dibasic sodium phosphate. Observed vibrational frequencies have been assigned to the various vibrational modes in a paper by Ramakrishnan (71). MAS-³¹P NMR and IR have been applied to study of the interaction of supported heteropoly acids with silica and silica-alumina supports (72).

Studies have been performed in-situ using transmission IR techniques. Several researchers described designs for spectroscopic vapor phase catalytic reactors based on transmission techniques (73-81). These spectroscopic reactors are typically designed so that vapor is fed across a thin catalyst disk enclosed in a chamber equipped with windows which are transparent to IR radiation. The catalyst disk must be thin enough that significant IR transmission occurs.

Another useful technique is Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFT) (82,83). With this technique, IR radiation is focused onto a small holder into which powdered or solid sample is placed. The reflected radiation is collected by mirrors surrounding the sample and directed to the detector. In either technique, gases may flow across or through the heated catalyst sample while performing FTIR spectroscopy.

Chapter 2 2.1. Int: Dehj strong a Zeolites also kno: ion inter Catalysts lactic a: suggeste: conversio activity, 2.2. Met) ^{2.2.1}. Ma . Lac in an 85: concentry Supply. Y-8; torn from n. activitized 1.5 mm di

Chapter 2. Lactic Acid Conversion over Zeolites in a Batch Reactor

2.1. Introduction

Dehydration of alcohols is known to be catalyzed by strong acids and proceeds via carbocation formation (41). Zeolites have both Brönsted and Lewis acid sites and are also known to catalyze hydrocarbon cracking via carbonium ion intermediates (43-45). For this reason, zeolite catalysts were considered good candidates for dehydration of lactic acid to acrylic acid. Several other considerations suggested zeolites would be good catalysts for the conversion of lactic acid: 1) high acidity, 2) high activity, 3) low coke formation and 4) regenerability (47).

2.2. Methods

2.2.1. Materials

Lactic acid was obtained from Aldrich Chemical Company in an 85% aqueous solution and diluted to the required concentration with reverse osmosis water from a house supply.

Y-82 and Y-62 zeolite catalysts were obtained in powder form from Union Carbide Corporation. HZSM-5 catalyst was acquired from Mobil Research and Development Corporation in 1.5 mm diameter extruded cylindrical pellets of varying

lengths purging Gas, Inc The Tercury and was Zeolites determin assumed discusse: diameter ^{2.2.2}. ca Cata turnace with a S. . ^{10aded} 1: Screws of the Vess Which so beneath ⁰⁻ring f ^{Catal}yst Wool in t ı. т<u>.</u>е eletett w lengths from 3-12 mm. Carbon dioxide and nitrogen gases for purging the reactor were obtained from Airco, Inc. and AGA Gas, Inc. in 99.5 and 99.99% purity, respectively.

The weighted mean macropore diameter was determined by mercury porosimetry using a Micromeritics Pore Sizer 9310 and was found to be 1310 and 1910 Å for Y-82 and Y-62 zeolites, respectively. The macropore diameter was not determined for HZSM-5 zeolite and the micropore size is assumed to correspond with the particular zeolite type, as discussed in the introduction. Calculation of the macropore diameter is presented in Appendix A.

2.2.2. Calcination Furnace

Catalysts were calcined in a calcination furnace. The furnace consisted of a insulated stainless steel (SS) vessel with a SS lid which bolts onto the top. The catalyst was loaded into a 0.5 inch ID × 5.5 inch long ceramic tube which screws onto the bottom of the lid and extends down inside the vessel. The tube connects to the lid by means of a nut which screws into threads in the lid and is installed beneath a small flange bonded to the top end of the tube. An O-ring forms a seal between the lid and the tube. The catalyst is held in the vertical tube by a plug of glass wool in the bottom end.

The tube is heated from the outside by an electric element which slides loosely around the tube. The heating

element is feedback f of the tub The c an inlet i center of and out th Gas then f and the ve The purge Gas supply formace i: 2.2.3. Ca Cata under nit ^a brisk f hissing s ^{2.2.4}. Ba A11 Reactor y legcror c ^{Seal}ed by by two ha and compr

element is controlled by an Omega PID controller receiving feedback from a thermocouple which extends down the center of the tube and into the catalyst.

The catalyst may be purged by introducing gas through an inlet in the center of the lid. The gas flows down the center of the tube, through the catalyst and glass wool plug and out the end of the tube near the bottom of the vessel. Gas then flows up through the annular space between the tube and the vessel insulation and exits at an outlet in the lid. The purge gas flow may be reversed simply by connecting the gas supply to the outlet. A diagram of the calcination furnace is presented in Figure 2.1.

2.2.3. Catalyst Calcination

Catalysts were calcined at 300-400°C for 4-16 hours under nitrogen purge. The nitrogen flow was not measured but a brisk flow was assured by adjusting the flow until a soft hissing sound was heard from the gas outlet connector.

2.2.4. Batch Reactor

All reactions were performed in a 300 ml Parr Mini Reactor Model 4561M constructed of T316 stainless steel. The reactor consists of a SS pressure vessel with a SS lid sealed by a flat Teflon seal. The lid connects to the vessel by two half circular clamps with bolts which tighten the lid and compress the seal. A SS retainer ring assures that the



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Figure 2.1. Calcination Furnace

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The lid is equipped with a mechanical stirrer which is sealed by a water cooled seal to prevent failure of the seal. Gas and liquid may be added to or removed from the reactor by way of a dip tube which extends nearly to the bottom of the vessel and by a gas outlet in the lid. Temperature inside the reactor is measured by a thermocouple which also extends nearly to the bottom of the vessel. The vessel is heated by an external electric heating mantle controlled by a dedicated Parr Controller Model 4841 receiving feedback from the thermocouple. Vessel pressure is measured by a pressure gage at the dip tube inlet. The whole apparatus is supported by a reactor stand equipped with a stirrer motor.

Products of early experiments were sometimes green or even purplish in color and white precipitates were often observed. This suggested that lactic acid was reacting with the metal in the reactor walls. T316 SS is composed of about 65% Fe, 12% Ni, 17% Cr, 2.5% Mo, 2.0% Mn and 1.0% Si, so some of these metals may account for the product color and precipitate. Many exposed surfaces were lined with or replaced with non-corrosive materials to alleviate this problem. A glass vessel liner, glass stirrer, Teflon dip tube fitting, glass dip tube and glass thermocouple sheath were improvements designed to reduce contact of lactic acid with metal. These changes improved the product color

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dramatically, but small amounts of precipitate were still observed.

The reaction vessel is rated for 3000 psig at 350°C, but a rupture disk limits its operation to 2000 psig as a safety measure. A reactor diagram is presented in Figure 2.2.

2.2.5. Batch Reactor Operation

The batch reactor was cleaned thoroughly before each run. The vessel was disassembled and each of the components was cleaned individually with water and acetone, if necessary, to remove as much residue as possible. A small brush usually removed everything except a few stains on the glass vessel liner. The reactor lid was cleaned by rinsing with water and flushing residue from the dip tube inlet and gas inlet. The reactor was towel dried after cleaning and the components assembled in the reactor lid.

The glass vessel liner was loaded with reagents and the catalyst, if any, was poured into the liquid reagent solution on the benchtop and stirred briefly to disperse the catalyst. The loaded liner was then placed inside the vessel and the reactor was assembled.

The stirrer was started and the reactor was purged with Carbon dioxide bubbled through the dip tube and exiting through the gas outlet for 10 minutes. At this time the Outlet valve was closed, the CO₂ pressure was increased to

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Figure 2.2. Batch Reactor


about 17 psig and the reactor sat for 10 additional minutes. The inlet valve was then closed, thus sealing the reactor, and heating was commenced. The reactor required about 50 minutes to heat from room temperature to 240°C. Temperature overshoot was typically less than 4°C and lasted for less than 5 minutes. Operator intervention reduced this overshoot to 1°C in later runs.

Upon reaching reaction temperature, the timer was started and the pressure and temperature were recorded at intervals until the end of the run. Typical batch reactor operating conditions are presented in Table 2.1.

Table 2.1. Batch Reactor Operating Conditions

Temperature (°C)	240-260
Starting Pressure (at 25°C) (psig)	16-18
Ending Pressure (at 240°C) (psig)	590-620
Ending Pressure (at 260°C) (psig)	960
Pressure after Quenching (at ~0°C) (psig)	95-140
Liquid Feed Concentration (wt%)	8.5-36
Liquid Feed Mass (g)	100.0
Reaction Time (hr)	2-3
Catalyst Mass (g)	1-3
Purge Gas	CO ₂

After the run, the heater was turned off, the heating mantle was removed from the reactor and the reaction was quenched. The bottom of the reactor was first submersed in hot water, then ice water, as the reactor cooled to less than ab 240°C to assembl refrige reactor refrige Af reactor into th then op and ana 2.2.6. 02 Particu With a standa: Analysi à glass Gas chi i:stal detect; on a He this sy âCetâte than about 100°C. We were able to cool the reactor from 240°C to less than 50°C within 10 minutes. The whole reactor assembly was then removed from the stand and placed in the refrigerator after cooling to about 10°C in ice water. The reactor was allowed to cool to about 0°C in the refrigerator, usually by leaving it overnight.

After cooling, the temperature and pressure in the reactor were recorded and the gases were bled off slowly into the fume hood to relieve the pressure. The reactor was then opened and the liquid product was collected, measured and analyzed.

2.2.6. Product Analysis

Crude liquid reaction products were filtered to remove particulate using disposable syringe filters, then mixed with a standard solution containing an internal calibration standard, 2-propanol, and a column conditioner, oxalic acid. Analysis was performed using a 1.0 µl sample injected into a glass 2 mm × 2 m 4% Carbowax 20M, 80/120 Carbopack B-DA gas chromatograph column from Supelco, Inc. The column is installed in a Varian 3700 GC with a flame ionization detector and helium carrier gas. Chromatograms were recorded on a Hewlett Packard HP3394 Integrator. Products analyzed by this system include acetaldehyde, ethanol, acetone, methyl acetate, 2-propanol, acetic acid, 2-butanone, acetol, 2,3-pent acid. Ear Spheroca Supelco, thermal Perkin-E nitroger ethane, later, ç 80/100 (Supelco, conducti Welch X: helium (Carbon ; acetyle: Jàs àr.a entered Yields Ð, Product of lact reprodu lactic 2,3-pentanedione, propanoic acid, acrylic acid and lactic acid.

Early gas samples were analyzed using a 1/8 inch x 6 ft Spherocarb 80-100 mesh in stainless steel GC column from Supelco, Inc. installed in a Perkin-Elmer 8500 GC with a thermal conductivity detector. Results were printed on a Perkin-Elmer GP-100 Graphics Printer. This GC setup detects nitrogen, oxygen, carbon monoxide, carbon dioxide, methane, ethane, ethene and acetylene using helium carrier gas. Later, gas samples were analyzed using a 1/8 inch x 5 ft 80/100 Carbosieve SII in stainless steel GC column from Supelco, Inc. installed in a Varian 3300 GC with a thermal conductivity detector. Results were recorded on a Sargent-Welch XKR Recorder with an electronic integrator. Using helium carrier gas, this GC system detects nitrogen, oxygen, carbon monoxide, carbon dioxide, methane, ethane, ethene and acetylene. The GC operating parameters for both liquid and gas analysis are presented in Table 2.2. GC results were entered into a spreadsheet in which mass balances, product yields and selectivities were calculated.

During the early stages of our studies of lactic acid products, we experienced considerable problems with analysis of lactic acid in the GC column. The GC peaks were not reproducible and calibration curves were nonlinear for lactic acid. This led to large errors in mass balances. This

Table 2. Liquid A Injecto: Initial Ramp Final C Detecto Gas Ana Injecto Initia] Ramp Final (Detecto IC EI proble lactic ile: àid lia techni 1 inser: is let :0 al: 001 Linn. . Actic s:_{Owl}y

Liquid Analysis Column	Supelco 4% Carbowax 20M 80/120 Carbopack B-DA in glass
Injector Temp.	200°C
Initial Column Temp.	100°C/0 mins
Ramp	25°C/min
Final Column Temp.	200°C/9 mins
Detector Temp. (FID)	200°C
Gas Analysis Column	Supelco 80/100 Carbosieve SII in Stainless Steel
Injector Temp.	200°C
Initial Column Temp.	50°C/2 mins
Ramp	20°C/min
Final Column Temp.	200°C/2 mins
Detector Temp. (TCD)	200°C
TCD Filament Temp.	300°C

Table 2.2. GC Operating Parameters

problem was found to be mostly due to holdup of high-boiling lactic acid in the dead space just beneath the septum on the inlet port to the column. Results were much more consistent and mass balances improved when we changed our injection technique by taking the following steps:

1) During sample injections, the injection needle is inserted, the plunger is depressed quickly, then the needle is left inserted in the septum for one minute before removal to allow the high boiling lactic acid to vaporize in the column. Immediate removal of the needle deposits a "drop" of lactic acid in the dead space beneath the septum, which slowly elutes into the column upon vaporization, leading to an eleva: calibrat: 2 aquecus equilibr 3) least tw 4) reproduc Car technig 2.2.6.1 Ξ. repeate Table 2 Çeaks a àrea. T highest an elevated baseline, poor reproducibility and nonlinear calibrations.

2) At startup, injection of a standard solution of 17% aqueous lactic acid saturates the column and brings it to equilibrium quickly.

 Repeated injections of the same sample (usually at least two injections).

4) Use of an internal standard, 2-propanol, insures reproducibility.

Carbon balances are typically within 10% using this technique.

2.2.6.1. Reproducibility of Product Analysis

The reproducibility of GC analysis was tested using 6 repeated runs of a representative sample and is presented in Table 2.3. The standard deviations of all major product peaks are between 1.5 and 7.5% of the mean value of the area. The standard deviation of the lactic acid peak is highest, at 14% of the mean value.

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Table 2.3. Reproducibility of GC Analysis

Compound	Standard Deviation (% o	f mean)
Acetaldehyde		4.7
2-Propanol		6.8
2,3-Pentanedione		6.2
Propanoic acid		6.7
Acrylic acid		1.5
Lactic acid		14.1
CO		7.5
CO ₂		6.2

2.3. Results

2.3.1. Definitions

The following definitions apply for discussions in this paper: Conversion (BOF) = 1 - (moles of reactant recovered/moles of reactant fed) Conversion (Adj) = Conversion (BOF) + Error(%C) Yield of A = (equivalents of A recovered/moles of reactant fed) Selectivity of A = (equivalents of A recovered/equivalents of all products recovered)

2.3.2. Effect of Temperature in Blank Runs

Blank runs of 34 wt% lactic acid with no catalyst were performed at 240, 250 and 260°C at a reaction time of 3 hrs. The products of lactic acid conversion included acetald acid, a 240 to 9.9%. 2 as the to etha rise. S to inc: to alm to bot} Same a C ethano favors acid s terper gCefol than 2 or pro 2.4. 2.3.3. С 1.000 Teacti: ^{zecli}t;

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acetaldehyde, ethanol, propanoic acid, acrylic acid, acetic acid, acetone and acetol. As the temperature was raised from 240 to 260°C, the conversion was seen to double from 5.2 to 9.9%. Acetaldehyde selectivity decreased from 57.3 to 25.6% as the temperature rose from 240 to 260°C while selectivity to ethanol rose from 20.9 to 47.9% over the same temperature rise. Selectivity to acetone and acetic acid were also seen to increase with temperature. Acetol selectivity dropped off to almost zero as temperature increased while selectivities to both propanoic acid and acrylic acid remained about the same at 13.5-16.5 and 3.7-4.0%, respectively.

Overall, an increase in reaction temperature favors ethanol and acetic acid formation while a lower temperature favors acetaldehyde formation. Acrylic acid and propanoic acid selectivities are unaffected by temperature. High temperatures also favor acetone while low temperatures favor acetol, but each of these two minor products contribute less than 2% to the overall conversion. The effect of temperature on product distribution in blank runs is presented in Table 2.4.

2.3.3. Effect of Y Zeolite Catalyst on Product Selectivities

Conversion of 34 wt% lactic acid was performed over 1.000 g of Y-82 zeolite catalyst at 240 and 250°C for a reaction time of 3.0 hours. A comparison of results over Y zeolite and blank runs reveals four striking differences

Table 2.

Temperat

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Propanc: Acetald

Acetol Acetone Ethanol

Acetic Belecti Acrylic Propano Acetald Acetol Acetone Ethanol hCetic 100.0 Lo ca ಭಾಂಗ ಕರೆ àCelaló increas formati COLVers gC670D6 i: I_{àbl} Ag terbera iecreas

Temperature (°C)	240	250	260
Conversion (Adj)(%)	5.2	6.6	9.9
Yield (%)			
Acrylic Acid	0.27	0.36	0.53
Propanoic Acid	0.97	1.42	2.21
Acetaldehyde	4.10	3.11	3.42
Acetol	0.07	0.06	0
Acetone	0.06	0.13	0.26
Ethanol	1.50	3.58	6.40
Acetic Acid	0.19	0.31	0.55
Selectivity (%)			
Acrylic Acid	3.7	4.0	3.9
Propanoic Acid	13.5	15.8	16.5
Acetaldehyde	57.3	34.7	25.6
Acetol	1.0	0.6	0.01
Acetone	0.8	1.5	1.9
Ethanol	20.9	39.9	47.9
Acetic Acid	2.7	3.5	4.1

Table 2.4. Effect of Temperature on Product Distribution in Blank Runs

* 100.0 g of 34.0 wt% lactic acid feed, reaction time 3 hrs, no catalyst.

upon addition of the catalyst: 1) a considerable decrease in acetaldehyde yield, 2) an increase in ethanol yield, 3) an increase in acetic acid yield and 4) suppression of acetol formation. Y zeolite catalyst has no significant effect on conversion or yields to acrylic acid, propanoic acid and acetone. The effect of Y zeolite on product yields is seen in Table 2.5.

As seen in blank runs, an increase in reaction temperature favors ethanol and acetic acid formation, while decreasing acetaldehyde selectivity.

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Catalyst	none	Y-82**	none	Y-82**
Temperature (°C)	240	240	250	250
Conversion (Adj)(%)	5.2	3.9	6.6	7.3
Yield (%)				
Acrylic Acid	0.26	0.23	0.36	0.36
Propanoic Acid	1.0	0.8	1.4	1.7
Acetaldehyde	4.1	1.9	3.1	2.3
Acetol	0.07	0	0.06	0
Acetone	0.06	0.07	0.13	0.15
Ethanol	1.5	1.9	3.6	4.8
Acetic Acid	0.19	0.37	0.31	0.43

Table 2.5. Effect of Y-82 Zeolite on Product Yields

* 100.0 g of 34.0 wt% aqueous lactic acid feed, 3 hr reaction time,

** 1.000 g Y-82 zeolite calcined 400°C/16 hr under N_2 purge.

2.3.4. Effect of Catalyst Mass on Conversion

The effect of tripling the catalyst mass was examined over both Y-82 and Y-62 zeolites at 240°C for a feed of 34 wt% lactic acid. The only major effect was an increase in the ethanol yield upon addition of more catalyst. A slight increase in the propanoic acid yield and a slight decrease in the acetaldehyde yield were also seen, but these effects were small. The effects of catalyst mass are shown in Table 2.6.

2.3.5. Effect of Feed Concentration

Conversion over Y-62 zeolite was studied at lactic acid feed concentrations of 8.5 and 36.0 wt%. Table 2.7. reveals that increasing the feed concentration produces an increase in the selectivity to acetaldehyde and ethanol while

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Catalyst"	Y-82		Y-62	2
Catalyst Mass (g)	1.00	3.00	1.00	3.00
Temperature (°C)	240	240	240	240
Conversion (Adj)(%)	3.9	4.9	3.7	4.1
Yield (%)		· · · · · · · · · · · · · · · · · · ·		
Acrylic Acid	0.23	0.24	0.22	0.20
Propanoic Acid	0.82	1.05	0.98	1.16
Acetaldehyde	1.88	1.66	1.48	1.27
Acetol	0	0	0.09	0
Acetone	0.07	0.08	0.06	0.06
Ethanol	1.87	3.41	1.55	2.13
Acetic Acid	0.37	0.28	0.52	0.54

Table 2.6. Effect of Catalyst Mass on Conversion over Y Zeolites

* 100.0 g of 34.0 wt% aqueous lactic acid feed, 3 hr reaction time, ** Catalysts calcined 400°C/16 hr under N_2 purge.

decreasing selectivity to propanoic acid, acetol, acetone and acetic acid. No effect was observed on the selectivity to acrylic acid.

2.3.6. Comparison of Catalysts at 240°C

Conversion of 34 wt% lactic acid was compared at 240°C over a blank run as well as Y-82, Y-62 and HZSM-5 zeolite catalysts for a reaction time of 3 hours. Catalysts were found to have little effect on conversion, which hovered at 3.7-5.3% for all runs. Acrylic acid yield was slightly suppressed by both Y and HZSM-5 catalysts, with the more acidic HZSM-5 having the greatest effect. Acetaldehyde yield was cut in half over Y zeolites and decreased 25% over Table 2. Lactic A Temperat Convers: Yield (Acrylic Propano Acetald Acetol Acetone Ethanol Acetic Select: Acryli Propan Acetal Acetol Acetor Ethan ACeti Ceti Cat 223Màgair acia ang : Nere વેર્દ્રનુ Ciay

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Lactic Acid Feed Concentration (wt%)	8.5	34.0
Temperature (°C)	240	240
Conversion (Adj)(%)	4.8	3.7
Yield (%)		
Acrylic Acid	0.28	0.22
Propanoic Acid	2.16	0.98
Acetaldehyde	0.86	1.48
Acetol	0.15	0.09
Acetone	0.12	0.06
Ethanol	1.22	1.55
Acetic Acid	1.05	0.52
Selectivity (%)		
Acrylic Acid	4.7	4.6
Propanoic Acid	37.0	19.9
Acetaldehyde	14.7	30.2
Acetol	2.6	1.8
Acetone	2.1	1.1
Ethanol	20.9	31.7
Acetic Acid	18.0	10.6

Table 2.7. Effect of Feed Concentration on Product Distribution over Y-62 Zeolite

* 100.0 g aqueous lactic acid feed, 3 hr reaction time, catalysts calcined 400°C/16 hr under N₂ purge.

HZSM-5. Ethanol yield was increased by both Y and HZSM-5, again with HZSM-5 producing the greatest increase. Acetic acid yield was also increased by a factor of two over HZSM-5 and increased by a factor of 3-4 over Y zeolite. Zeolites were observed to have little effect on yields of propanoic acid, acetol and acetone. Product yields and selectivities over the catalysts are compared in Table 2.8. Table 2. Catalyst Conversi Yield (S Acrylic Propano Acetald Acetol Acetone Ethanol Acetic Selecti korylia Propano Acetal Acetol Aceton Ethano Acetic illo '' Cat 2.4. °℃7°° teact of _{Ca} ಯಿರಿ

Catalyst"	None	Y-82	Y-62	HZSM-5
Conversion (Adj)(%)	5.2	3.9	3.7	5.3
Yield (%)				
Acrylic Acid	0.27	0.23	0.22	0.19
Propanoic Acid	0.97	0.82	0.98	1.03
Acetaldehyde	4.10	1.88	1.48	2.99
Acetol	0.07	0	0.09	0.05
Acetone	0.06	0.07	0.06	0.08
Ethanol	1.50	1.87	1.55	2.53
Acetic Acid	0.19	0.37	0.52	0.37
Selectivity (%)				
Acrylic Acid	3.7	4.5	4.6	2.6
Propanoic Acid	13.5	15.7	19.9	14.2
Acetaldehyde	57.3	35.9	30.2	41.3
Acetol	1.0	0.0	1.8	0.6
Acetone	0.8	1.3	1.1	1.1
Ethanol	20.9	35.7	31.7	35.1
Acetic Acid	2.7	7.1	10.6	5.1

Table 2.8. Conversion over Zeolites at 240°C*

* 100.0 g of 34.0 wt% aqueous lactic acid feed, 3 hr reaction time, ** Catalysts calcined 400°C/16 hr under N_2 purge.

2.4. Discussion

The reaction temperature was seen to affect the overall conversion. Conversion increased from 5.2 to 9.9% as the reaction temperature increased from 240 to 260°C. Addition of catalysts, variation of catalyst mass and the feed concentration did not affect conversion significantly.

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Increasing the lactic acid feed concentration from 8.4 to 34 wt% increased yields to acetaldehyde and ethanol and cut yields to propanoic acid, acetol, acetone and acetic acid nearly in half. Little change was noted in the overall conversion.

Acrylic acid yield decreased slightly with increasing acidity of the catalyst. The yield of acetaldehyde was suppressed by both Y and HZSM-5 zeolites, with Y zeolites producing only 36-46% as much acetaldehyde as blank runs. Both Y and HZSM-5 zeolites increase ethanol production, with HZSM-5 producing the highest yield. Acetic acid yields were increased by a factor of 2-3 over zeolites, when compared to no catalyst. Catalysts had little effect on yields of propanoic acid, acetol and acetone.

2.5. Summary

Conversion of aqueous lactic acid over Y and HZSM-5 zeolites were studied in a batch reactor at 240-260°C and were found to produce mostly acetaldehyde and ethanol at selectivities of 30-42%, as well as propanoic acid at 14-20% selectivity. Acetic acid and acrylic acid were formed with selectivities of 5-11% and 2-5%, respectively. Less than 2% selecti Overall acid fe Ze . iesira to the propar less ; conve not h under Were ació

selectivity to acetol and acetone were also observed. Overall conversions were 3.7-5.3% at 240°C based on lactic acid fed.

Zeolite catalysts produced poor selectivities to the desirable product acrylic acid, and considerable selectivity to the undesirable products acetaldehyde, ethanol and propanoic acid. The lactic acid conversions observed were less than 10% at reaction temperatures of 240-260°C. These conversions are rather small and indicate that zeolites do not have much catalytic activity at these temperatures and under these batch reaction conditions. Overall, zeolites were found to be poor catalysts for conversion of lactic acid to valuable products.

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Chapter 3. Lactic Acid Conversion over Phosphate Salt Catalysts

3.1. Introduction

Reactions of lactic acid were performed in the vapor phase in a downflow differential packed bed reactor over both supported and neat sodium phosphate salts. Effects of temperature and residence time on the yields and selectivities to products were observed. Product selectivities and conversion were compared for various sodium phosphate salts.

3.2. Methods

3.2.1. Materials

Lactic acid was obtained from Aldrich Chemical Company in an 85% syrup solution in water, from which aqueous lactic acid feed solutions were prepared by dilution with HPLC grade water. HPLC grade water was obtained from Sigma-Aldrich, J.T. Baker, Inc. and Baxter Scientific and was reported to have a maximum evaporation residue of 3 ppm. Reverse osmosis (RO) water used in catalyst impregnation was obtained from a house supply. Sodium lactate was obtained from Aldrich in solid crystalline form. Silica alumina (Si/Al) catalyst support (93% alumina, 7% silica) was purchased from Johnson-Matthey in cylindrical pellets with

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the dimensions 2.3 mm diameter by 2.3 mm long. $NaH_2PO_4 \cdot H_2O_1$, Na_2HPO_4 and $Na_4P_2O_7$ were obtained from Aldrich in solid lumps or crystals. $Na_3PO_4 \cdot 12H_2O$ was obtained from EM Science in a solid form. $(NaPO_3)_n$, $Na_5P_3O_{10}$ and $Na_3P_3O_1$, were obtained as practical grade solids from Sigma. Reagent grade phosphoric acid, H_3PO_4 , was obtained from Mallinckrodt in an 85% aqueous solution. Bovine dental enamel was obtained from the meat packing laboratory at MSU. Helium carrier gas was purchased from AGA Gas, Inc. in 99.99% purity.

3.2.2. Catalyst Preparation

Catalysts consisted of inorganic salts impregnated into silica-alumina supports. Before impregnation, catalyst support pellets were crushed with a mortar and pestle until all pellets were at least broken in half. All particles retained in a #16 USA wire mesh sieve were used as catalyst support. The catalyst salt was added to RO water in a glass beaker and stirred to dissolve. Heating on a hotplate was used to speed dissolution, if necessary. Crushed catalyst support was added to the aqueous salt solution and stirred to wet all the support. The salt was dissolved in sufficient water to completely cover the catalyst support. In all cases, the aqueous salt solution was immediately taken up into the support to replace air, as evidenced by the vigorous expulsion of tiny air bubbles upon addition of the support. The slurry of catalyst pellets was heated on a

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hotplate with occasional stirring to boil off the water. When most of the liquid was gone, the supported catalyst was removed from the hotplate and placed in an oven. Overnight heating at about 100°C dried the catalyst completely. Complete drying was checked gravimetrically. Catalyst loading was 1.0 mmol/g support unless otherwise stated. Takeup of catalyst salt into the support was typically greater than 95%, based on the residue left in the preparation vessels. After impregnation, the supported catalyst was then weighed and loaded into a quartz liner tube which was inserted inside the reactor tube.

Bovine dental enamel used as catalyst was prepared by boiling in water to remove flesh, then crushing and sieving to 16 \times 30 USA wire mesh. The catalyst was then calcined at 800°C for 1.0 hr in air.

3.2.3. Vapor-phase Reactor

All reactions were performed in a downflow differential packed bed vapor-phase reactor lined with quartz. The reactor body consists of a stainless steel tube 19.5" long ,1.25" OD, and 0.55" ID, with a 6.5" long and 0.5" thick copper heat sink around the heated section to heat the reactor evenly. The bottom of the reactor is removable to allow access to the catalyst, which is supported on a coarse quartz frit fused into a 19" long and 0.50" OD quartz liner tube. The catalyst and liner tube is inserted into the react gas i betwe react well botto react spri Heli tibe ând bure Stal disp read Ĵas 2 the : Lêĝ ins 9<u>75</u> Set

reactor from the bottom. Bypassing of the catalyst bed by gas is prevented by a Viton O-ring which seals the annulus between the liner and the inside reactor wall. The inside reactor temperature is measured inside a quartz thermocouple well which extends from the bottom of the reactor up to the bottom of the frit supporting the catalyst. The removable reactor end is sealed to the main body of the reactor by a spring-loaded metal to metal seal ring manufactured by the Helicoflex Company. Stainless steel liquid and gas feed tubes enter the top of the reactor through a Conax fitting and extend down inside the quartz liner tube.

Liquid feed solutions are fed from a 50 ml titration buret with graduations of 0.1 ml, through an in-line stainless steel filter and into an Eldex HPLC positive displacement metering pump. Liquid is pumped into the reactor through 1/16" stainless steel tubing. Helium carrier gas or air for calcination may be fed to the reactor.

The reactor is heated by a clamshell electric heater. An Omega PID temperature controller receives feedback from a thermocouple mounted outside the reactor walls between the heating element and the copper heat sink. The temperature inside the reactor is measured by a thermocouple inserted into the thermocouple well at the bottom of the reactor and extending to just below the catalyst bed.

Temperature control is achieved by adjusting the setpoint of the controlled outer temperature until the

temperature inside the reactor achieves the desired temperature. The outside temperature is about 30°C higher than inside at an inside reactor temperature of 300°C. An attempt was made to control the temperature using feedback from the thermocouple inside the reactor, but the lag time was too great and instability resulted.

The cooler ends of the reactor are heated to 150-180°C by heat tape controlled by an Omega controller. The cool ends of the reactor are heated to prevent condensation and collection of products in these zones. A diagram of the reactor setup is presented in Figure 3.1. Typical reactor operating conditions are given in Table 3.1.

Temperature (°C)	280-350
Pressure (psig)	60
Liquid Feed Concentration (wt%)	36
Liquid Feed Flowrate (ml/min)	0.05-0.50
Residence Time (s)	0.2-8.0
Catalyst Weight (g)	2-6
Catalyst Bed Length (cm)	2.5-7.6
Feed Composition (mol%)	8% Lactic Acid 77% H ₂ O 15% He

Table 3.1. Reactor Operating Conditions



Figure 3.1. Vapor-phase Reactor

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3.2.4. Product Collection

Reactor effluent passes to a pair of stainless steel ice traps in parallel. One trap accommodates a 40 ml volume and is used for product collection during reactor equilibration between runs. The other trap is used for product collection during a run and accommodates only 10 ml. It is cleaned between each run. Both traps are immersed in ice water while in use. Trap selection is made by a set of two-way valves.

After passing through the ice trap, reactor effluent gases flow through a filter, gas metering valve and a ball flowmeter. Gases may then either be collected in a evacuated gas collection bag for analysis, or allowed to flow through a bubblemeter and out to the vent. A reactor flow diagram is shown in Figure 3.2.

3.2.5. Reactor Operation

Each catalyst is loaded into the reactor then heated under helium flow until the temperature approaches 280°C, when the lactic acid feed solution is fed at a high flowrate of 0.5 ml/min. After product flow is established, helium and lactic acid feed flow rates as well as reactor temperature are adjusted to the desired values. The reactor is operated at these conditions for about 15 minutes to allow equilibration. The reactor run is then commenced with the collection of liquid product in the ice trap and gas product



Figure 3.2. Reactor Flow Diagram

in Saran gas bags for a length of time required to collect 2-7 ml of liquid product. This process is repeated at each set of reaction conditions.

3.2.6. Product Analysis

Methods of product analysis and the reproducibility thereof are discussed in Section 2.2.6.

3.3. Results

Conversion of lactic acid over supported and neat phosphate salt catalysts yields the major products acrylic acid, propanoic acid, 2,3-pentanedione and acetaldehyde. Minor products include ethanol, acetone, acetic acid, hydroxyacetone (acetol), 2-butanone, pyruvic acid and unknowns.

The condensation product, 2,3-pentanedione, was first observed as a product of lactic acid condensation in our laboratory. The identity of 2,3-pentanedione was confirmed by GCMS and by matching the residence time in GC analysis. The combination of elevated pressures, low temperatures and basic catalysts leads to observed 2,3-pentanedione selectivities approaching 60% based on conversion of lactic acid.

3.3.1. Definitions

The definition of "other" products includes all minor products listed above except acetol, which is listed separately, and unknowns, which are not included. Conversion, yield and selectivity are defined in Section 2.3.1.

3.3.2. Reactor Characterization

A series of experiments was performed to establish the catalytic effect of the phosphate salts on conversion of lactic acid. Reactions were first carried out in a tubular pressure reactor made of 316 stainless steel with a stainless steel liner in a horizontal flow configuration. This configuration led to poor mass balances due to excessive coking caused by incomplete vaporization of the high boiling lactic acid (b.p. 190°C). The reactor was changed to a vertical configuration to insure complete lactic acid vaporization.

Experiments were performed on 0.43 mmol Na₃PO₄/g silica-alumina support in this vertical configuration to determine the effect of the stainless steel and quartz liners. Results indicate that the quartz liner has a dramatic effect on the selectivity to all desired products. Conversion (BOF) at 280°C increased from 10% in quartz to 71% in stainless steel. Selectivity to acrylic acid triples and the 2,3-pentanedione selectivity increases by a factor

of four in quartz. In contrast, the propanoic acid selectivity decreases an order of magnitude and the acetaldehyde selectivity is cut in half in quartz. Formation of 2,3-pentanedione and acetaldehyde account for most of the CO and CO₂ formed with the quartz liner, but in stainless steel, formation of these two products accounts for only about 70% of the gases. This indicates either significant cracking or coking of lactic acid or secondary reactions. A comparison of results in the stainless steel and quartz liner tubes is presented in Table 3.2. Unless otherwise stated, all reactions reported below were performed with the quartz liner in place.

The effect of the reactor liner and support was examined by performing experiments in the empty quartz liner tube and over blank Si/Al support with no salt impregnated. Conversion for the empty blank liner at 0.7 seconds residence time was less than 5% even for high temperature runs at 350°C. The only products observed in significant quantities were propanoic acid and acetaldehyde. At 300°C, there was virtually no reaction with an adjusted conversion of less than 1%. The Si/Al support gave conversions from 4% at 280°C to 19% at 350°C. As with the empty blank, the Si/Al support exhibited selectivity to propanoic acid and acetaldehyde with acetaldehyde selectivity increasing up to 62% at higher temperatures of 350°C. Measurable yields of

Catalyst	Na ₃ PO ₄ on Si/Al (SS)	Na ₃ PO ₄ on Si/Al (Quartz)
Temperature (°C)	280	280
Residence Time (s)	1.60	1.53
Error (%C)	-32.8	7.29
Conversion (BOF)(%)	70.6	10.4
Conversion (Adj)(%)	37.9	17.7
Yield (%)		
Acrylic Acid	1.4	3.4
Propanoic Acid	9.3	0.6
2,3-Pentanedione	2.3	8.2
Acetaldehyde	6.3	2.5
Acetol	1.1	1.6
Other	1.1	0.9
coʻ	1.6	1
CO ₂ *	8.7	4.4
Selectivity (%)		
Acrylic Acid	6.4	19.8
Propanoic Acid	43.4	3.4
2,3-Pentanedione	10.9	47.4
Acetaldehyde	29.3	14.7
Acetol	5.0	9.4
Other	5.1	5.4

Table 3.2. Comparison of Results in Stainless Steel and Quartz Liner Tubes

* Yields of gases are reported as moles gas/moles lactic acid fed.

all the major products were observed at this temperature. The catalytic effect of the blank Si/Al support and the empty quartz tube are presented in Table 3.3.

3.3.3. Catalytic Effect of Phosphate Salts

Studies at three different residence times revealed that the addition of Na_3PO_4 to the Si/Al support produced a catalytic effect with strong selectivity to acrylic acid and 2,3-pentanedione. The yields of acrylic acid and 2,3pentanedione were increased by an order of magnitude over the phosphate catalyst while the yield of propanoic acid remained about the same. The yield of acetaldehyde stayed the same or even decreased at higher temperatures of 320-350°C.

The phosphate catalyst produced double the conversion of the blank support at 280-320°C and contact times of 0.4-4.0 seconds. As the temperature increased to 350°C, the phosphate catalyst continued to affect more conversion than the support, but the difference was not as pronounced. Product yields for lactic acid reaction over Na₃PO₄ supported on Si/Al and over blank Si/Al support as a function of temperature are shown in Table 3.4. for three different residence times.

Catalyst	Empty Quartz	Tube	Blank Si/Al	Support
Т(°С)	300	350	300	350
Residence Time (s)	0.69	0.62	0.46	0.42
Error (%C)	9.1	2.4	0.8	1.3
Conversion (BOF)(%)	-8.4	1.7	5.7	17.4
Conversion (Adj)(%)	0.7	4.2	6.5	18.6
Yield (%)				
Acrylic Acid	0	0.11	0.07	0.79
Propanoic Acid	0.09	1.26	0.52	1.21
2,3-Pentanedione	0	0	0.22	0.28
Acetaldehyde	0.12	1.47	1.49	9.00
Acetol	0	0	0.09	0.37
Other	0.25	0.19	0.41	2.87
CO*	0	1.01	1.11	10.57
CO ₂ *	0.43	2.56	0.24	1.95
Selectivity (%)				
Acrylic Acid	0	3.7	2.4	5.5
Propanoic Acid	20.0	41.6	18.6	8.3
2,3-Pentanedione	0	0	7.9	1.9
Acetaldehyde	25.6	48.5	53.3	62.0
Acetol	0	0	3.3	2.5
Other	54.4	6.2	14.5	19.8

Table 3.3. Catalytic Effect of Si/Al Support on Product Yields for Lactic Acid Conversion

* Yields of gases are reported as moles gas/moles lactic acid fed.

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Catalyst	Blá	ank Si/Al	Support			Na3PO4 on	Si/Al	
Temperature (°C)	280	300	320	350	280	300	320	350
Error (%C)	4.8	0.8	7.8	1.3	12.0	-5.8	4.5	-7.3
Conversion (BOF)(%)	-0.87	5.7	1.2	17.4	-3.3	19.9	15.3	39.9
Conversion (Adj)(%)	з . 9	6.5	0.6	18.6	8.7	14.1	19.9	32.6
Yield(%)								
Acrylic Acid	0.05	0.07	0.24	0.79	0.81	1.96	4.00	9.83
Propanoic Acid	0.50	0.52	1.26	1.21	0.61	0.87	0.87	1.47
2,3-Pentanedione	0	0.22	0.12	0.28	2.28	4.34	5.65	7.04
Acetaldehyde	0.98	1.49	2.15	9.00	0.78	1.89	2.61	5.17
Acetol	0	0.09	0	0.37	0.09	0.58	1.52	2.91
Other	0.37	0.41	0.87	2.87	0.43	0.49	0.72	1.15 9
20 1	0.82	1.11	2.17	10.57	0.43	0.63	1.40	2.97
co2"	0.35	0.24	0.42	1.95	2.92	4.97	8.41	10.19
Selectivity(%)								
Acrylic Acid	2.7	2.4	5.2	5.5	16.2	19.3	26.0	35.7
Propanoic Acid	26.0	18.6	27.2	8.3	12.1	8.6	5.6	5.3
2,3-Pentanedione	0	7.8	2.5	1.9	45.8	42.9	36.8	25.5
Acetaldehyde	51.7	53.3	46.4	62.0	15.5	18.7	17.0	18.7
Acetol	0	3.3	0	2.5	1.7	5.7	6.6	10.6
Other	19.6	14.5	18.7	19.8	8.6	4.8	4.7	4.2
* Residence time 0.39-0.	.47 s.							

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** Yields of gases are reported as moles gas/moles lactic acid fed.

Table 3.4. Catalytic Effect on Product Yields of Addition of Na₃PO4 to Si/Al Support^{*}

Catalyst	BI	ank Si/Al	Support			Na,PO, on	Si/Al	
Temperature (°C)	280	300	320	350	280	300	320	350
Error (%C)	0.3	-22.8	7.8	-22.2	12.0	-16.5	-14.0	-19.5
Conversion (BOF)(%)	10.6	36.4	19.8	75.7	14.2	59.0	73.6	85.4
Conversion (Adj)(%)	10.9	14.0	27.6	53.4	26.3	42.5	59.6	65.9
Yield (%)								
Acrylic Acid	0.43	0.26	0.83	2.48	3.11	7.36	11.50	9.22
Propanoic Acid	0.75	0.97	1.50	3.80	0.88	1.71	3.08	3.98
2,3-Pentanedione	0.12	0.26	0.36	1.73	9.07	11.81	11.11	5.53
Acetaldehyde	3.16	5.04	14.09	24.78	3.06	7.16	8.60	18.46
Acetol	0.23	0.25	0.92	3.16	1.05	3.96	5.27	2.93
Other	0.40	0.92	2.24	6.28	0.59	2.14	2.98	3.850
o	3.02	5.00	13.78	37.22	1.49	4.22	00.6	22.49
co2.	0.69	0.73	2.31	9.65	9.77	17.61	31.61	16.46
Selectivity (%)								
Acrylic Acid	8.4	3.4	4.2	5.9	17.5	21.6	27.0	21.0
Propanoic Acid	14.7	12.6	7.5	0.6	4.9	5.0	7.2	0.6
2,3-Pentanedione	2.3	3.4	1.8	4.1	51.1	34.6	26.1	12.6
Acetaldehyde	62.3	65.4	70.6	58.7	17.2	21.0	20.2	42.0
Acetol	4.5	3.2	70.6	7.5	5.9	11.6	12.4	6.7
Other	7.9	11.9	11.2	14.9	3.3	6.3	7.0	8.8

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Catalyst	Blank	Si/Al Suppor	t.	Na,PC), on Si/Al	
Temperature (°C)	280	300	350	280	300	350
Error (%C)	5.6	-12.4	-5.3	8.2	-4.3	-7.9
Conversion (BOF)(%)	16.8	28.9	69.1	31.6	56.5	82.0
Conversion (Adj)(%)	22.5	16.5	63.8	39.8	52.2	74.1
Yield (%)						
Acrylic Acid	0.38	0.51	1.82	4.42	8.19	3.40
Propanoic Acid	0.93	1.22	3.81	1.46	2.47	4.31
2,3-Pentanedione	0.15	0.34	1.40	13.43	13.41	3.17
Acetaldehyde	5.23	10.19	35.63	6.25	10.58	36.44
Acetol	0.34	0.80	1.90	2.17	4.92	1.68 0
Other	0.52	1.17	6.07	1.89	2.18	4.77
co	5.21	7.41	39.22	3.87	7.05	31.26
co,	0.89	1.32	9.37	14.03	19.24	20.98
Selectivity (%)						
Acrylic Acid	5.0	3.6	3.6	14.9	19.6	6.3
Propanoic Acid	12.3	8.6	7.5	4.9	5.9	8.0
2,3-Pentanedione	2.0	2.4	2.8	45.4	32.1	5.9
Acetaldehyde	69.3	71.6	70.4	21.1	25.3	67.8
Acetol	4.5	5.6	3.7	7.3	11.8	3.1
Other	6.9	8.2	12.0	6.4	5.2	8.9
* Residence time 3.83-4.5 ** Yields of gases are rep	0 s. orted as moles	gas/moles lact	ic acid fed.			

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3.3.4. Studies of Catalyst Loading over Supported Salts and Neat Salts

Conversion of lactic acid was performed over various loadings of Na_3PO_4 supported on Si/Al and over neat Na_3PO_4 . The effects of catalyst loading and support are seen in Table 3.5.

No significant trends were observed in either the yields or selectivities to liquid products over Na₃PO₄ supported on Si/Al at loadings of 0.43, 0.86 and 1.00 mmol salt/g support. A slight increase in the conversion was observed upon increased loading at 280°C, but the effect is small. Conversion increased from 17.7 to 26.3% upon more than doubling the loading at 280°C. Selectivities to propanoic acid change significantly, but the changes appear to be unrelated to catalyst loading.

Significantly lower conversions were observed over the neat salt, compared to the supported salt, at all temperatures studied. Conversions over the neat salt were typically half of those observed over the supported salt, although this difference became less pronounced at the high temperature of 350°C.

Employing a support enhanced the catalyst activity, but the selectivity to products remained unchanged. This suggests that the support serves only to increase the surface area of the catalyst and is not involved mechanistically in the catalysis. The neat salt was found to have melted onto the liner walls and frit upon removal of

IANTE J.J. HITECL OF	Carar		m AllTh		400						
Catalyst			N	a,PO, o	n Si/A]				Ne	at Na ₃ P	01
Loading (mmol/g support)	0.	43		0.86			1.00			N/A	
Temperature(°C)	300	350	280	300	350	280	300	350	280	300	350
Error(%C)	-19.4	-22.3	-65.5	-48.4	-39.6	12.0	-5.8	-7.3	17.2	10.4	-10.6
Conversion (BOF)(%)	27.0	69.9	70.6	58.8	88.0	-3.3	19.9	39.9	-15.3	-5.6	46.6
Conversion (Adj)(%)	7.6	47.5	5.1	10.3	48.4	8.7	14.1	32.6	1.9	4.9	36.1
Yield (%)											
Acrylic Acid	1.41	10.76	0.93	1.83	11.66	0.81	1.96	9.83	0.23	0.94	7.01
Propanoic Acid	0.29	7.60	0.22	0.71	10.90	0.61	0.87	1.47	0.03	0.15	6.29
2,3-Pentanedione	3.86	7.11	2.50	3.93	8.02	2.28	4.34	7.04	0.91	2.12	4.56
Acetaldehyde	1.47	9.04	1.10	2.46	12.48	0.78	1.89	5.17	0.34	0.96	10.03
Acetol	0.44	3.42	0	0.35	2.58	0.09	0.58	2.91	0	0.30	4.00
Other	0.42	1.96	0.53	0.34	1.21	0.43	0.49	1.15	0.14	0.12	1.23
co**	0	3.87	0.27	0.48	2.39	0.43	0.63	2.97	0.13	0.74	1.69
co2	0.56	16.91	1.83	3.33	11.23	2.92	4.97	10.19	0.36	1.14	7.33
Selectivity (%)											
Acrylic Acid	17.9	27.0	17.7	19.0	24.9	16.2	19.3	35.7	14.2	20.4	21.2
Propanoic Acid	3.6	19.1	4.2	7.4	23.3	12.1	8.6	5.3	1.6	3.2	19.0
2,3-Pentanedione	49.0	17.8	47.2	40.8	17.1	45.8	42.9	25.5	55.1	46.3	13.8
Acetaldehyde	18.6	22.7	20.9	25.6	26.6	15.5	18.7	18.7	20.5	21.0	30.3
Acetol	5.6	8.6	0	3.6	5.5	1.7	5.7	10.6	0	6.5	12.1
Other	5.3	4.9	10.0	3.5	2.6	8.6	4.8	4.2	8.7	2.6	3.7
* Residence time 0.29-0.	44 s. '	** Yield	s of gas	es are 1	reported	as mole	s gas/mo	les lac	tic acid	l fed.	

Table 3.5. Effect of Catalyst Loading and Support

		1	ł		1							
Catalyst				Na,PC	on S	i/Al				Ne	at Na ₃	PO4
Loading (mmol/a support)		0.43			0.86			1.00			N/A	
Temperature (°C)	280	300	350	280	300	350	280	300	350	280	300	350
Error (%C)	7.3	-26.1	-21.8	-41.9	-42.9	-18.9	12.0	-16.5	-19.5	-0.1	-7.8	-16.3
Conversion (BOF)(%)	10.4	71.1	94.4	64.3	85.8	97.1	14.2	59.0	85.4	6.0	28.4	72.5
Conversion (Adj)(%)	17.7	45.0	72.7	22.5	42.9	78.2	26.3	42.5	65.9	5.9	20.6	56.2
Yield (%)												
Acrylic Acid	3.42	7.86	5.19	4.39	7.14	8.23	3.11	7.36	9.22	0.98	4.05	7.16
Propanoic Acid	0.59	7.68	18.89	0.44	6.73	27.94	0.88	1.71	3.98	0.03	1.09	14.39
2,3-Pentanedione	8.19	10.73	3.50	13.15	13.32	6.05	9.07	11.81	5.53	3.92	8.76	3.49
Acetaldehyde	2.53	8.48	14.01	4.02	10.70	21.91	3.06	7.16	18.46	0.89	4.24	14.09.
Acetol	1.63	4.32	3.58	0.83	1.97	3.43	1.05	3.96	2.93	0.18	2.38	4.86
Other	0.93	1.47	2.53	0.81	1.22	2.28	0.59	2.14	3.85	0.15	0.30	2.50
	0.96	1.52	7.28	0.66	1.51	4.20	1.49	4.22	22.49	0.14	0.47	1.92
co2	4.38	8.42	25.79	5.39	11.18	19.11	9.77	17.61	16.46	0.74	2.64	7.10
Selectivity (%)												
Acrylic Acid	19.8	19.4	10.9	18.6	17.4	11.8	17.5	21.6	21.0	16.0	19.4	15.4
Propanoic Acid	3.4	18.9	39.6	1.8	16.4	40.0	4.9	5.0	0.6	0.4	5.2	31.0
2,3-Pentanedione	47.4	26.5	7.3	55.6	32.4	8.7	51.1	34.6	12.6	63.7	42.1	7.5
Acetaldehyde	14.7	20.9	29.4	17.0	26.0	31.4	17.2	21.0	42.0	14.5	20.4	30.3
Acetol	9.4	10.7	7.5	3.5	4.8	4.9	5.9	11.6	6.7	3.0	11.4	10.5
Other	5.4	3.6	5.3	3.4	3.0	3.3	3.3	6.3	8.8	2.4	1.5	5.4
* Residence time 1.40-2.	06 s.	** Yiel	ds of g	ases are	e repor	ted as	moles g	as/mole	s lacti	c acid	fed.	

Table 3.5. Effect of Catalyst Loading and Support' (Continued)

the catalyst from the reactor.

Nitrogen BET results indicate that the surface area of the Si/Al support is about 5 m^2/g . At our catalyst loadings of 0.4 to 1.0 mmol/g, there is plenty of salt present to cover the support surface with many molecular layers, assuming uniform dispersion of the salt on the support. Because the neat salt melted and flowed at reaction conditions, we expect the catalyst to be in a hydrated, liquid phase on the support during reaction. The dispersion of the salt on the support has not been measured.

3.3.5. Selectivity over Supported Orthophosphate Salts

Reactions of lactic acid were performed over monobasic, dibasic and tribasic sodium phosphate salts all supported on Si/Al. Conversion was found to increase with basicity of the salt. Increased basicity also increases selectivity to acrylic acid and 2,3-pentanedione while lowering selectivity to acetaldehyde and other products. The effect of catalyst basicity on propanoic acid and acetol selectivity showed no clear trend. The effect of catalyst basicity on product yields may be seen in Table 3.6.

3.3.6. Reactions over Bovine Dental Enamel and Trisodium Phosphate

Comparisons of reactions over tribasic sodium phosphate and calcium hydroxyapatite in bovine dental enamel showed from three to seven times greater conversion over Na_3PO_4 .

Catalyst	Si/Al B	lank	NaH ₂ PO ₄ on	Si/Al	Na ₂ HPO ₄ or	lSi/Al	Na,PO, on	Si/Al
Temperature (°C)	300	350	300	350	300	350	300	350
Error (%C)	0.8	1.3	4.3	-8.9	-2.2	-12.1	-5.8	-7.3
Conversion (BOF)(%)	5.7	17.4	-2.5	17.6	5.5	45.5	19.9	39.9
Conversion (Adj)(%)	6.5	18.7	1.8	8.7	3.4	33.4	14.1	32.6
Yield (%)								
Acrylic Acid	0.07	0.79	60.0	1.55	0.58	9.69	1.96	9.83
Propanoic Acid	0.52	1.21	0.10	1.72	0.16	2.65	0.87	1.47
2,3-Pentanedione	0.22	0.28	0.17	1.26	1.59	8.10	4.34	7.04
Acetaldehyde	1.49	9.00	0.37	2.47	0.67	6.24	1.89	5.17
Acetol	0.09	0.37	0.10	0.44	0.11	3.29	0.58	2.91
Other	0.41	2.87	0.54	0.69	0.15	1.12	0.49	1.15
	1.11	10.59	0.37	1.64	0.25	2.14	0.63	2.97
co2**	0.24	1.95	0.24	2.06	0.94	9.69	4.97	10.19
Selectivity (%)								
Acrylic Acid	2.4	5.5	6.3	19.1	17.9	31.2	19.3	35.7
Propanoic Acid	18.6	ю. З	7.4	21.2	4.8	8.5	8.6	5.3
2,3-Pentanedione	7.8	1.9	12.5	15.5	48.8	26.1	42.9	25.5
Acetaldehyde	53.3	62.0	27.0	30.3	20.4	20.1	18.7	18.7
Acetol	3.3	2.5	7.4	5.4	3.3	10.6	5.7	10.6
Other	14.5	19.8	39.3	8.5	4.7	3.6	4.8	4.2
* Residence time 0.28-0.	46 s. ** Y	ields of g	Jases are rej	ported as	moles gas/m	oles lacti	ic acid fed.	

Table 3.6. Product Yields over Phosphate Salts'

Since the nitrogen BET surface areas of the sodium phosphate and the hydroxyapatite are 5 and 6.2 m²/g, respectively, this indicates Na_3PO_4 has an inherently greater activity since the surface areas of the two catalysts are comparable. Selectivities to both acrylic acid and propanoic acid were similar for the two catalysts over all conditions studied. Na_3PO_4 exhibited selectivities to 2,3-pentanedione nearly four times greater than hydroxyapatite at 280°C and 1.0 second residence time. Raising either the temperature or the residence time quickly erodes this advantage. Selectivity to acetaldehyde over Na_3PO_4 is one half to two thirds the selectivity over hydroxyapatite for all conditions studied. Results of the reactions over tribasic sodium phosphate and calcium hydroxyapatite are presented in Table 3.7.

3.3.7. Effect of Temperature and Residence Time on Product Yields

Lactic acid conversion over Na₃PO₄ on Si/Al was performed at a series of temperatures of 280-350°C and a series of residence times from 0.39-4.08 seconds. Yields of acrylic acid, 2,3-pentanedione and acetol were all found to go through a maximum at a temperature of 300-320°C for residence times of two and four seconds. Yields of acetaldehyde, propanoic acid and other products were found to increase with temperature for all conditions studied. The effect of temperature on product yields may be seen in Figure 3.3.

Dec Br Br <th>intal Na₃PO₄ Dental Na₃PO₄ namel on Si/Al Enamel on Si/Al</th> <th>2-1.07 0.40-0.44 5.49-6.18 2.04-2.06</th> <th>300 320 280 300 320 280 300 280 300</th> <th>7.5 4.7 12.0 -5.8 4.5 7.5 2.8 12.0 -16.5</th> <th>-5.4 -1.2 -3.3 19.9 15.3 -2.1 9.3 14.2 59.0</th> <th>2.0 3.5 8.7 14.1 19.9 5.5 12.1 26.3 42.5</th> <th></th> <th>0.24 0.41 0.81 1.96 4.00 0.66 1.99 3.11 7.36</th> <th>0.08 0.12 0.61 0.87 0.87 0.15 0.47 0.88 1.71</th> <th>0.30 0.56 2.28 4.34 5.65 1.13 2.43 9.07 11.81</th> <th>0.56 0.81 0.78 1.89 2.61 1.30 2.93 3.06 7.16</th> <th>0.05 0.19 0.09 0.58 1.52 0.41 1.49 1.05 3.96⁴</th> <th>0.32 0.29 0.43 0.49 0.72 0.48 0.56 0.59 2.14</th> <th>0.13 0.39 0.43 0.63 1.40 0.39 0.92 1.49 4.22</th> <th>0.66 1.19 2.92 4.97 8.41 1.30 2.55 9.77 17.61</th> <th>15.7 17.3 16.2 19.3 26.0 16.0 20.2 17.5 21.6</th> <th>5.1 4.9 12.1 8.6 5.6 3.6 4.7 4.9 5.0</th> <th>19.2 23.6 45.8 42.9 36.8 27.4 25.6 51.1 34.6</th> <th>35.7 34.1 15.5 18.7 17.0 31.4 29.7 17.2 21.0</th> <th>3.5 8.0 1.7 5.7 9.9 10.0 15.1 5.9 11.6</th>	intal Na ₃ PO ₄ Dental Na ₃ PO ₄ namel on Si/Al Enamel on Si/Al	2-1.07 0.40-0.44 5.49-6.18 2.04-2.06	300 320 280 300 320 280 300 280 300	7.5 4.7 12.0 -5.8 4.5 7.5 2.8 12.0 -16.5	-5.4 -1.2 -3.3 19.9 15.3 -2.1 9.3 14.2 59.0	2.0 3.5 8.7 14.1 19.9 5.5 12.1 26.3 42.5		0.24 0.41 0.81 1.96 4.00 0.66 1.99 3.11 7.36	0.08 0.12 0.61 0.87 0.87 0.15 0.47 0.88 1.71	0.30 0.56 2.28 4.34 5.65 1.13 2.43 9.07 11.81	0.56 0.81 0.78 1.89 2.61 1.30 2.93 3.06 7.16	0.05 0.19 0.09 0.58 1.52 0.41 1.49 1.05 3.96 ⁴	0.32 0.29 0.43 0.49 0.72 0.48 0.56 0.59 2.14	0.13 0.39 0.43 0.63 1.40 0.39 0.92 1.49 4.22	0.66 1.19 2.92 4.97 8.41 1.30 2.55 9.77 17.61	15.7 17.3 16.2 19.3 26.0 16.0 20.2 17.5 21.6	5.1 4.9 12.1 8.6 5.6 3.6 4.7 4.9 5.0	19.2 23.6 45.8 42.9 36.8 27.4 25.6 51.1 34.6	35.7 34.1 15.5 18.7 17.0 31.4 29.7 17.2 21.0	3.5 8.0 1.7 5.7 9.9 10.0 15.1 5.9 11.6
Dental Ename1Na ₃ PO ₄ on Si/A11.02-1.07 $0.40^{-0.444}$ 2803003202803003202803003208.37.5 4.7 -5.5-5.4 -1.2 2.82.03.58.37.5 4.7 2.82.03.58.37.5 4.7 1.02-1.0712.0 -5.8 -5.5 -5.4 -1.2 8.37.5 4.7 12.0 -5.8 0.14 0.24 0.41 0.18 0.61 0.87 14.1 0.81 0.20 0.30 0.61 0.18 0.61 0.87 0.20 0.30 0.61 0.48 0.56 0.43 0.49 0.63 0.43 0.56 0.12 0.43 0.63 0.66 1.19 0.63 0.66 1.19 2.8 5.1 4.97 13.4 19.2 23.6 45.8 5.1 45.8 45.8 5.1 45.8 13.4 16.2 18.7 32.6 35.7 34.1 15.7 1.7 1.7 5.7 34.1 1.7 5.7 34.1 1.7 5.7 34.1 1.7 5.7 34.1 1.7 5.7 34.1 1.7 5.7 34.1 1.7 5.7 34.1 1.7			320	4.5	15.3	19.9		4.00	0.87	5.65	2.61	1.52	0.72	1.40	8.41	26.0	5.6	36.8	17.0	9.9
Dental Dental Fnamel 00.4 1.02-1.07 0.4 280 300 320 280 300 320 280 281 7.5 4.7 0.4 283 7.5 4.7 12.0 -5.5 -5.4 -1.2 -3.3 2.8 0.14 0.24 0.41 0.14 0.20 0.12 0.61 0.20 0.30 0.56 0.43 0.14 0.24 0.41 0.78 0.20 0.30 0.56 0.43 0.20 0.32 0.12 0.43 0.20 0.32 0.29 0.43 0.26 0.13 0.39 0.43 0.56 0.13 0.39 0.43 0.65 0.13 0.39 0.43 0.56 0.13 0.39 0.43 13.4 19.2 1.19 2.92 13.4 19.2 34.1 15.7 13.5 8.0 1.17 15.7	la ₃ PO4 Si/Al	10-0.44	300	-5.8	19.9	14.1		1.96	ò.87	4.34	1.89	0.58	0.49	0.63	4.97	19.3	8.6	42.9	18.7	5.7
Dental Enamel 1.02-1.07 1.02-1.07 280 300 320 280 300 320 280 300 320 280 300 320 280 300 320 280 300 320 280 300 320 283 7.5 4.7 -5.5 -5.4 -1.2 2.8 2.0 3.5 2.8 2.0 3.5 0.14 0.24 0.41 0.20 0.30 0.56 0.48 0.56 0.12 0.48 0.56 0.12 0.56 0.32 0.29 0.56 0.13 0.39 0.56 0.13 0.39 0.56 0.13 0.39 0.58 0.166 1.19 13.4 19.2 23.6 32.6 35.7 34.1 0 3.5 8.0	4 uo	0.4	280	12.0	-3.3	8.7		0.81	0.61	2.28	0.78	0.09	0.43	0.43	2.92	16.2	12.1	45.8	15.5	1.7
Dental Enamel 1.02-1.07 280 300 8.3 7.5 -5.5 -5.4 -5.5 -5.4 2.8 2.0 8.3 7.5 -5.5 -5.4 0.14 0.24 0.18 0.08 0.20 0.30 0.214 0.24 0.20 0.30 0.214 0.24 0.20 0.30 0.214 0.24 0.226 0.32 0.56 0.32 0.56 0.13 0.56 0.13 0.56 0.13 0.56 0.13 0.56 0.13 0.56 0.13 0.56 0.13 13.4 19.2 32.6 35.7 0 3.5			320	4.7	-1.2	3.5	-	0.41	0.12	0.56	0.81	0.19	0.29	0.39	1.19	17.3	4.9	23.6	34.1	8.0
DD2802801.02802801.08.3-5.52.80.140.140.140.260.260.550.560.560.5613.432.600.6300.63	ental namel	12-1.07	300	7.5	-5.4	2.0		0.24	0.08	0.30	0.56	0.05	0.32	0.13	0.66	15.7	5.1	19.2	35.7	3.5
	Ŭ Ŭ	1.0	280	8.3	-5.5	2.8		0.14	0.08	0.20	0.48	0	0.56	0.26	0.63	9.7	5.8	13.4	32.6	0

on Si/Al and Bovine Dental Enamel of Lactic Acid over Na.PO. Conversion 5 Table 3



Effect of Temperature on Product Yields over Trisodium Phosphate on Si/Al Figure 3.3. This suggests that acrylic acid, 2,3-pentanedione and acetol are destroyed by secondary reactions which convert them to other products. No conversion of 2,3-pentanedione was observed at 280°C, as discussed in Section 3.4.1., but conversion may take place at higher temperatures. Acrylic acid may be hydrogenated to propanoic acid, but this does not account for all the propanoic acid formed. Some propanoic acid results from direct reduction of lactic acid. Acetaldehyde and propanoic acid are terminal products which do not break down to a significant extent.

The highest acrylic acid yield of 15.6% is obtained at a moderate retention time of one second and a high temperature of 350°C. The maximum acrylic acid selectivity is observed at a contact time of 0.4 seconds and 350°C. Effects of temperature and contact time on acrylic acid yield are presented in Figure 3.4.

A long contact time of four seconds and a low temperature of 280°C favors the formation of 2,3pentanedione, with a maximum yield of 13.4%.

2,3-Pentanedione selectivity is very sensitive to temperature. Selectivities of 45-52% are seen at 280°C for all contact times studied. These selectivities drop to less than 26% upon raising the temperature to 350°C.

At 280°C, the residence time has little effect on 2,3pentanedione selectivity. However, at 350°C, the selectivity decreases from 26 to 6% upon increasing the residence time





from 0.4 to 4 seconds. Effects of temperature and residence time on 2,3-pentanedione yields are seen in Figure 3.5.

The maximum yield and maximum selectivity to acetol are 5.3 and 12.4%, respectively, and both occur at 320°C and 2 seconds contact time.

Propanoic acid selectivity decreases from 12 to 5% with increasing temperature at a short contact time of 0.4 seconds. This trend reverses at a long contact time of 2-4 seconds, with selectivity increasing from 4.9 to 9.0% upon raising the temperature from 280 to 350°C.

At temperatures of 280-320°C, acetaldehyde selectivity is insensitive to contact time, remaining at 15-25%. Upon raising the temperature to 350°C, the selectivity shows a strong dependence on contact time. Acetaldehyde selectivity increases from 19 to 68% upon increasing the contact time from 0.4 to 4 seconds. Results of lactic acid conversion over Na₃PO₄ supported on Si/Al are presented in Table 3.8.

3.4. Discussion

3.4.1. Mechanisms

Acrylic acid dehydration is proposed to occur via cycloelimination. Lactic acid condenses with sodium phosphate to yield lactic acid-2-phosphate which subsequently cycloeliminates with the phosphate oxygen attacking the β-hydrogen of lactic acid. With the



RT 4s

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- RT 0.4s

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RT 1s

RT 2s

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	5				4) + CY		4				:		
Contact Time (s)		0.39	-0.44		0.98-	1.12		1.93	-2.06		3.	83-4.0	8
Temperature (°C)	280	300	320	350	280	350	280	300	320	350	280	300	350
Error (%C)	12.0	-5.8	4.5	-7.3	12.7	-18.1	12.0	-16.5	-14.0	-19.5	8.2	-4.3	-7.9
Conversion(BOF)(%)	-3.3	19.9	15.3	39.9	4.3	78.8	14.2	59.0	73.6	85.4	31.6	56.5	82.0
Conversion(Adj)(%)	8.7	14.1	19.9	32.6	17.0	60.7	26.3	42.5	59.6	65.9	39.8	52.2	74.1
Yield (%)													
Acrylic Acid	0.81	1.96	4.00	9.83	1.86	15.6	3.11	7.36	11.50	9.22	4.42	8.19	3.40
Propanoic Acid	0.61	0.87	0.87	1.47	0.68	3.42	0.88	1.71	3.08	3.98	1.46	2.47	4.31
2,3-Pentanedione	2.28	4.34	5.65	7.04	5.69	8.28	9.07	11.81	11.11	5.53	13.43	13.41	3.17
Acetaldehyde	0.78	1.89	2.61	5.17	1.72	17.04	3.06	7.16	8.60	18.46	6.25	10.58	36.44
Acetol	0.09	0.58	1.52	2.91	0.57	4.39	1.05	3.96	5.27	2.93	2.17	4.92	1.68
Other	0.43	0.49	0.72	1.15	0.46	2.37	0.59	2.14	2.98	3.85	1.89	2.18	4.77
co,	0.43	0.63	1.40	2.97	1.52	13.73	1.49	4.22	9.00	22.49	3.87	7.05	31.26
co2	2.92	4.97	8.41	10.19	7.57	14.87	9.77	17.61	31.61	16.46	14.03	19.24	20.98
Selectivity (%)													
Acrylic Acid	16.2	19.3	26.0	35.7	16.9	30.5	17.5	21.6	27.0	21.0	14.9	19.6	6.3
Propanoic Acid	12.1	8.6	5.6	5.3	6.2	6.7	4.9	5.0	7.2	0.0	4.9	5.9	8.0
2,3-Pentanedione	45.8	42.9	36.8	25.5	51.8	16.2	51.1	34.6	26.1	12.6	45.4	32.1	5.9
Acetaldehyde	15.5	18.7	17.0	18.7	15.7	33.3	17.2	21.0	20.2	42.0	21.1	25.3	67.8
Acetol	1.7	5.7	6.6	10.6	5.2	8.6	5.9	11.6	12.4	6.7	7.3	11.8	3.1
Other	8.6	4.8	4.7	4.2	4.2	4.6	3.3	6.3	7.0	8.8	6.4	5.2	8.9
* Yields of gases are	e repor	ted as	moles	gas/mol	es lact	ic acid	l fed.						

Table 3.8. Lactic Acid Conversion over Na_3PO_4 on Si/Al

abstraction of the β -hydrogen, a double bond is formed between the α - and β -carbons of lactic acid, and the phosphate group leaves. This process produces acrylic acid, as well as regenerating the phosphate salt catalyst, which loses a water molecule and repeats the cycle. This mechanism is shown in Figure 3.6.

The proposed mechanism for condensation of lactic acid to 2,3-pentanedione is shown in Figure 3.7. The phosphate first combines with the acid group of lactic acid to form an ester. The α -hydrogen of the ester is abstracted by a base with the resulting enolate anion being stabilized by resonance. The enolate anion attacks the carbonyl carbon of another ester resulting in the substitution of the phosphate group. This substitution product then decarboxylates and rearranges to yield 2,3-pentanedione.



Figure 3.6. Proposed Mechanism for the Dehydration of Lactic Acid to Acrylic Acid



Figure 3.7. Proposed Mechanism for the Condensation of Lactic Acid to 2,3-Pentanedione

In a study of this condensation mechanism, an aqueous feed solution of acetaldehyde and propanoic acid yielded no conversion over supported Na₃PO₄ catalyst at 280°C and 1.5 seconds residence time. This rules out the condensation of acetaldehyde and propanoic acid to form 2,3-pentanedione and demonstrates that there is no simple decomposition of either acetaldehyde or propanoic acid under these conditions. Reaction of an aqueous solution of 2,3-pentanedione under identical conditions produced virtually no products, thus eliminating the possibility of acetaldehyde and propanoic acid resulting from 2,3-pentanedione decomposition.

Glycolic acid, $CH_2(OH)COOH$, an analog of lactic acid, was also studied in an effort to determine if this condensation mechanism could be applied to an entire class of α -hydroxy carboxylic acids. If glycolic acid reacts by a condensation mechanism analogous to that of 2,3pentanedione, one would expect to form 2-oxo-propanaldehyde.

A 28.7 wt% aqueous glycolic acid feed solution was chosen so the molar concentration was identical to the concentration in the 34 wt% lactic acid feed solutions used in lactic acid studies. Reaction of the glycolic acid solution at 280°C and residence times of 0.3 and 1.5 seconds gave no yield of 2-oxo-propanaldehyde over Na₃PO₄ on Si/Al. The conversion of glycolic acid was less than 5% for both runs and products were mostly acetaldehyde, acetic acid, CO

and CO_2 , as well as minor amounts of 2,3-butanedione and unidentified products.

A mixed condensation between lactic acid and glycolic acid, following an analogous mechanism, would yield 2-oxobutanaldehyde and or 2,3-butanedione. An aqueous feed solution of 17.0 wt% lactic acid and 14.4 wt% glycolic acid was chosen to provide a combined molar concentration identical to that used in lactic acid studies. This solution was reacted under identical conditions as the glycolic acid feed. The reaction produced no 2-oxo-butanaldehyde and only minor amounts of 2,3-butanedione.

These results may be rationalized by noting that the enol which is formed after hydrogen abstraction from the lactyl phosphate is stabilized by the methyl group, causing the α -hydrogen to be acidic. This causes the condensation step of the mechanism to be favorable for lactic acid, but not for glycolic acid, leading to no formation of the glycolic acid condensation product, 2-oxo-propanaldehyde. By electron donation, the methyl group also stabilizes the anion formed after nucleophilic attack of the enolate anion on the carboxyl group. The absence of this methyl group in glycolic acid thus impedes the formation of the enol from the glycolic acid-phosphate ester and impedes the condensation pathway.

The observed product of the mixed condensation between lactic and glycolic acids, 2,3-butanedione, arises from the

attack of the lactic enol on the carboxylate carbon of the glycolic acid ester. Since the glycolic enol is not stabilized by the methyl group, it is not formed and thus the product of the reverse condensation, 2-oxobutanaldehyde, is not observed.

3.4.2. Mass Transfer Limitations

The reactions in this catalytic system may be considered free from mass transport limitations according to the Weiss-Prater criterion. The observable modulus is about 0.04 for the worst case in which a high feed rate and high temperature are used.

3.4.3. Kinetics

Product yields from the conversion of lactic acid over Na₃PO₄ on Si/Al were analyzed to determine rates and orders of reaction. Rate constants and kinetic parameters were calculated by integrating the molar balances of each product using an in-house software package (KINFIT). Kinetic analysis indicates that the formation of 2,3-pentanedione is second order with respect to lactic acid. A second order fit was much better than an attempted first order fit, which was nonlinear. Kinetic data suggests a secondary reaction which converts the dione to unspecified products. This secondary pathway was included in the kinetic analysis, but the reaction rate constant was not able to be calculated accurately as a function of temperature.

As discussed in Section 3.4.1., no reaction was observed when an aqueous solution of 2,3-pentanedione was fed over Na_3PO_4 on Si/Al at 280°C and 1.5 seconds residence time. This indicates that the secondary reaction of 2,3pentanedione is not a simple decomposition at this temperature. However, we cannot rule out the possibility that the dione is reacting with another compound, or more likely, that simple decomposition occurs to a significant extent only at elevated temperatures.

The formation of acrylic acid was found to be first order with respect to lactic acid. A secondary reaction which destroys acrylic acid is occurring and was accounted for in the kinetic analysis, but as in the case of 2,3pentanedione, the rate at which it is occurring cannot be accurately calculated. Propanoic acid is formed by hydrogenation of acrylic acid, but this does not account for all the secondary reaction of acrylic acid. A secondary reaction to unspecified product is also included. Propanoic acid is also formed directly from lactic acid via a first order reduction pathway.

The formation of acetaldehyde was found to be first order with respect to lactic acid and, as previously discussed, acetaldehyde does not undergo a simple decomposition. The reaction pathways are presented in Figure 3.8. Reaction rate constants for the various pathways are

given in Table 3.9. Activation energies and frequency factors for the formation of major products are presented in Table 3.10. An Arrhenius plot for the primary reaction pathways is presented in Figure 3.9.

3.4.4. Catalyst Stability over Extended Reactor Run

34 wt% aqueous lactic acid was reacted over calcined calcium hydroxyapatite catalyst at 320°C and 5.0 seconds residence time for 102 hours in order to study catalyst stability. The overall adjusted conversion stayed constant around 13.7%. Acrylic acid and propanoic acid yields increased from about 2.2 and 1.1%, respectively, at the beginning of the run, to 2.9% and 1.4% near the end of the 102 hour run. The yield of 2,3-pentanedione remained constant at about 2.6% while the yield to acetaldehyde increased significantly from 1.6 to 3.2%. Both decarboxylation and decarbonylation increased to account for the increase in acetaldehyde yield. The average carbon recovery was 109.2% with a standard deviation of 8.3%. The results of this extended run are shown in Table 3.11. Overall, the hydroxyapatite catalyst exhibited good stability with yields to the desired products acrylic acid and 2,3-pentanedione remaining stable.



Figure 3.8. Reaction Pathways of Lactic Acid Conversion over $Na_3 PO_4$ on Si/Al

Table 3.9. Reaction Rate Constants of Lactic Acid Conversion Pathways

Ter	nperature (°C)	280	300	320	350
К1	(Lactic → Acrylic)(s ⁻¹)	0.021	0.052	0.12	0.49
К2	(Lactic \rightarrow Propanoic)(s ⁻¹)	0.0024	0.011	0.010	0.030
кз	(Acrylic → Propanoic)(s ⁻¹)	0.016	0.025	0.11	0.12
K4	(Lactic → 2,3-Pentanedione) (1/mol·s)	9.7	18	31	66
К5	(Lactic \rightarrow Acetaldehyde)(s ⁻¹)	0.017	0.043	0.065	0.13

Table 3.10. Activation Energies and Frequency Factors for Lactic Acid Conversion

Rat	e Constant	Activation Energy (kJ/mol)	Frequency Factor (s ⁻¹)
K1	(Lactic → Acrylic)	133.6	7.80x10 ¹⁰
К2	(Lactic → Propanoic)	106.4	2.42×10^{7}
К3	(Acrylic → Propanoic)	83.1	1.20x10 ⁶
K4	(Lactic → 2,3-Pentanedione)	78.1	2.31x10 ⁸ *
К5	(Lactic → Acetaldehyde)	73.6	1.98×10 ⁵

* Units are (1/mol·s).



Table 3.11. Ex	tended	l Lact	ic Aci	d Run	over	Calci	um Hyo	lroxya	patit€	e Cata	lyst'			
Time (hr)	1.2	1.8	7.9	8.4	12.6	13.1	20.9	22.1	29.9	30.3	35.6	36.1	45.5	46.1
Error (%C)	5.6	6.7	7.0	8.0	8.3	-0.1	10.6	-17.5	5.1	16.1	1.0	0.5	5.1	12.8
Conversion(BOF)(%)	6.0	4.6	3.0	6.1	5.1	10.8	2.8	28.6	6.2	-0.4	14.1	14.7	7.3	2.6
Conversion(Adj)(%)	11.6	11.3	10.0	14.1	13.4	10.7	13.5	11.0	11.3	15.6	15.1	15.3	12.4	15.3
Yield (%)														
Acrylic Acid	2.12	2.04	2.11	2.73	2.45	2.22	2.97	2.93	2.37	2.44	2.91	2.83	2.92	3.18
Propanoic Acid	0.95	0.95	1.07	1.35	1.24	1.11	1.54	1.17	1.15	1.21	1.55	1.43	1.45	1.60
2,3-Pentanedione	2.52	2.50	2.51	2.38	3.04	2.75	2.89	2.51	2.82	3.03	2.91	2.89	2.55	3.11
Acetaldehyde	1.25	2.47	1.55	0.98	3.35	1.83	1.31	0.63	2.15	2.82	3.59	2.13	0.97	3.13
Acetol	1.47	1.69	1.66	2.12	1.97	1.54	2.28	1.54	1.56	1.89	2.17	1.64	2.22	2.23
Other	0.37	0.67	0.61	0.67	0.48	0.40	0.51	0.45	0.52	0.55	0.75	0.44	0.67	0.69
	I	0.18	I	0.26	I	0.06	I	0.61	I	0.57	I	0.68	ı	0.57
co ₂	I	1.10	ı	1.72	Т	0.96	ı	1.94	I	1.77	I	1.79	ı	1.31
Selectivity (%)														
Acrylic Acid	24.4	19.8	22.2	26.7	19.6	22.6	25.8	31.8	22.5	20.5	20.9	24.9	27.4	22.8
Propanoic Acid	10.9	9.2	11.2	13.2	6.6	11.3	13.4	12.7	10.8	10.1	11.2	12.6	13.6	11.4
2,3-Pentanedione	29.1	24.2	26.4	23.3	24.2	27.9	25.2	27.2	26.7	25.4	21.0	25.4	23.9	22.3
Acetaldehyde	14.4	23.9	16.3	9.5	26.8	18.6	11.4	6.8	20.3	23.6	25.9	18.8	9.1	22.5
Acetol	17.0	16.4	17.5	20.7	15.7	15.7	19.8	16.7	14.8	15.8	15.6	14.4	20.8	16.0
Other	4.2	6.5	6.4	6.5	3.8	4.0	4.5	4.8	4.9	4.6	5.4	3.9	5.3	5.0
* 320°C, 4.71-5.	46 s co	ntact t	cime.	** Yiel	ds of	gases a	are rep	orted a	ts mole:	s gas/m	ole la	ctic ac	id fed	

Table 3.11. Ex	tended	Lacti	c Acid	Run o	ver Ca	lcium	Hydrox	yapat	ite Ca	talyst	. (Con	tinued)	
Time (hr)	54.2	54.7	63.9	64.4	71.0	71.5	79.0	79.5	85.2	85.7	93.7	94.2	101.8
Error (%C)	10.9	-0.9	19.9	17.2	13.7	14.0	24.0	15.6	19.4	14.0	14.1	10.9	6.6
Conversion(BOF)(%)	3.4	15.2	-4.1	-2.6	0.4	-0.1	-7.5	-2.2	-5.0	0.1	1.4	3.0	7.7
Conversion(Adj)(%)	14.3	14.3	15.8	14.5	14.1	13.9	16.5	13.4	14.5	14.1	15.5	13.9	14.3
Yield (%)													
Acrylic Acid	2.81	2.95	3.11	2.72	2.81	2.83	2.94	3.00	2.99	2.71	3.21	2.91	2.86
Propanoic Acid	1.39	1.46	1.55	1.32	1.34	1.38	1.42	1.47	1.38	1.25	1.52	1.35	1.38
2,3-Pentanedione	2.65	2.33	2.70	2.75	2.65	2.41	2.73	2.07	2.49	2.13	2.81	2.73	2.48
Acetaldehyde	4.21	1.60	3.88	3.27	3.13	1.96	4.92	1.22	3.71	1.87	4.71	2.42	3.71
Acetol	1.67	1.74	2.26	1.91	2.06	2.19	2.05	2.14	1.99	1.73	2.03	1.83	1.63
Other	0.94	0.67	0.62	0.74	0.77	0.61	0.43	0.51	0.45	0.54	0.45	0.46	0.71
oo	I	0.68	ı	0.88	I	0.22	I	0.23	I	0.91	I	1.21	I
co ₂	I	1.78	1	1.66	I	1.11	I	1.07	1	2.19	I	2.24	I
Selectivity (%)													
Acrylic Acid	20.5	27.5	22.0	21.4	22.0	24.9	20.3	28.8	23.0	26.5	21.8	24.9	22.4
Propanoic Acid	10.2	13.6	11.0	10.4	10.5	12.1	9.8	14.1	10.6	12.2	10.3	11.6	10.8
2,3-Pentanedione	19.4	21.7	19.1	21.6	20.8	21.2	18.8	19.9	19.1	20.9	19.1	23.3	19.4
Acetaldehyde	30.8	14.9	27.5	25.7	24.5	17.2	34.0	11.8	28.6	18.3	32.0	20.7	29.1
Acetol	12.2	16.2	16.0	15.0	16.2	19.3	14.2	20.5	15.3	16.9	13.8	15.6	12.7
Other	6.9	6.2	4.4	5.8	6.0	5.3	3.0	4.9	3.5	5.3	3.0	3.9	5.5
* 320°C, 4.71-5.	46 s cor	tact ti	me. **	Yields	of gas	es are	reporte	d as mo	les gas	/mole 1	actic a	Icid fed	
3.4.5. Mass Balance Accuracy

To determine carbon loss due to coking of the catalyst, reactions were performed over two batches of blank Si/Al support and two batches of Na_3PO_4 on Si/Al catalyst. These used catalysts were then calcined at 550°C in air for 24 hours and the weight loss of the samples was measured. Weight loss accounted for 1.7 to 4.4% of the carbon fed over Si/Al support, while accounting for 6.7 to 7.6% over Na_3PO_4 on Si/Al catalyst. For reactions over supported trisodium phosphate, the amount of carbon deposited on the catalyst accounts for most of the unrecovered carbon.

3.5. Summary

Lactic acid is converted to acrylic acid, propanoic acid, 2,3-pentanedione and acetaldehyde as well as other minor products, over sodium phosphate salts supported on silica alumina. Acrylic acid formation is favored at a high temperature of 350°C and short residence time of 0.4 seconds, while 2,3-pentanedione is favored at a low temperature of 280°C and long residence times of 4.0 seconds. The more basic trisodium phosphate catalyst exhibited more activity and selectivity to both acrylic acid and 2,3-pentanedione than the more acidic sodium orthophosphate salts, monosodium and disodium phosphate.

All primary reaction products result from first order decomposition of lactic acid except for the second order condensation of lactic acid to form 2,3-pentanedione. Propanoic acid is formed by both a first order reduction of lactic acid as well as a hydrogenation of acrylic acid.

The condensation product, 2,3-pentanedione, is proposed to result from a Claisen condensation between two cyclic lactyl phosphate molecules, with subsequent decarboxylation and rearrangement. Acrylic acid dehydration is proposed to occur via a cycloelimination in which phosphate is cleaved from lactic acid-2-phosphate, leaving acrylic acid.

Kinetic analysis suggests that 2,3-pentanedione selectivity may be enhanced by increasing contact time, greater lactic acid concentration and lower temperature.

Sodium phosphate salts possess significant selectivity to several valuable products including acrylic acid and 2,3pentanedione. Manipulation of the reaction conditions may be used to enhance the selectivity to a particular product. Catalyst activity of sodium phosphates is also high, with conversions greater than 80% at 350°C under certain conditions.

Chapter 4. Lactic Acid Conversion over Supported Sodium Salt Catalysts-A Catalyst Screening Study

4.1. Introduction

The proposed mechanism for 2,3-pentanedione formation includes the combination of the phosphate catalyst with the acyl group of lactic acid to form an acyl phosphate. The proposed mechanism for acrylic acid formation depends on the phosphate forming an ester linkage with the hydroxyl group on the C2 of lactic acid to yield a cyclic structure. The formation of cyclic intermediates suggested a catalyst survey to study the catalytic performance of various catalyst salts with different central atoms and oxygen ligands similar to phosphates in structure. Sodium catalyst salts were systematically chosen by the central atoms which form an adjacent series on the periodic table. The performance of these sodium salts are directly comparable to sodium phosphate salt catalysts. The sodium salt catalysts surveyed are listed in Table 4.1. The relationship of the central atoms on the periodic table is shown in Table 4.2.

Table 4.1. Catalyst Salts Surveyed

Sodium Tetraborate	Na ₂ B ₄ O ₇
Sodium Carbonate	Na ₂ CO ₃
Sodium Nitrate	NaNO3
Sodium Metasilicate	Na ₂ SiO ₃
Trisodium Phosphate	Na ₃ PO ₄
Sodium Sulfate	Na ₂ SO ₄
Sodium Chlorate	NaClO ₃
Dibasic Sodium Arsenate Heptahydrate	$Na_{2}HAsO_{4} \cdot 7H_{2}O$
Sodium Bromate	NaBrO ₃
Sodium Molybdate	Na ₂ MoO ₃

Table 4.2. Periodic Relationship of Catalyst Salt Central Atoms

			Group				
		VIB	IIIA	IVA	VA	VIA	VIIA
	2		5 B	6 C	7 N		
Period	3			14 	15 P	16 S	17 C1
	4				33 As		35 Br
	5	42 Mo				_	

4.2. Methods

4.2.1. Materials

All catalyst salts except trisodium phosphate (EM Science) were obtained in solid lumps or crystals from Aldrich Chemical Company. The origin of all other materials and catalyst preparation methods are discussed in Sections 3.2.1. and 3.2.2.

4.2.2. Vapor-phase Reactor

All reactions were performed in a downflow differential packed bed vapor-phase reactor lined with quartz. Descriptions of the reactor and operating conditions are discussed in Section 3.2.3. Product analysis techniques are discussed in Section 2.2.6.

4.3. Results

Conversion of lactic acid was performed over each of the catalysts supported on Si/Al support. Reactions were performed at 280-350°C and a residence time of 1.5-3.5 seconds.

Silicate is a moderately active catalyst with conversions (BOF) from 26.3% at 280°C to 81.8% at 350°C. Silicate produces the highest selectivity to acrylic acid which increases with temperature to 35.9% at 350°C. The propanoic acid selectivity is one of the lowest of the catalysts surveyed increasing from 3.7% to a maximum of 9.9% at 350°C. The selectivity to 2,3-pentanedione for silicate is very similar to that for trisodium phosphate. This selectivity decreases from 52.9% at 280°C to 22.5% at 350°C. The selectivity to acetaldehyde remains low and fairly constant at 12-15% for all temperatures studied while the selectivity to acetol is the highest of all the catalysts at 10-14%. Selectivity to other products is moderate, hovering at 5-7%. Overall, silicate shows high conversion and high selectivity to acrylic acid as well as low selectivity to propanoic acid and acetaldehyde. Silicate also exhibits the highest selectivity to acetol of 10-14%.

Trisodium phosphate is an active catalyst with conversions (BOF) from 14.2-85.4% as temperature increases from 280 to 350°C. The selectivity to acrylic acid is high with a maximum of 27.0% at 320°C. The selectivity of phosphate to propanoic acid is low, increasing from 4.9% to 9.0% at 350°C. Phosphate also has a high selectivity to 2,3pentanedione which is surpassed only by arsenate and silicate. This selectivity has a maximum of 51.1% at 280°C. Phosphate has a moderate acetaldehyde selectivity which increases from 17.2% at 280°C to a maximum of 42.0% at 350°C. A moderate selectivity to other products increases from 3.3 to 8.8%. Overall, trisodium phosphate exhibits good

selectivity to acrylic acid and 2,3-pentanedione and also a low selectivity to the undesirable product propanoic acid.

The activity of arsenate is second only to bromate and molybdate. This is especially evident at low temperatures where the conversion starts at 42.2% at 280°C and increases to 95.9% at 350°C. Arsenate exhibits a moderate selectivity to both acrylic acid and propanoic acid which hover at 15-24% and 5-13%, respectively. The selectivity to 2,3pentanedione is outstanding with a maximum of 63.8% at 280°C. This selectivity decreases precipitously with increasing temperature to 22.5% at 350°C. The acetaldehyde selectivity increases from 13-30% with a selectivity to other products of 2-7%. Overall, arsenate proves a very active catalyst with the highest selectivity to 2,3pentanedione of all catalysts surveyed.

Carbonate is a moderately active catalyst. Conversion based on lactic acid recovery ranges from 24.3% at 280°C to 88.1% at 350°C. Carbonate has a high selectivity to acrylic acid ranging from 15.1% at 280°C to 25.4% at 320°C. Propanoic acid selectivity for carbonate is moderate, increasing from 4.0% at 280°C to 14.4% at 350°C. Carbonate shows a moderate selectivity to 2,3-pentanedione of 47.0% at 280°C. This selectivity decreases with increasing temperature to 18.5% at 350°C. The moderate selectivity to acetaldehyde increases from 20.6% at 280°C to 32.3% at 350°C. Carbonate selectivity to other products is low at 4-

8%. Overall, carbonate shows high conversion and moderate selectivity to desirable products.

Borate is a moderately active catalyst with conversion (BOF) increasing from 17.4% at 280°C to 91.5% at 350°C. Acrylic acid selectivities are low, ranging from 9-22%, going through a maximum near 320°C. Borate and sulfate share the lowest selectivities to acrylic acid of all the catalysts surveyed except molybdate. Propanoic acid selectivities are moderate at 5-14% for borate. Borate has moderate selectivity to 2,3-pentanedione. The maximum 2,3pentanedione selectivity of 43.2% for borate occurs near 320°C. All catalysts except borate show a maximum 2,3pentanedione selectivity near 280°C. Borate has a high acetaldehyde selectivity which decreases with increasing temperature from 59.6% at 280°C to 22.8% at 320°C. The selectivity to other products is 4-10%. Overall, borate shows poor conversion and poor to moderate selectivity to desirable products.

The catalyst with the lowest activity is sulfate. The conversion (BOF) increases from 4 to 52% as the temperature rises from 280 to 350°C. Sulfate has low selectivity to acrylic acid and 2,3-pentanedione. Acrylic and propanoic acid selectivities hover at 10-14% over the temperature range studied. The maximum 2,3-pentanedione selectivity is 24.5% at 280°C. The acetaldehyde selectivity of sulfate is one of the highest of all the catalysts surveyed with a

maximum of 53.5% at 350°C. The selectivity to other products is high at 7-12%. Overall, sulfate is a poor catalyst with low conversion and low selectivity to desirable products and high selectivity to undesirable acetaldehyde and propanoic acid.

Bromate is an active catalyst with conversions from 45-96%. Bromate has a high selectivity to acrylic acid which is second only to silicate and increases with temperature from 19 to 33% from 280 to 350°C. The propanoic acid selectivity is also high at 17-20% and the low 2,3-pentanedione selectivity stays at 18-26%. Bromate has a moderate acetaldehyde selectivity which hovers at 19-26%. Bromate shows a low selectivity to other products at 4-7%. Overall, bromate is an active catalyst with high selectivity to acrylic acid and propanoic acid.

Chlorate produces low conversion increasing from 14% at 280°C to 90% at 350°C. The selectivity to acrylic acid is also moderate, increasing to a maximum at 350°C of 23.6%. The high propanoic acid selectivity follows a similar trend with a maximum at 350°C of 19.2%. The 2,3-pentanedione selectivity is moderate with the maximum of 29.4% occurring at 280°C. The moderate acetaldehyde selectivity hovers at 22-26% while the high selectivity to other products is 5-11%. Overall, chlorate produces no outstanding conversions to any of the major products, but all products are formed in rather even proportions.

Nitrate is an active catalyst with conversion (BOF) which increases from 25% at 280°C to 92% at 350°C. Nitrate has a high selectivity to acrylic acid which hovers at 17-23%. The selectivity to propanoic acid is moderate, increasing from 6.2% at 280°C to 15.1% at 350°C. Nitrate has a high 2,3-pentanedione selectivity which decreases from 50.1% at 280°C to 24.3% at 350°C. Nitrate shows a moderate selectivity to acetaldehyde which ranges from 16-29% while the selectivity to other products ranges from 4-9%. Overall, nitrates exhibit high conversions and good selectivity to acrylic acid and 2,3-pentanedione.

Molybdate, the only salt included in this study with a transition metal central atom, behaves differently than all other catalysts surveyed. Molybdate produced mostly propanoic acid in selectivities from 70-84%. Propanoic acid selectivity decreases with increasing temperature. Molybdate is the most active catalyst with very high conversion (BOF) of 87.2% at the lowest temperature of 280°C. This conversion increases slightly to 92.6% at 350°C. The acrylic acid and 2,3-pentanedione selectivities were the lowest of all the catalysts at less than 2.7% and 1.7%, respectively. The acetaldehyde selectivity was also low at 10-20%. Selectivity to other products was less than 5%. Unlike the other catalysts, molybdate affected much cracking to produce much CO₂ and some CO accounting for 14-17% of the carbon balance. Overall, molybdate is the most active catalysts surveyed but

produces mostly propanoic acid and CO_2 . Product distribution over catalyst salts surveyed is presented in Table 4.3.

4.4. Discussion

The various catalysts do not always attain the maximum selectivity to a product at the same temperature. An excellent example of this occurrence is the fact that borate achieves a maximum 2,3-pentanedione selectivity at 320°C, while all other catalysts have a maximum near 280°C. For this reason, it was instructive to compare the maximum selectivity attained by a catalyst at any temperature instead of considering the selectivities at only one temperature. In the following discussion, this selectivity will be referred to as the "maximum selectivity".

4.4.1. Catalyst Activity

Sulfate has the lowest activity of all catalysts surveyed while molybdate has the highest. Arsenate, bromate, nitrate and phosphate are also active catalysts. Molybdate shows little effect of temperature on conversion with conversions of 86.5-92.6% for temperatures from 280-350°C. Generally, the greater the activity of the catalyst, the higher the cracking to produce CO and CO₂.

Silicate	Phosphate	Arsenate	Carbonate
12.6	12.0	12.0	11.6
2.06-2.23	1.93-2.06	1.81-2.01	3.06-3.37
280 300 320 350	280 300 320 350	280 300 320 350	280 300 320 350
.9 -12.2 -31.5 -29.1	12.0 -16.5 -14.0 -19.5	3.5 -14.2 -37.5 -32.5	5.7 9.8 -13.9 -8.8
.3 50.8 81.7 81.8	14.2 59.0 73.6 85.4	42.2 85.0 96.2 95.9	24.3 41.6 76.5 88.1
.4 38.5 50.2 52.7	26.3 42.5 59.6 65.9	45.7 70.9 58.8 63.4	30.0 51.3 62.6 79.3
:			
.32 7.79 11.96 16.52	3.11 7.3611.50 9.22	5.44 11.82 11.59 12.25	4.61 10.02 13.32 12.84
.82 1.16 2.19 4.56	0.88 1.71 3.08 3.98	1.98 4.01 5.73 6.60	1.23 2.21 4.20 9.16
.74 13.41 12.57 10.33	9.07 11.81 11.11 5.53	23.84 25.32 16.47 11.36	14.35 17.31 13.99 11.81
.76 4.65 6.17 6.50	3.06 7.16 8.6018.46	4.82 10.44 11.52 15.04	6.28 10.48 12.87 20.56
.22 4.82 5.71 5.30	1.05 3.96 5.27 2.93	0.42 4.90 3.79 1.58	2.64 5.48 5.54 4.60
.32 1.72 2.72 2.77	0.59 2.14 2.98 3.85	0.88 2.01 2.89 3.75	1.44 1.85 2.46 4.78
.46 0.88 1.63 2.64	1.49 4.22 9.00 22.49	1.63 2.32 2.06 7.57	1.05 2.46 4.56 7.91
.63 9.81 10.58 10.91	9.77 17.61 31.61 16.46	11.3614.13 9.7219.06	3.24 6.38 11.25 14.77
.0 23.2 29.0 35.9	17.5 21.6 27.0 21.0	14.6 20.2 22.3 24.2	15.1 21.2 25.4 20.1
.7 3.5 5.3 9.9	4.9 5.0 7.2 9.0	5.3 6.9 11.0 13.1	4.0 4.7 8.0 14.4
.9 40.0 30.4 22.5	51.1 34.6 26.1 12.6	63.8 43.3 31.7 22.5	47.0 36.6 26.7 18.5
.4 13.9 14.9 14.1	17.2 21.0 20.2 42.0	12.9 17.9 22.2 29.7	20.6 22.1 24.6 32.2
.0 14.4 13.8 11.5	5.9 11.6 12.4 6.7	1.1 8.4 7.3 3.1	8.7 11.6 10.6 7.2
.0 5.1 6.6 6.0	3.3 6.3 7.0 8.7	2.4 3.4 5.6 7.4	4.7 3.9 4.7 7.5
e reported as moles	gas/moles lactic acid f	fed.	
	12.6 2.06-2.23 280 300 320 350 9 -12.2 -31.5 -29.1 3 50.8 81.7 81.8 4 38.5 50.2 52.7 .2 4.65 6.17 6.50 .74 13.41 12.57 10.33 .74 13.41 12.57 10.33 .75 5.71 5.30 .63 9.81 10.58 10.91 .63 9.81 10.58 10.91 .63 9.81 10.58 10.91 .7 3.5 5.3 9.9 .9 40.0 30.4 22.5 .14.1 13.8 11.5 .0 14.4 13.8 11.5 .0 14.4 13.8 11.5 .0 5.1 6.6 6.0 reported as moles	12.612.0 $2.06-2.23$ $1.93-2.06$ 280 300 320 350 280 300 320 350 280 300 320 350 280 300 320 350 350 320 350 350 350 320 350 350 350 81.7 81.8 14.2 59.0 $7.7911.9616.52$ 3.11 $7.3611.50$ 9.22 82 1.16 2.19 4.56 0.88 1.71 305 $7.7911.9616.52$ 3.11 $7.3611.50$ 9.22 82 1.16 2.19 4.56 0.88 1.71 3.08 $7.14112.5710.33$ $9.0711.8111.11$ 5.53 7.2449 4.55 3.06 7.16 $8.6018.46$ $2.224.82$ 5.71 5.3 1.05 3.96 5.27 $2.224.82$ 5.71 5.3 1.05 3.96 5.27 $2.224.82$ 5.71 5.3 1.05 3.96 5.27 $2.224.82$ 5.71 5.3 1.05 3.96 5.27 $2.224.82$ 5.71 5.3 1.05 3.96 5.27 $2.224.82$ 5.71 5.3 1.05 2.90 2.90 $2.224.82$ 5.71 5.9 1.75 2.90 2.90 $2.224.82$ 5.27 2.90 2.90 2.90 2.90 $2.321.0532.99$ $9.0711.81$ 1.75 2.90 2.90	12.612.012.01.93-2.061.81-2.01 $2.06-2.23$ $1.93-2.06$ $1.81-2.01$ $1.81-2.01$ 280 300 320 350 320 350 280 300 320 350 320 350 280 300 320 350 320 350 350 320 350 320 350 320 350 81.7 81.8 14.2 59.0 73.6 81.7 81.7 81.8 14.2 59.0 73.6 4 38.5 50.2 52.7 26.3 42.5 59.6 59.1 12.0 11.7 511.7 70.9 58.8 61.6 $7.7911.9616.52$ 3.11 $7.3611.50$ 9.22 $5.4411.8211.5912.25$ 32 $7.7911.9616.52$ 3.11 $7.3611.50$ 9.22 $5.4411.5216.47$ 74 38.5 6.59 65.9 45.7 70.9 58.8 63.4 74 38.5 1.98 1.75 3.96 5.73 297.2 573 74 31.11 $7.3611.11$ 553 28.201 2.97 575.7 74 $3.14112.5710.33$ $9.0711.8111.11$ 553 28.201 289 3.75 74 3.12 2.72 2.93 0.42 4.90 3.79 1.58 74 3.12 2.72 2.92 3.96 5.73 29.2 $5.4411.52$ 52 9.82 1.69 1.72

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						24+0	רמרמ.	575 Å			172				
Catalyst		Borate			Sulf	ate			Brom	ate			Chlor	ate	
Catalyst pH		9.2			7.	4			7.	8			7.	0	
Residence Time (s)	1	.49-1.6	9		3.27-	3.48			2.25-	2.48			2.67-	3.10	
Temperature (°C)	280	300 3	20 350	280	300	320	350	280	300	320	350	280	300	320	350
Error (%C)	-6.1 -1	9.7-22	.7 -37.1	4.5	5.2	17.2 -	-16.6	-18.8 -	23.1-	15.1 -	-27.4	-1.0	5.9	- 6.7 -	22.3
Conversion (BOF)(%)	17.4 37	1.2 77.	3 91.5	3.7	10.1	6.1	51.5	45.2	56.3	72.8	95.7	14.2	24.2	50.0	39.7
Conversion (Adj)(%)	11.3 17	7.5 54.	6 54.4	8.3	15.3	23.3	34.9	26.5	33.2	57.7	68.3	13.2	30.1	43.3	57.4
Yield (%)															
Acrylic Acid	0.75 3	3.03 10.	38 3.88	0.70	0.87	2.69	4.31	3.08	6.56	11.16	15.67	1.69	4.35	8.04	12.30
Propanoic Acid	0.52 (0.95 2.	53 6.25	0.70	0.97	2.46	3.66	3.24	5.13	7.98	8.16	1.38	2.88	5.95	10.01
2,3-Pentanedione	0.73 (5.3620.	90 16.37	1.28	1.27	1.65	1.89	4.22	7.32	9.88	8.32	3.23	6.24	8.82	9.86
Acetaldehyde	4.12 5	5.67 11.	03 12.85	1.82	3.22	9.49	18.08	4.18	6.81	11.18	8.95	2.80	4.94	7.85	12.64
Acetol	0.14 (1.39 1.	77 1.97	0.36	0.48	0.64	1.98	0.55	1.24	2.45	2.81	0.72	2.21	3.39	3.96
Other	0.66 (0.85 1.	74 3.38	0.37	0.72	1.93	3.88	0.74	1.01	1.74	3.19	1.17	0.98	2.28	3.39
.oo	1.85 2	2.13 3.	26 4.24	0.63	1.10	2.64	7.28	2.38	1.55	3.86	7.89	0.75	1.66	2.51	4.39
co,	0.63 1	l.87 6.	9517.86	0.50	0.84	1.76	3.20	3.32	3.75	8.93	14.21	1.49	3.40	6.28	10.91
Selectivity (%)															
Acrylic Acid	10.8 17	7.6 21.	5 8.7	13.3	11.5	14.3	12.7	19.3	23.4	25.1	33.3	15.4	20.2	22.1	23.6
Propanoic Acid	7.4 5	5.5 5.	2 14.0	13.3	12.9	13.1	10.8	20.2	18.3	18.0	17.3	12.5	13.3	16.4	19.2
2,3-Pentanedione	10.6 36	5.9 43.	2 36.6	24.5	16.9	8.7	5.6	26.3	26.1	22.3	17.7	29.4	28.9	24.3	18.9
Acetaldehyde	59.6 32	2.8 22.	8 28.7	34.8	42.8	50.3	53.5	26.1	24.3	25.2	19.0	25.5	22.9	21.6	24.2
Acetol	2.1	2.3 3.	7 4.4	7.0	6.3	3.4	5.9	3.4	4.4	5.5	6.0	6.5	10.2	9.3	7.6
Other	9.5 4	1.9 3.	6 7.6	7.1	9.6	10.2	11.5	4.6	3.6	3.9	6.8	10.6	4.5	6.3	6.5
* Yields of gases	are repo	rted as	s moles	jas/mo.	les la	ictic ;	acid f	ed.							

Product Distribution over Sodium Salt Catalvsts (Continued) ٣ Table 4.

Catalyst pH7.0Residence Time (s)2.25-2.48Temperature (°C)280300Temperature (°C)280300Error (%C)280300320Error (%C)280300320Error (%C)280300320Error (%C)280300320Error (%C)280300320Error (%C)280300320Conversion (BOF) (%)37.264.473.5Conversion (Adj) (%)37.264.473.5Yield (%)37.264.473.5Acrylic Acid1.964.126.602,3-Pentanedione15.9719.0814.54Acetol1.962.346.965.78Acetol1.212.173.33Co'1.152.163.60Co'0.012.173.33Co'1.152.163.60Co'1.152.163.60Co'1.152.163.60Co'1.152.163.60Co'0.136.722.7Acrylic Acid6.27.812.6Propanoic Acid50.136.227.82.3-Pentanedione50.136.227.82.3-Pentanedione50.136.227.8			с с	
Residence Time (s) 2.25-2.48 Temperature (°C) 280 300 320 Error (%C) 280 300 320 Error (%C) 280 300 320 Error (%C) 12.3 3.0 -19.6 Conversion (BOF) (%) 37.2 64.4 73.5 Vield (%) 5.39 11.94 11.76 Yield (%) 5.39 11.94 11.76 Acrylic Acid 1.96 4.12 6.60 2, 3-Pentanedione 1.96 4.12 6.60 2, 3-Pentanedione 1.96 4.12 6.60 2, 3-Pentanedione 1.96 2.17 3.33 Other 1.96 2.17 3.33 Other 1.15 2.16 3.60 Co' 1.15 2.16 3.60 Co' 1.15 2.17 3.33 Co' 1.15 2.16 3.60 Co' 1.12 2.17 3.33 Co' 1.15 2.16 3.60 Co' 6.76 9.72 3			κ.۶	
Temperature (°C)280300320Error (%C)Error (%C)12.33.0-19.6Conversion (BOF) (%)24.961.493.0Conversion (Adj) (%)37.264.473.5Yield (%)37.264.473.5Yield (%)5.3911.9411.76Acrylic Acid1.964.126.602,3-Pentanedione15.9719.0814.54Acetal1.964.126.602,3-Pentanedione15.9719.0814.54Acetal1.912.346.965.78Acetol1.212.173.33Other2.346.965.78Other1.152.163.60Co'1.152.163.60Co'5.316.92.72Selectivity (%)6.769.7213.05Acrylic Acid6.27.812.6Propanoic Acid50.136.22.782,3-Pentanedione50.136.22.78	8	2.3	0-2.72	
Error (%C)12.33.0-19.6Conversion (BOF) (%)24.961.493.0Conversion (Adj) (%)37.264.473.5Yield (%)5.3911.9411.76Acrylic Acid5.3911.9411.76Propanoic Acid1.964.126.602,3-Pentanedione1.964.126.602,3-Pentanedione1.964.126.602,3-Pentanedione1.964.126.602,3-Pentanedione1.912.346.963,710.322.346.965.78Acetol2.346.965.78Acetol2.346.965.78Other1.152.173.30Co1.152.163.60Co26.769.7213.05Selectivity (%)6.769.7213.05Acrylic Acid6.27.812.6Propanoic Acid50.136.227.8	20 350	280 3	00 320	350
Conversion (BOF) (%)24.961.493.0Yield (%)37.264.473.5Yield (%)5.3911.9411.76Acrylic Acid1.964.126.602,3-Pentanedione15.9719.0814.54Acetol2,3-Pentanedione15.9719.0814.54Acetol2,3-Pentanedione1.212.173.33Acetol2.346.965.78Acetol1.152.163.60Co'1.152.163.60Co'1.152.163.60Co'1.152.163.60Co'1.152.163.60Co'1.152.163.60Co'1.152.163.60Co'1.152.163.60Co'1.152.163.60Co'1.152.163.60Co'1.152.163.60Co'1.152.163.60Co'1.152.163.60Co'1.152.163.60Co'1.152.173.25Acrylic Acid6.27.812.6Propanoic Acid50.136.22.782.3-Pentanedione50.136.22.78	6 -14.6	-8.5 -4.	0 -7.1 -	9.8
Conversion (Adj)(%)37.2 64.4 73.5Yield (%)5.3911.9411.76Acrylic Acid5.3911.9411.76Propanoic Acid1.96 4.12 6.602,3-Pentanedione15.9719.0814.54Acetaldehyde4.99 8.3710.32Acetol2.34 6.96 5.78Other2.34 6.96 5.78Other1.21 2.17 3.33Co'1.15 2.16 3.60Co'1.15 2.16 3.60Co'2.34 6.96 5.78Acetol2.34 6.96 5.78Acetol2.34 6.96 5.78Acetol2.34 6.96 5.78Acetol1.21 2.17 3.33Co'1.15 2.16 3.60Co'5.76 9.7213.05Selectivity (%)6.76 9.7213.05Acrylic Acid6.2 7.8 12.6Propanoic Acid6.2 7.8 12.62,3-Pentanedione50.1 36.2 27.8	0 91.8	87.2 86.	5 89.8 9	2.6
Yield (%)Acrylic Acid5.3911.9411.76Propanoic Acid1.962,3-Pentanedione1.962,3-Pentanedione15.9719.0814.54Acetaldehyde4.998.3710.32Acetol2.346.965.78Acetol2.346.965.78Acetol1.212.173.33Other1.152.163.60Co1.152.163.60Co1.152.1305Selectivity (%)6.769.7213.05Acrylic Acid16.922.722.5Propanoic Acid6.27.812.62,3-Pentanedione50.136.227.8	5 77.2	78.8 82.	6 82.7 8	2.8
Acrylic Acid5.3911.9411.76Propanoic Acid1.964.126.602,3-Pentanedione15.9719.0814.54Acetaldehyde4.998.3710.32Acetol2.346.965.78Acetol1.21212.173.33Other1.1522.163.60co'1.1522.163.60co'5.7697.13.05Selectivity (%)6.769.7213.05Propanoic Acid6.27812.62,3-Pentanedione50.136.22.7				
Propanoic Acid1.964.126.602,3-Pentanedione15.9719.0814.54Acetaldehyde4.998.3710.32Acetol2.346.965.78Acetol1.212.173.33Other1.212.163.60Co'1.152.163.60Co'1.152.163.60Co'1.152.163.60Co'1.152.163.60Co'1.152.163.60Co'2.7812.6Acrylic Acid6.27.812.6Propanoic Acid50.136.227.8	76 9.89	0.95 0.	93 1.02	1.23
2,3-Pentanedione15.9719.0814.54Acetaldehyde4.998.3710.32Acetol2.346.965.78Acetol1.21211.313.33Other1.1521.3173.33Co'1.1522.163.60Co'1.1522.163.60Co'1.1522.163.60Co'1.1522.163.60Co'1.1522.163.60Co'2.7697.13.05Selectivity (%)6.7697.7213.05Acrylic Acid16.922.722.5Propanoic Acid6.27812.62,3-Pentanedione50.13622.78	60 8.89	30.5626.	69 30.43 3	2.38
Acetaldehyde4.998.3710.32Acetol2.346.965.78Other2.346.965.78Other1.212.173.33CO'1.152.163.60CO'1.152.163.60CO'1.152.163.60CO'1.152.163.60CO'1.152.163.60CO'1.152.163.60Selectivity (%)6.769.7213.05Acrylic Acid16.922.722.5Propanoic Acid6.27.812.62.3-Pentanedione50.136.227.8	5414.34	0.35 0.	48 0.68	0.95
Acetol2.346.965.78Other1.212.173.33CO'1.152.163.60CO'1.152.163.60CO'6.769.7213.05Selectivity (%)6.769.7213.05Acrylic Acid16.922.722.5Propanoic Acid6.27.812.62,3-Pentanedione50.136.227.8	3216.99	3.78 4.	95 6.59	9.25
Other1.212.173.33CO'1.152.163.60CO'6.769.7213.05Selectivity (%)6.769.7213.05Acrylic Acid16.922.722.5Propanoic Acid6.27.812.62,3-Pentanedione50.136.227.8	78 3.85	0.10 0.	13 0.24	0.43
CO [*] CO ₂ [*] CO ₂ [*] Selectivity (%) Acrylic Acid Propanoic Acid 6.2 7.8 12.6 6.3 - 10.1 36.2 27.8 2.3 - Pentanedione 50.1 36.2 27.8 12.6	33 5.05	0.68 1.	15 1.39	2.15
CO2 6.76 9.72 13.05 Selectivity (%) 16.9 22.7 22.5 Acrylic Acid 16.9 22.7 22.5 Propanoic Acid 6.2 7.8 12.6 2,3-Pentanedione 50.1 36.2 27.8	60 5.53	3.70 3.	60 4.09	5.40
Selectivity (%) Acrylic Acid 16.9 22.7 22.5 Propanoic Acid 6.2 7.8 12.6 2,3-Pentanedione 50.1 36.2 27.8	0516.24	40.6237.	95 29.52 3	3.07
Acrylic Acid 16.9 22.7 22.5 Propanoic Acid 6.2 7.8 12.6 2,3-Pentanedione 50.1 36.2 27.8				
Propanoic Acid 6.2 7.8 12.6 2,3-Pentanedione 50.1 36.2 27.8	5 16.8	2.6 2.	7 2.5	2.6
2,3-Pentanedione 50.1 36.2 27.8	6 15.1	83.9 77.	7 75.4 6	9.8
	8 24.3	1.0 1.	4 1.7	2.0
Aceraiaenyae 13.1 V. 19.19.	7 28.8	10.4 14.	4 16.3 1	6.6
Acetol 7.3 13.2 11.0	0 6.5	0.3 0.	4 0.6	0.9
Other 3.8 4.1 6.4	48.6	1.9 3.	4 3.4	4.6

Product Distribution over Sodium Salt Catalysts (Continued) Table 4.3.

4.4.2. Acrylic Acid

Silicate and bromate exhibit high selectivities to acrylic acid. These catalysts have maximum selectivities at 350°C of 35.9 and 33.3%, respectively. Molybdate shows the lowest acrylic acid selectivity of 2.5-2.7%. Sulfate is second lowest with selectivities of 11.5-14.3%.

Acrylic acid yields generally increase with temperature, but for some catalysts, the yield goes through a maximum near 320°C, indicating secondary reaction of acrylic acid.

4.4.3. Propanoic Acid

Propanoic acid production is highest over molybdate with selectivities of 70-84%. Bromate comes in second with propanoic acid selectivities of 17-20%. Chlorate also produces much propanoic acid at 13-19% selectivity. Silicate and phosphate produce the least amounts of propanoic acid with selectivities of 3-10% and 5-9%, respectively.

Yields to propanoic acid increase with temperature for all catalysts surveyed, indicating that it is a terminal product.

4.4.4. 2,3-Pentanedione

2,3-Pentanedione selectivity is highest for arsenate at 63.8%. Silicate, phosphate and nitrate produce almost identical amounts of 2,3-pentanedione with selectivities of 52.9, 51.1 and 50.1%, respectively, at 280°C. Carbonate has a selectivity of 47.0%. All of these catalysts have a maximum selectivity at 280°C which falls off with increasing temperature to less than 25% at 350°C. Borate is the only catalyst which has a maximum selectivity at a temperature higher than 280°C. Borate goes through a maximum of 43.2% at 320°C. Molybdate exhibits the lowest selectivity of 1-2%.

4.4.5. Acetaldehyde

Production of acetaldehyde is highest over borate and sulfate with selectivities of 23-60% and 35-54%, respectively. Silicate and molybdate have the lowest selectivities at 12-15% and 10-20%, respectively.

Acetaldehyde yield increases with temperature in all cases except for bromate, where it goes through a maximum near 320°C. Acetaldehyde is believed to be a terminal product.

4.4.6. Acetol

Selectivity to acetol is greatest over silicate at 10-14%. Nitrate, phosphate and carbonate produce maximum selectivities of 13.2, 12.4 and 11.6%, respectively. Molybdate produces the lowest acetol selectivity of 0.3-0.9%.

4.4.7. Other Products

Selectivities to other products vary from 7-12% for sulfate to 2-5% for molybdate. Other products observed are listed in Section 3.3.

4.4.8. Effect of Catalyst Salt Acidity on Selectivity and Conversion

The catalyst salts were analyzed on the basis of their acidity in an aqueous solution. The pH of a 0.1 M aqueous solution of each of the catalyst salts was determined either from measured values reported in literature or by calculation from published acid dissociation constants, K_a (84-87). No correlation was observed between the acidity of the salts and their activity as catalysts or their selectivity to acrylic acid.

The selectivity to 2,3-pentanedione follows a strong trend with respect to catalyst acidity. With the exception of nitrate, the 2,3-pentanedione selectivity increases as the catalyst becomes more basic. Basic catalysts (pH > 9) exhibit the highest 2,3-pentanedione selectivities of 43-64%. As the catalyst becomes more acidic, the maximum 2,3pentanedione selectivity decreases to 25-29% for chlorate, bromate and sulfate. The basic arsenate (pH = 12.0) produces the greatest 2,3-pentanedione selectivity at 63.8%. The trend in maximum 2,3-pentanedione selectivities may be seen in Figure 4.1.





Nitrate does not follow the trends observed by the other catalysts. One reason that has been suggested is that sodium nitrate may decompose or condense to form another species after heating to reaction conditions. This may change the acidity of the actual surface species and affect the selectivity to 2,3-pentanedione. Efforts are currently being made to test this hypothesis using transmission FTIR studies similar to those discussed in Chapter 6.

Propanoic acid selectivity increases with catalyst acidity. The neutral chlorate and bromate catalysts produce the most propanoic acid with maximum selectivities of 20.2 and 19.2%, respectively, while the most basic phosphate and silicate produce the least at 9.0 and 9.9%, respectively. Again, nitrate does not fit this trend, presumably for the reasons stated above. The effect of catalyst acidity on propanoic acid selectivity is presented in Figure 4.2.

Moderately basic catalysts exhibit the greatest selectivity to acetaldehyde. Sulfate and borate produce selectivities of 35-54 and 23-60%, respectively. The most basic silicate catalyst produces the lowest acetaldehyde selectivities of 12-15%. Acetaldehyde selectivity also falls off for the relatively acidic catalysts chlorate, bromate and nitrate. The effect of catalyst acidity on acetaldehyde selectivity may be seen in Figure 4.3.









The selectivity to acetol is greatest over the most basic catalyst silicate. However, acetol selectivity exhibits no clear trend with respect to catalyst acidity.

Selectivity to other products is greatest over relatively acidic chlorate and sulfate at 10.6 and 11.5%, respectively, but no trend with catalyst acidity is observed. The effect of catalyst salt acidity on product selectivities at 300°C is illustrated in Figure 4.4.

4.4.9. Periodic Considerations

Catalyst salts with central atoms from Group IVa and Va produce the highest selectivities to 2,3-pentanedione.

The activity of the catalyst is related to the highest occupied electronic shell of the central atom. This trend becomes obscured as the reaction approaches completion at high temperature, but is very clear at the low conversions of 280°C, as shown in Table 4.4. Molybdate exhibits the greatest conversion of 87.2% with a partially filled 0 shell $(5s^{1})$ for ground state molybdenum. Arsenate and bromate produce conversions of 42.2 and 45.2%, respectively, with partially filled N shells $(4p^{3} \text{ and } 4p^{5})$ for ground state arsenic and bromine. All other central atoms with highest occupied atomic orbitals of L and M produce less than 27% conversion at 280°C. No correlation was observed between conversion and the highest occupied shell L and M.



Figure 4.4. Effect of Catalyst Acidity on Product Selectivities at 300°C

We believe both acrylic acid and 2,3-pentanedione to arise by mechanisms in which the formation of a five membered cyclic transition state or intermediate is required. Formation of charged transition states are required by these mechanisms. Oxygen ligands of the catalyst salt must also be readily eliminated in both of these schemes, as discussed in Section 3.4.1. Since the reaction mechanisms are similar in these respects, the same factors may affect the rates of both mechanisms.

Three factors may be responsible for this phenomenon of increased conversion with the increase in highest occupied atomic orbital.

1) Steric factors may be preventing the smaller "hard" central atoms from allowing bond angle deformation to easily form rings while larger, more "soft" central atoms with loosely held bonding electrons allow more flexibility for bond angle deformation.

2) The simple geometric steric consideration of the size of the central atom may allow larger atoms to form larger rings with larger bonding angles on the opposite side of the ring from the central atom. Smaller atoms must form smaller rings with tighter bond angles thus making the transition state less favorable. Figure 4.5. illustrates how the size of the central atom may affect the bond angles of a transition state.

Catalyst Salt	Highest Occupie Atom Electro	ed Shell of Central nic Ground State	Conversion BOF at 280°C (%)
Borate	L	(2p ¹)	17.4
Carbonate	L	$(2p^{2})$	24.3
Nitrate	L	$(2p^{3})$	24.9
Silicate	М	$(3p^2)$	26.3
Phosphate	М	$(3p^{3})$	14.2
Sulfate	М	(3p ⁴)	3.7
Chlorate	М	$(3p^5)$	14.2
Arsenate	N	$(4p^{3})$	42.2
Bromate	N	$(4p^{5})$	45.2
Molybdate	0	(5 <i>s</i> ¹)	87.2

Table 4.4. Effect of Electronic State of Catalyst Salt Central Atom on Conversion at 280°C





Figure 4.5. Effect of Size of Catalyst Salt Central Atom on Bond Angles in Cyclic Transition States

3) Atoms with large, loosely held electron clouds may delocalize electronic charge easier, thus facilitating formation of charged transition states.

4.4.10. Carbon Balance

Carbon balance errors generally increase with increasing temperature as shown in Table 4.5. Mean carbon balance errors vary from 0.2% at 280°C to nearly 22% at 350°C. Borate and arsenate exhibit the highest observed carbon balance errors of -37.1 and -37.5%, respectively.

Gravimetric calcination studies were performed on selected lots of used catalyst and discussed in Section 3.4.5. These studies indicate that about 7% of carbon fed over a series of runs at temperatures of 280-350°C is deposited on the catalyst in the form of coke. We know from mass balances that much coking occurs at high temperatures and almost none at low temperatures, so this accounts for most of the carbon balance error observed.

The standard deviation of the carbon balance error is almost identical to the reproducibility of the lactic acid peak in product analysis. As mentioned in Section 2.2.6.1., the standard deviation of the lactic acid peak area observed in GC analysis is 14.1% of the mean. This compares very well with the standard deviation of the carbon balance errors in the catalyst survey, which is 10-15%. This indicates that most of the deviation observed in the carbon balance is caused by deviation in the analysis method.

Table 4.5. Analysis of Carbon Balance Error

Temperature (°C)	280	300	320	350
Mean Error (%)	0.2	-6.6	-15.1	-21.8
Standard Deviation of Error (%)	9.6	12.0	15.0	9.6

4.5. Summary

Group V catalyst salts (nitrate, phosphate and arsenate) show the greatest selectivities to 2,3pentanedione, with selectivities up to 64%.

Catalyst salt acidity affects product selectivity. Basic salts (pH > 9) exhibit higher selectivity to desirable 2,3-pentanedione. Relatively acidic catalysts promote formation of propanoic acid. Moderately basic catalysts (7.4 < pH < 10) promote production of acetaldehyde.

Conversion increases with increasing level of occupied orbitals in the catalyst salt central atom. Salts with central atoms having N and O shell electrons produce much higher conversions than those with only L and M shells.

Chapter 5. Characterization of Sodium Phosphate Salt Catalysts using MAS-³¹P-NMR

5.1. Introduction

Sodium phosphate salts are known to undergo dehydration and condensation upon heating (58). The sodium phosphate salts which serve as catalysts in our reactors are heated to temperatures up to 400°C before and during reactions, which leads to a need to identify which chemical species are present on the catalyst surface. The purpose of this study is to determine the form of the phosphate catalyst under reaction conditions employing Magic Angle Spinning-³¹P-Nuclear Magnetic Resonance (MAS-³¹P-NMR). The conclusions which are made have also been compared to results of a study of surface species using transmission FTIR.

Chemical shifts reported are relative to 85% phosphoric acid, H_3PO_4 , where $\sigma = -\delta$ and the chemical shift, δ , is reported according to IUPAC convention with $\delta > 0$ representing a downfield shift and deshielding.

5.2. Methods

5.2.1. Materials

The origin of materials used is discussed in Section 3.2.1.

5.2.2. Sample Preparation

Neat salts were used as received without purification. Salts which appeared clumpy were ground with a mortar and pestle to achieve uniform consistency.

Before impregnation of catalyst supports with salt, the support was crushed with a mortar and pestle and sieved to 30x60 USA wire mesh. The catalyst support was crushed finer for use in NMR spectroscopic studies than for use as a catalyst support in the vapor phase reactor. The finer consistency of the NMR samples was necessary for better balance and higher spinning speeds for Magic Angle Spinning (MAS) spectroscopy.

Crushed supports were impregnated with phosphate salts using the same method described in Section 3.2.2. Catalyst loading was 1.0 mmol/g support for all samples.

Bovine dental enamel was prepared by boiling for two hours to remove organic material, then crushing, grinding and sieving to 60×100 mesh.

Samples were heated in a Thermolyne 1300 furnace controlled by an Omega PI controller. Neat or supported salts were prepared as described above, placed in glass beakers or ceramic crucibles, then placed in the furnace which had been preheated to a designated temperature. Samples were heated for 4.3-5.6 hours at constant temperature, then removed from the furnace and allowed to cool in air. The furnace door was opened for as short a time

as possible upon addition or removal of samples. At temperatures less than 500°C, the furnace temperature dropped less than 15°C upon addition of the sample and returned to within 5° of the setpoint within 5 minutes after the start of the calcination run. For calcination of biomineral hydroxyapatite at 800°C, the temperature dropped 50°C but returned to within 20° of the setpoint within 5 minutes. After heating, samples were stored in glass vials with plastic screw-on lids tightly shut until ready for use.

5.2.3. NMR Spectrometer

5.2.3.1. Spectrometer Hardware and Data Acquisition

Magic Angle Spinning Phosphorus-31 Nuclear Magnetic Resonance (MAS-³¹P-NMR) spectra were obtained at room temperature by weighted Fourier transformation of free induction decays (FIDs) observed using quadrature detection at 161.903 MHz. Hardware consisted of a Varian VXR-400S spectrometer with an Oxford cryomagnet generating a magnetic field of 9.395 T. Appendix B details calculation of the magnetic field strength. A Varian 400VT CP/MAS sample probe was used with a 7 mm diameter rotor and a top speed of about 8 kHz. The computer operating system was VNMR Version 4.1 run on a Sun workstation network.

Normal data acquisition was accomplished using a single pulse sequence shown in graphical form in Figure 5.1.

Typical operating parameters for normal data acquisition are presented in Table 5.1.



Figure 5.1. Normal Data Acquisition Sequence

Table 5.1. Typical Parameters for Normal Data Acquisition

Observed Nucleus	³¹ P
Transmitter Frequency (MHz)	161.903
Spectral Width (kHz)	100
Number of Data Points	16,000
Acquisition Time (s)	0.080
Number of Scans	64
First Delay, dl (s)	10.0
Pulse Width, pw (µs)	4.0

5.2.3.2. Spectrometer Setup

The account was started on the workstation and a setup procedure was run as outlined in the operating manuals to set the acquisition parameters for the observe nucleus, ³¹P. The transmitter was turned on in preparation for tuning the probe.

The spectrometer probe required tuning at the start of every daily session on the spectrometer. The tuning wand for ³¹P was inserted into the sample probe and the probe assembly was installed in the magnet. The observe port of the probe was connected to the tuning port of the spectrometer junction box located on the leg of the magnet. The "tune" mode was selected on the selector knob of the junction box. The probe was tuned to the minimum signal possible using both coarse and fine tuning knobs on the bottom of the probe. The tune range was changed several times before a minimum was found at the most sensitive range setting. The probe was disconnected from the junction box, the probe was removed from the magnet and the tuning wand was removed from the probe in preparation for sample loading.

5.2.3.3. Sample Loading

Visible residue was loosened from the rotor using a wooden toothpick or similar sharp, soft object to prevent scratching and grooving the rotor. The rotor was tapped lightly with the mouth down on a solid surface or blown into in order to dislodge residual particles. Any residual powder was wiped out using a lintless wipe rolled into a cylindrical shape. This procedure was repeated until the rotor was clean by visual inspection.

The rotor was filled with loose sample and tapped lightly on a solid surface to pack the sample evenly. This was repeated until the rotor was full up to the level at which the end cap contacts the sample. The sample was checked for evenness on top before the end cap was firmly pressed into the rotor. Handling the rotor by the end cap, any residual material was wiped from the rotor, being careful to look for grease from fingers and powder from sample loading since any foreign material on the outside of the rotor may decrease spinning frequency or affect sample balance.

The access door to the sample compartment of the probe was opened and the rotor was inserted into the spinner housing until it was firmly seated. The access door was closed and the probe was installed in the magnet. The observe port of the probe was connected with the observe port of the junction box. The decoupler transmitter cable from the spectrometer was connected to the decouple port of the probe if performing proton decoupling experiments.

5.2.3.4. Sample Spinning

The two quick-connect fittings of the spinner air control unit, located on the leg of the magnet, were connected with the respective connectors on the probe. One is labeled "bearing" for the air bearing of the spinner and the other is labeled "drive" denoting the air drive or speed

control. The fittings were tightened firmly, taking care to not break the glass connectors. The fiber-optic tachometer connector was plugged into the respective port in the probe. The air bearing pressure on the air control unit was increased before increasing the drive pressure. The sample started spinning as evidenced by the accompanying whine of the rotor and the readout of the tachometer. The complete procedure for bringing the spinner up to speed is given in the instruction manual. Once the spinner had reached the appropriate frequency for the experiment, the drive pressure required frequent observation and periodical adjustment since the spinning frequency had a tendency to drift. The spinning frequency was typically maintained within 15 Hz of the designated frequency.

Spectra were obtained at spinning frequencies, u_r , of 4-7 kHz. A constant spinning frequency was difficult to maintain at frequencies greater than 7 kHz, resulting in peak broadening. At frequencies lower than 4 kHz, broad peakwidths and multiple isotropic peaks led to sideband overlap, thus complicating interpretation of the spectra.

5.2.3.5. Collection of Free Induction Decays

The parameters to set up the spectrometer for the particular observe nucleus had already been selected as described above, but it was necessary to select the acquisition parameters for each experiment. These parameters included the spectral width, number of scans, block size, delay and pulse width. Several of these parameters are listed in Table 5.1.

The experiment was started and free induction decays (FIDs) were collected for at least 32 scans. At this point the data was examined by performing a weighted Fourier transform of the FIDs to generate an NMR spectrum. Phasing was adjusted to produce a flat baseline and improve the appearance of the spectrum. If the data exhibited a reasonably high signal to noise ratio (S/N) by visual inspection and the phasing was good, data collection was terminated and the data was saved. If S/N or the phasing of the spectrum was poor, additional scans were collected until either the spectrum improved or no improvement was realized with many additional scans.

5.2.3.6. Reference Sample

The spectrometer required referencing to a known standard at the start of each daily session. Synthetic calcium hydroxyapatite, $Ca_{10}(OH)_2(PO_4)_6$, (Aldrich) was chosen as a reference because it is a solid at room temperature and may be analyzed in the same probe setup as the other solid samples. The reference of choice for many NMR spectra is 85% phosphoric acid, but it was deemed inappropriate for our experiments since use of a liquid reference required the use of a different probe. This has the possibility of introducing error because of inconsistent sample placement in the magnetic field, magnetic field inhomogeneity and differences in probe tuning.

A spectrum of calcium hydroxyapatite was collected and the transmitter offset was adjusted to place the chemical shift of the isotropic central peak of calcium hydroxyapatite at the literature value of 2.8 ppm ± 0.2 (65). The hydroxyapatite chemical shift of 2.8 ppm is relative to the standard reference of 85% phosphoric acid.

5.2.4. Experiments

5.2.4.1. Data Quality

The chemical shift of isotropic peaks is reproducible to \pm 0.50 ppm for a typical spectrum with a signal to noise ratio (S/N) of 44 for the largest peak. Typical reproducibility of chemical shifts in spectra of identical samples repeated during the same session is \pm 0.21 ppm. Typical reproducibility of chemical shifts in spectra repeated during subsequent sessions is \pm 0.50 ppm. Fluctuations in the magnetic field over several days between sessions may be responsible for the lesser reproducibility for samples repeated during different sessions than for samples repeated during the same session. Table 5.2. shows typical and worst-case reproducibility and S/N for NaH₂PO₄ spectra. S/N for spectra of various compounds are presented in Table 5.3.
Table 5.2. Reproducibility for NMR Spectra of NaH, PO₄

	Typical	Worst Case
Chemical Shift (ppm)	± 0.21	± 1.1
S/N ·	38	11
Chemical Shift (ppm)	± 0.50	± 1.1
S/N**	38	11

* Identical samples repeated during same session.

** Identical samples repeated during subsequent sessions.

Sample	S/N Range	Typical S/N
Hydroxyapatite	150-760	507
NaH ₂ PO ₄	11-166	38
Na ₂ HPO ₄	38-378	162
Na ₃ PO ₄	68-740	232
Na ₄ P ₂ O ₇	76-300	184

Table 5.3. Signal to Noise Ratios (S/N) for NMR Spectra

Peakwidths (FWHM) for the spectra cover a range from 1.05-18.3 ppm with a typical peakwidth of about 2.5 ppm. Error in chemical shift values is attributed largely to uncertainty in identifying the center of the isotropic peak due to noise and large peakwidth. The average error associated with the chemical shift increases with an increase in peakwidth. This trend is clearly seen in Table 5.4. A wider peak has a broader apex and thus a less easily established center. Transmitter drift is believed to be insignificant compared to other errors.

Peakwidth (FWHM), ppm	Error in Chemical Shift, ppm
2.5	0.06
2.8	0.35
5.4	0.43
2.8	0.56
7.5	0.67
8.9	0.91
8.9	1.15
18.3	1.30

Table 5.4. Effect of Peakwidth on Chemical Shift Reproducibility

5.2.4.2. Variation of Spinning Frequency

For each NMR signal in a sample, MAS spectroscopy produces one band at the isotropic chemical shift frequency accompanied by spinning sidebands flanking the isotropic peak on each side. These sidebands are evenly spaced at integer multiples of the spinning frequency. Variation of the spinning frequency may be used to discriminate between isotropic peaks and spinning sidebands. The chemical shifts of isotropic peaks are independent of the spinning frequency, while the apparent chemical shifts of spinning sidebands change with spinning frequency. This technique involves acquiring spectra at several different spinning frequencies and observing which peaks change position.

5.2.4.3. Determination of Chemical Shift Anisotropy

The intensities of the sidebands relative to the isotropic peak depend on several factors including the magnetogyric ratio of the observe nucleus, the chemical shift, anisotropy of the chemical shift tensor, the strength of the magnetic field and the spinning frequency. A graphical method by Herzfeld and Berger was used to determine the three primary values of the chemical shift tensor from the intensities of the sidebands and other system parameters (88). A detailed example of the method is presented in Appendix B.

The anisotropy of the chemical shift tensor may be used to determine if two signals with nearly identical chemical shifts are really identical signals, or merely have similar chemical shifts.

5.2.4.4. Sideband Suppression

Heated samples of NaH₂PO₄ exhibit at least six isotropic peaks with a large anisotropy associated with four of the signals to produce intense sidebands. This produces very complicated spectra in which it is difficult to distinguish overlapping sidebands from isotropic peaks.

VNMR Version 4.1 software contains a method for suppression of spinning sidebands called Total Sideband Suppression (TOSS). This method uses a cross-polarized 180° pulse sequence to create timed spin-echoes to suppress

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spinning sidebands. The method employs the principle that as the echoes interact with the nucleus from opposite sides, the spinning sideband signals cancel each other while the isotropic signal is reinforced. The method requires setting the initial pulse width and the spinning frequency. A recipe is then invoked within the program to calculate the pulse widths and delay times of the echo pulses. The method requires optimization of the initial pulse width for the particular sample by performing several runs at various pulse widths to optimize sideband suppression. The optimum pulse width was about 6.0 µs for the heated samples of NaH₂PO₄. A diagram of the TOSS pulse sequence used for heated NaH₂PO₄ is shown in Figure 5.2. and parameters are listed in Table 5.5.

The TOSS sequence worked well for suppression of sidebands in NaH_2PO_4 samples, but S/N is sacrificed. Typical values of S/N decreased from 38 for the standard acquisition sequence to 8.2 for the TOSS sequence.

5.2.4.5. Proton Decoupling

AX coupling is caused by oscillation of the coupled nucleus X between spin states at the frequency of the coupling constant J_{AX} . The energy driving this oscillation is derived from the observed nucleus A causing an identical splitting J_{AX} in the spectrum of A. In $A{X}$ decoupling experiments, the sample is irradiated with two RF fields



Figure 5.2. Total Sideband Suppression (TOSS) Pulse Sequence

p1	0	
pw	6.0	μs
d1	10.0	s
d2	0	
d3	4.6	μs
d4	1.0	μs
d5	25.5	μs
d6	163.0	μs
d7	113.9	μs

Table 5.5. Parameters for TOSS Pulse Sequence

* Calculated for 6 kHz spinning frequency and optimized for heated NaH_2PO_4 .

simultaneously. The observe transmitter irradiates the sample with an RF field B_3 at the observe frequency of A, u_A , while the decoupler transmitter irradiates the sample with another strong RF field B_2 near the resonant frequency of the decoupled nucleus X, u_X . If B_2 is strong enough that the frequency of the oscillations induced in X by B_2 are greater than J_{AX} , the energy driving the oscillations is then derived from B_2 instead of from the coupling with A and the spin states are no longer seen separately by A, thus suppressing the splitting (89).

A range of magnitudes of selected coupling constants for ${}^{31}P^{1}H$ and ${}^{31}P^{31}P$ coupling are presented in Table 5.6. The second order coupling constant, ${}^{2}J_{PH}$, is expected to be of the same order of magnitude as ${}^{2}J_{PP}$ which is about 0.1 ppm (90). With typical peakwidths (FWHM) of 2.5 ppm, it would be very difficult to observe any second order coupling since ${}^{2}J_{PH}$ is an order of magnitude smaller than the peakwidth. Several heteronuclear ${}^{21}P({}^{1}H)$ proton decoupling experiments were performed to determine if some of the peaks observed in complicated spectra were caused by splitting of phosphorus signals due to coupling with hydrogen. No ${}^{31}P^{1}H$ coupling was observed and all signals were found to be either distinct ${}^{31}P$ signals or spinning sidebands. These observations are developed further in Section 5.3.

Coupling Type	Functional Group	J (Hz)	J (ppm)**
¹ J _{PH}	R ₂ PH=O	490-760	3.0-4.7
¹ J _{pp}	R ₂ PPR ₂	220-400	1.4-2.5
$^{1}J_{PP}$	$R_2P(=0)P(=0)R_2$	330-500	2.0-3.1
² J _{PCH}	R ₂ PCH ₃	1-5	0.006-0.031
² J _{PCH}	$R_2P(=O)CH_3$	7-15	0.04-0.09
² J _{P⊖P}	$R_2P(=0)OP(=0)R_2$	15-20	0.09-0.12
³ J _{PH}	POCH ₃	6-15	0.04-0.09
* Erom Emalou a	nd Unii (00)		

Table 5.6. Spin-Spin Coupling Constants

* From Emsley and Hall (90) ** At $u_o = 161.903$ Mhz

5.3. Results

5.3.1. Neat Salts

5.3.1.1. Calcium Hydroxyapatite

Synthetic calcium hydroxyapatite, Ca₁₀(OH)₂(PO₄)₆, was used as a reference standard and its chemical shift was set at the reference value of 2.8 ± 0.2 ppm (65). Synthetic calcium hydroxyapatite was observed at spinning frequencies of 4-7 kHz and exhibited one narrow isotropic peak. The principal values of the chemical shift tensor agree with the literature values within the error of the experiment.

Bovine dental enamel was studied after heating to 100°C and 800°C. At 100°C, one signal was observed at 3.0 ppm. This signal has the same chemical shift, within experimental error, as synthetic calcium hydroxyapatite and the principal values of the chemical shift tensor also agree within

experimental error, except the literature value for σ_{33} is outside of experimental error. At 800°C, three signals were observed at 2.9, 0.5 and -4.5 ppm. The peak at 2.9 ppm accounts for 78% of the ³¹P signal intensity. The two small peaks probably correspond to a pyrophosphate which is formed upon heating and possibly a non-stoichiometric hydroxyapatite species. Both of these have been reported to exhibit small upfield peaks in heated hydroxyapatites (65). The anisotropy of the 2.9 ppm peak remains unchanged upon heating to 800°C.

We conclude that calcium hydroxyapatite is the sole component of both synthetic calcium hydroxyapatite and bovine dental enamel heated to 100° C. Bovine enamel remains 78% hydroxyapatite upon heating to 800° C, with the remainder probably composed of calcium pyrophosphate, $Ca_2P_2O_7$. Spectra of calcium hydroxyapatites are shown in Figure 5.3. Chemical shifts and anisotropies for calcium hydroxyapatites are presented in Table 5.7. Linewidths (FWHM) of both biomineral and synthetic hydroxyapatite were typically 2.0-3.0 ppm, as seen in Table 5.8.

5.3.1.2. Neat Monosodium Orthophosphate

Neat monosodium orthophosphate monohydrate, $NaH_2PO_4 \cdot H_2O$, exhibits a single isotropic chemical shift at 1.8 ± 0.4 ppm. The literature value of 2.3 ppm lies just outside the experimental error (67). The principal values of the



a) Commercial sample synthetic $Ca_{10}(OH)_{2}(PO_{4})_{6}$, $v_{r} = 6$ kHz. b) Bovine dental enamel boiled at 100°C, $v_{r} = 6$ kHz. c) Bovine dental enamel calcined in air at 800°C, $v_{r} = 6$ kHz. Bars indicate isotropic peaks.

Figure 5.3. MAS-³¹P-NMR Spectra of Calcium Hydroxyapatites

Compound	Chemical Shift, ppm	Principal Values of Chemical Shift Tensor, ppm	Ref.
	δ	σ_{11} σ_{22} σ_{33}	
Ca ₁₀ (OH) ₂ (PO ₄) ₆	2.8	18 ± 9 -3 ± 8 -24 ± 10	*
Ca ₁₀ (OH) ₂ (PO ₄) ₆	2.8 ± 0.2	19 ± 3 4 ± 6 -15 ± 1	(65)
Bovine Dental Enamel, 100°C	3.0	30 ± 17 6 ± 22 -46 ± 19	*
Bovine Dental	2.9 (78)**	30 ± 11 -3 ± 12 -35 ± 11	*
Enamel, 800°C	0.5 (21)**		
	-4.5 (1)**		
Human Dental Enamel	3.3		(65)

Table 5.7. Chemical Shifts of Calcium Hydroxyapatites

* This work

** Parenthetical values are percentages of the total signal.

Table	5.8.	Linewidths	of	³¹ P	Signals
TUDIC	5.0.		O L	-	Dignard

Compound	Linewidth FWHM, ppm	Ref.
Ca ₁₀ (OH) ₂ (PO ₄) ₅	1.9-2.6	*
Bovine Dental Enamel, 100°C	3.1	*
Bovine Dental Enamel, 800°C	1.7	*
Human Dental Enamel	3	(65)

* This work

chemical shift tensor also lie just outside experimental error.

Upon heating to 300°C, six peaks become visible at 2.0, -8.3, -15.6, -19.4, -24.1 and -26.3 ppm. Analysis by both spinning frequency variation and spinning sideband suppression (TOSS) confirm that all six peaks are unique signals and are not spinning sidebands. ³¹P(¹H) proton decoupling experiments confirm that there is no splitting into multiple peaks due to ${}^{31}P^{1}H$ coupling.

Upon further heating to 450°C, five signals appear at -5.4, -15.3, -19.0, -24.0 and -26.2 ppm. Again, additional experiments confirm that all peaks are unique signals and not sidebands or split peaks, as described above. TOSS analysis indicated an additional signal at about 9.0 ppm, but spinning frequency variation revealed that this was due to either noise or a lingering spinning sideband in the TOSS spectrum.

Linewidths (FWHM) were typically 2.5-4.0 ppm for neat heated and unheated NaH_2PO_4 samples. Reproducibility of chemical shifts was typically better than ± 0.5 ppm.

The signal at 2.0 ppm is assigned to NaH₂PO₄ and decreases in size as the temperature increases, indicating NaH₂PO₄ is converting to other species. This signal has virtually disappeared by 450°C. A signal appears at -8.3 ppm at 300°C, but disappears again by 450°C, to be replaced by another peak at -5.4 ppm. These peaks match the central phosphate units of the linear sodium triphosphates in literature, Na₅P₃O₁₀-I at -8.0 ppm and Na₅P₃O₁₀-II at -5.6 ppm (61,62,64,68,70). However, the signal near -5.6 ppm is believed to arise from the trimeric ring, trimetaphosphate, Na₃P₃O₃, because of several considerations detailed in Section 5.4.1. The linear sodium polyphosphates, (NaPO₃), and (NaPO₃)_n, also show a small peak near -6 ppm which is

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assigned to a terminal phosphate unit in the literature (64). We assign the peak at -8.3 ppm to $Na_5P_3O_{10}$ -I and the peak at -5.4 ppm to $Na_3P_3O_9$. There is a strong possibility that the -6 ppm peak which was assigned to $(NaPO_3)_n$ in the literature is actually due to small amounts of $Na_5P_3O_{10}$ -II or $Na_3P_3O_9$ in the polyphosphate sample.

We were able to determine the anisotropy of the -8.3 ppm peak, but the anisotropy was not reported in the literature. Conversely, the anisotropy of the -5.6 ppm peak was reported in literature, but we were unable to determine an anisotropy because the sidebands were too small. Therefore, no comparison of anisotropy was able to be made in order to confirm the peak assignments.

We assign all the peaks at -15.3, -19.0, -24.0 and -26.2 ppm to linear sodium polyphosphate, $(NaPO_3)_n$. Each of these signals was observed by Prabhakar, *et al.*, while the peaks near -16 and -19 were also observed by other researchers (63,64,66). The MAS-³¹P-NMR spectra from normal acquisition, spinning frequency variation, TOSS and ³¹P{¹H} decoupling of neat monosodium phosphates after calcination are presented in Figure 5.4. The chemical shifts and tensors are listed in Table 5.9.

Neat $NaH_2PO_4 \cdot H_2O$ converts partly to $Na_5P_3O_{10}-I$ and $(NaPO_3)_n$ at 300°C and then completely to $Na_3P_3O_9$ and $(NaPO_3)_n$ at 450°C. The four polyphosphate peaks correspond to various phosphate units with different thermal stabilities. The units giving



a) Commercial sample NaH₂PO₄·H₂O, $v_{r} = 7$ kHz. b) NaH₂PO₄·H₂O calcined in air at 300°C, $v_{r} = 4$ kHz. c) ;300°C, $v_{r} = 6$ kHz. d) ;300°C, $v_{r} = 7$ kHz. e) ;300°C, TOSS, $v_{r} = 6$ kHz. f) ;300°C, without ³¹Pl⁴H decoupling, $v_{r} = 6$ kHz. Bars indicate isotropic peaks.

Figure 5.4. MAS-³¹P-NMR Spectra of Neat Monosodium Phosphates



g) NaH,PO₄•H,O calcined in air at 300°C, with ³¹P[¹H] decoupling, $v_r = 6$ kHz. h) ;450°C, $v_r = 7$ kHz. i) ;450°C, TOSS, $v_r = 6$ kHz. j) ;450°C, without ³¹P[¹H] decoupling, $v_r = 6$ kHz. k) ;450°C, with ³¹P[⁴H] decoupling, $v_r = 6$ kHz. Bars indicate isotropic peaks.

Figure 5.4. MAS-³¹P-NMR Spectra of Neat Monosodium Phosphates (Continued)

Table	5.9.	Chemical	Shifts	of	Monosodium	Orthophosphates

Sample	Chemical	Fraction	Principal Values of				
Compound	Shirt,ppm	or Signal,∛	Chemica.	I SNIIT T	ensor,ppm		
	δ		σ_{11}	σ_{22}	σ_{33}		
NaH ₂ PO ₄ _25°C							
NaH ₂ PO ₄ •H ₂ O	1.8±0.4	100	66±10	10±12	-81±10	*	
NaH ₂ PO ₄ 30	<u>0°C</u>						
NaH ₂ PO ₄ •H ₂ O	2.0±0.7	13				*	
Na ₅ P ₃ O ₁₀ -I	-8.3	19	89±13	10±2	-73±13	*	
(NaPO ₃) _n	-15.6	9	137±15	65±24	-154±17	*	
(NaPO ₃) _n	-19.4	23	128±7	60±7	-129±9	*	
(NaPO ₃) _n	-24.1	23	131±13	64±14	-121±16	*	
(NaPO ₃) _n	-26.3	13	141±18	65±16	-126±21	*	
NaH_2PO_4 45	<u>0°C</u>		·				
Na ₃ P ₃ O ₉	-5.4	21				*	
(NaPO ₃) _n	-15.3	26	129±21	68±22	-141 ±2 5	*	
(NaPO ₃) _n	-19.0	42	130±8	66±9	-138±9	*	
(NaPO ₃) _n	-24.0	6	140±11	62±8	-130±14	*	
(NaPO ₃) _n	-26.2	5				*	
NaH ₂ PO ₄ Si	/Al 100°C						
NaH ₂ PO ₄ •H ₂ O	2.4	79				*	
Na ₃ P ₃ O ₉	-5.9	21				*	
NaH ₂ PO ₄ Si/Al 300°C							
Na ₅ P ₃ O ₁₀ -I	-8.8	44	102±13	16±14	-92±13	*	
(NaPO ₃) _n	-19.5	56	122±10	45±13	-108±10	*	
NaH ₂ PO ₄ Si	/A1 450°C						
Na ₃ P ₃ O ₉	-5.8	100	88±6	9±7	-81±6	*	

	(Continued)						
Sample	Chemical	Fraction	Principa	l Values	of	Ref.	
Compound	Shift	of	Chemical	Shift T€	ensor,ppm		
	δ	Signal, 8	J.	σ.,	σ		
T					0,;	L	
Literature	<u>e values</u>						
Monosodiu			77 2	22 1	<i>c</i> 1 1	1671	
Sodium Tr			11.5	-23.1	-01.1	(67)	
No DO T		2	ſ			(70)	
$Na_5P_3O_{10} = 1$						(70)	
	-8.0					(70)	
$Na_5P_3O_{10}-11$	5.0					(01)	
	-0.2		60	2 7	110	(01)	
$Na_5P_3O_{10}-11$	4.0 5.7°		02	27	-113	(62)	
			118	-22	= 7 9	(62)	
$Na_5P_3O_{10}-11$	5.1 5.2		0Z	3Z	-109	(64)	
	-5.6		120	-24	- / 9	(64)	
$Na_5P_3O_{10}-11$	4.6		69	24	-107	(68)	
	-5.6		11/	-20	-80	(68)	
$Na_5P_3O_{10}-11$	4.6					(70)	
	-6.6	·				(70)	
Sodium Po.	Lyphosphat (25	4.7				
$Na_6P_4O_{13}$	1.5		4/	47	-98	(64)	
(), , , , , , , , , , , , , , , , , , ,	-16.4		152	-18	-85	(64)	
$(NaPO_3)_6$	-6.0			1.0	0.5	(64)	
	-19.6		165	-19	-87	(64)	
$(NaPO_3)_n$	2.0		45	45	-95	(63)	
	-19.0		160	-13	-90	(63)	
(NaPO ₃) _n	-15.6					(66)	
	-18.5					(66)	
	-19.9					(66)	
	-24.1					(66)	
	-26.8					(66)	
(NaPO ₃) _n	1.0					(64)	
	-6.2 ^T					(64)	
			165	-20	-85	(64)	

Table 5.9. Chemical Shifts of Monosodium Phosphates

* This work

C Central phosphate unit T Terminal phosphate unit

rise to signals at -15.3 and -19.0 ppm are more thermally stable at 450°C than those at -24.0 and -26.2 ppm. Table 5.10. shows that the less stable species convert to the more stable species as the temperature rises so that 68% of the signal is due to the -15.3 and -19.0 ppm peaks at 450°C.

Table 5.10. Conversion of Phosphate Units to Thermally Stable Species for Neat NaH,PO₄•H₂O

Phosphate Species	Chemical Shift, ppm	Percentage of ³¹ P Signal at Temperature T, %		
	δ	$T = 25^{\circ}C$	300°C	450°C
NaH ₂ PO ₄ •H ₂ O	2.0	100	13	
Na ₅ P ₃ O ₁₀ -I	-8.3		19	
Na ₃ P ₃ O ₉	-5.4			20
(NaPO ₃) _n	-15.3		9	26
(NaPO ₃) _n	-19.0		23	42
(NaPO ₃) _n	-24.0		23	7
(NaPO ₃) _n	-26.2		13	5

5.3.1.3. Neat Disodium Orthophosphate

A single peak is present at 6.3 ppm in the spectrum of neat disodium orthophosphate, Na_2HPO_4 . This chemical shift is within 0.3 ppm of the literature value (67) and the anisotropy also compares well with literature.

After heating to 300°C, complete conversion occurs to form sodium pyrophosphate with a signal at 1.9 ppm and a small amount of unknown at 10.8 ppm, which only makes up 1.3% of the signal. Further heating to 450°C again produces mostly pyrophosphate at 2.2 ppm and a small amount of unknown at 13.6 ppm. This unknown makes up only 2.8% of the signal and has a chemical shift that corresponds with trisodium orthophosphate, Na_3PO_4 . The peak was too small to calculate the chemical shift anisotropy, so it is impossible to ascertain whether its anisotropy is comparable with that of Na_3PO_4 . The spectra of neat disodium phosphate are presented in Figure 5.5. and the chemical shifts and tensors are tabulated in Table 5.11.

Both the chemical shift and anisotropy of Na_2HPO_4 compare well with values reported in the literature. The chemical shifts of pyrophosphate also agree with literature, but the anisotropies do not. The chemical shift anisotropies are self-consistent with samples calcined at other temperatures and also with commercial samples of pyrophosphate, but our results for pyrophosphate chemical shift tensors differ from literature results by typically 23 ppm for both σ_{11} and σ_{33} after accounting for experimental error. A possible explanation for this discrepancy is suggested in Section 5.3.2.4.

5.3.1.4. Neat Trisodium Orthophosphate

The only transformation observed upon calcination of neat $Na_3PO_4 \cdot 12H_2O$ is a simple dehydration to the anhydrous form, Na_3PO_4 . One peak is present at 7.5-7.9 ppm for a commercial sample of $Na_3PO_4 \cdot 12H_2O$ at 25°C. This chemical



a) Commercial sample Na₂HPO₄, $v_r = 6$ kHz. b) ; $v_r = 7$ kHz. c) Na₂HPO₄ calcined in air at 300°C, $v_r = 6$ kHz. d) ;450°C, $v_r = 6$ kHz. Bars indicate isotropic peaks.

Figure 5.5. MAS-³¹P-NMR Spectra of Neat Disodium Phosphates

Sample	Chemical	Fraction	Principal Values of R				
Compound	Shift,ppm	of	Chemical Shift Tensor,				
		Signal,%	ppm				
	δ		σ_{11}	σ_{22}	σ_{33}		
Na ₂ HPO ₄ 25°	C						
Na ₂ HPO ₄	6.3±0.3		67±10	-19±11	-67±10	*	
$Na_2HPO_4_300$	<u>)°C</u>					-	
Unknown	10.8	1.3				*	
$Na_4P_2O_7$	1.9	98.7				*	
Na_2HPO_4 450	<u>)°C</u>						
Na_3PO_4 (?)	13.6	2.8				*	
Na ₄ P ₂ O ₇	2.2	97.2	84±10	-34±16	-57±9	*	
Na ₂ HPO ₄ Si/	'Al 100°C						
Na ₂ HPO ₄	6.5	89				*	
$Na_4P_2O_7$	1.3	11				*	
Na ₂ HPO ₄ _Si/	'Al 300°C						
Na ₄ P ₂ O ₇	2.9	100				*	
Na ₂ HPO ₄ Si/	Al 450°C						
Na ₄ P ₂ O ₇	2.3	91	78±5	-29±5 ·	-55±4	*	
Na ₄ P ₂ O ₇ •nH ₂ O	-2.0	9				*	
Literature	Values						
Disodium O	rthophosph	ates					
Na ₂ HPO ₄	6.6		48.9	5.7	-74.5	(67)	
Na ₂ HPO ₄	-16.6		69.8	35.5	-55.4	(68)	
•12H ₂ O				· · · · · · · · · · · · · · · · · · ·			
Trisodium	Orthophosp	hate	· · · · · · · · · · · · · · · · · · ·				
Na ₃ PO ₄	14.0					(64)	
Na ₃ PO ₄	13.0					(69)	
Na ₃ PO ₄	13.7					(66)	
Sodium Pyr	ophosphate	S					
$Na_4P_2O_7$	2.4		37	37	-80	(63)	
	1.2		37	37	-80	(63)	
$Na_4P_2O_7$	3.0		40	40	-89	(64)	
	2.2		40	40	-89	(64)	
$Na_4P_2O_7$	3.2					(66)	
	2.1					(66)	
Na ₄ P ₂ O ₇	2.7		46	33	-87	(68)	
	1.3		50	27	-81	(68)	
$Na_4P_2O_7$	-1.4					(64)	
•10H ₂ O	-2.3		38	38	-70	(64)	
$Na_4P_2O_7$	-1.7		49	32	-76	(68)	
•12H ₂ O	-2.0		58	26	-78	(68)	

Table 5.11. Chemical Shifts of Disodium Orthophosphates

* This work

shift agrees with literature results within 0.3 ppm (64,67).

By 300°C, complete dehydration has occurred, yielding anhydrous Na_3PO_4 , indicated by a single shift at 14.2 ppm. No further change is seen up to 450°C, with a single signal observed at 13.9 ppm. The anisotropy changes very little upon dehydration, as seen by the results in Table 5.12. Spectra of neat trisodium phosphates are presented in Figure 5.6.

5.3.1.5. Neat Sodium Pyrophosphate

Commercial samples of neat sodium pyrophosphate, Na₄P₂O₇, exhibit only one peak corresponding to anhydrous pyrophosphate at a chemical shift of 2.3 \pm 0.3 ppm. The same signal is observed at calcination temperatures of 25, 300 and 450°C. The spectra are shown in Figure 5.7. and the chemical shifts and anisotropies are presented in Table 5.13. Data quality, chemical shift anisotropy and comparisons with literature results are discussed in Section 5.3.2.4.

5.3.2. Supported Salts

5.3.2.1. Supported Monosodium Orthophosphate

Monosodium orthophosphate supported on silica alumina also undergoes changes in composition as the calcination temperature increases. At 100°C, two signals are present at



a) Commercial sample Na,PO, \cdot 12H,O, v, = 6 kHz. b) ;v, = 7 kHz. c) Na,PO, \cdot 12H,O calcined in air at 300°C, v, = 6 kHz. d) ;450°C, v, = 6 kHz. Bars indicate isotropic peaks.

Figure 5.6. MAS-³¹P-NMR Spectra of Neat Trisodium Phosphates

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Table 5.12. Chemical Shifts of Trisodium Orthophosphates

Sample	Chemical	Fraction	Principa	l Values	of	Ref.
Compound	Shift,ppm	of	Chemical	Shift Te	ensor,	
		Signal,%	ppm			
	δ		σ_{11}	σ ₂₂	_σ <u>33</u>	
<u>Na,PO₄ 25°C</u>						
Na ₃ PO ₄ •12H ₂ O	7.7±0.2	100	22±16	-8±22	-38±16	*
<u>Na₃PO₄ 300°C</u>						
Na ₃ PO ₄	14.2	100	12±21	-14±23	-40±21	*
<u>Na₃PO₄ 450°C</u>						
Na ₃ PO ₄	13.9	100	11±22	-14±23	-39±22	*
Na ₃ PO ₄ Si/Al	100°C					
Na ₃ PO ₄	13.6	84.7				*
$Na_3PO_4 \cdot 12H_2O$	8.2	11.3				*
Na ₅ P ₃ O ₁₀ -II	3.9	4.0				*
Na ₃ PO ₄ Si/Al	<u>300°C</u>					
Na ₃ PO ₄	14.0	96.8				*
Unknown	6.6	3.2				*
<u>Na₃PO₄ Si/Al</u>	<u>450°C</u>					
Na ₃ PO ₄	13.7	100	9±19	-14±21	-37±19	*
Literature	Values					
<u>Trisodium C</u>	rthophosph	ates				
Na ₃ PO ₄	14.0					(64)
Na ₃ PO ₄	13.0					(69)
Na ₃ PO ₄	13.7					(66)
$Na_3PO_4 \bullet 10H_2O$	7.7					(64)
$Na_3PO_4 \cdot 12H_2O$	7.8					(67)
Sodium Trip	hosphate					
Na ₅ P ₃ O ₁₀ -II	5.6 ^T					(61)
	-6.2					(61)
Na ₅ P ₃ O ₁₀ -II	4. 0 ^T		62	37	-113	(62)
	-5.7		118	-22	-79	(62)
$Na_5P_3O_{10}-II$	5.1 ^{T}		62	32	-109	(64)
	-5.6°		120	-24	-79	(64)
$Na_5P_3O_{10}-II$	4.6		69	24	-107	(68)
	-5.6		117	-20	-80	(68)
Na ₅ P ₃ O ₁₀ -II	4 .6 ^T					(70)
	-6.6°					(70)

*

This work Terminal phosphate unit Central phosphate unit Т С



a) Commercial sample Na,P,O., v, = 7 kHz. b) Na,P,O. calcined in air at 300°C, v, = 6 kHz. c) ;450°C, v, = 6 kHz. d) Na,P,O. on Si/Al calcined in air at 100°C, v, = 6 kHz. e) ;300°C, v, = 6 kHz. f) ;450°C, v, = 6 kHz. Bars indicate isotropic peaks.

Figure 5.7. MAS-³¹P-NMR Spectra of Sodium Pyrophosphates

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Table 5.13. Chemical Shifts of Sodium Pyrophosphates

Sample	Chemical Fraction		Princi	Ref.		
Compound	Shift,ppm	or Signal,%	Chemical	Snift Ten	sor,ppm	
	δ		σ_{11}	σ_{22}	σ_{33}	
$Na_4P_2O_7_25^{\circ}C_7$				·····		
Na ₄ P ₂ O ₇	2.6	100	84±12	-37±13	-55±10	*
$Na_4P_2O_7_300$	°C				_	
Na ₄ P ₂ O ₇	2.0	100				*
<u>Na₄P₂O₇ 450</u>	<u>°C</u>					
Na ₄ P ₂ O ₇	2.4	100	85±9	-38±12	-54±8	*
$Na_4P_2O_7$ Si/	<u>Al 100°C</u>					
$Na_4P_2O_7$	2.4	100				*
$Na_4P_2Q_7_Si/$	<u>Al 300°C</u>					
$Na_4P_2O_7$	2.2	100				*
$Na_4P_2Q_7$ Si/	<u>Al 450°C</u>					
$Na_4P_2O_7$	2.4	100	84±12	-35±16	-57±11	*
Literature	Values					
<u>Sodium Pyr</u>	ophosphate	<u>s</u>				
$Na_4P_2O_7$	2.4		37	37	-80	(63)
	1.2		37	37	-80	(63)
$Na_4P_2O_7$	3.0	х х	40	40	-89	(64)
	2.2		40	40	-89	(64)
$Na_4P_2O_7$	3.2					(66)
	2.1					(66)
$Na_4P_2O_7$	2.7		46	33	-87	(68)
	1.3		50	27	-81	(68)
Na ₄ P ₂ O ₇	-1.4					(64)
•10H ₂ O	-2.3		38	38	-70	(64)
Na ₄ P ₂ O ₇	-1.7		49	32	-76	(68)
•12H ₂ O	-2.0		58	26	-78	(68)
$Na_2H_2P_2O_7$	-13.0		80	24	-65	(68)

Na * This work 2.4 and -5.9 ppm, which are assigned to $NaH_2PO_4 \cdot H_2O$ and $Na_3P_3O_9$, respectively.

At 300°C, two peaks are observed at chemical shifts of -8.8 and -19.5 ppm. These are assigned to $Na_{s}P_{3}O_{1c}$ -I and $(NaPO_3)_n$, respectively. The principal values of the chemical shift tensor also agree within experimental error with both literature and experimental values except for σ_{13} for -19.5 ppm, which is slightly outside of experimental error, but still close. A third signal at about 17.2 ppm was indicated by TOSS analysis, but we were unable to confirm the peak by spinning speed variation due to sideband overlap by the other strongly anisotropic signals. No corresponding signals were observed in our experiments or in literature which suggest a possibility for the identity of this peak. The peak is located at an interval of one spinning frequency downfield from the signal at -19.5 ppm, suggesting the possibility that it is a lingering spinning sideband. In any case, the signal is weak and only contributes 12% to the total signal in the TOSS spectrum. ³¹P(¹H) decoupling experiments demonstrate that both signals at -8.8 and -19.5 ppm are unique signals.

One signal is observed at 450° C at a chemical shift of -5.8 ppm which is attributed to $Na_3P_3O_9$. This signal is very broad (FWHM 18 ppm), the spectrum is noisy and a large anisotropy contributes to large sidebands. These factors combine to make it difficult to determine whether there is

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only one signal or several signals in close proximity. The peakshapes suggest the latter. Spinning frequency variation and ³¹P(¹H) decoupling experiments show that if there is indeed more than one peak, they are within about 5 ppm of each other. The principal values of the chemical shift tensor are close to the literature values, but σ_{11} and σ_{22} are not within experimental error. The spectra for supported monosodium phosphate are presented in Figure 5.8. and the chemical shifts and tensors are shown in Table 5.9.

Supported monosodium phosphate converts to different phosphate species as the temperature rises. The percentage of the total 31 P signal that is assigned to each species is shown in Table 5.14. The reproducibility of the chemical shifts is ± 1.1 ppm at 300°C and 450°C. The peakwidth (FWHM) is typically 5.4 ppm at 100°C, 9 ppm at 300°C and 18 ppm at 450°C.

5.3.2.2. Supported Disodium Orthophosphate

When supported on silica alumina, disodium orthophosphate undergoes the same basic transformations as neat samples. The peakwidths (FWHM) for both neat and supported disodium phosphate are 2.1-3.5 ppm. At 100°C, two signals are seen at 6.5 and 1.3 ppm, which correspond to Na_2HPO_4 and $Na_4P_2O_7$, respectively. By 300°C, complete conversion to pyrophosphate has been achieved. At 450°C,

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a) NaH₂PO₄·H₂O on Si/Al calcined in air at 100°C, $v_1 = 6$ kHz. b) ;300°C, $v_1 = 4$ kHz. c) ;300°C, $v_2 = 6$ kHz. d) ;300°C, $v_2 = 7$ kHz. e) ;300°C, TOSS, $v_1 = 6$ kHz. f) ;300°C, without ³¹Pl¹H¹ decoupling, $v_2 = 6$ kHz. Bars indicate isotropic peaks.

Figure 5.8. MAS-³¹P-NMR Spectra of Supported Monosodium Phosphates



g) NaH,PO,•H,O on Si/Al calcined in air at 300°C, with ${}^{31}P{}^{1}H{}$ decoupling, v, = 6 kHz. h) ;450°C, v, = 6 kHz. i) ;450°C, v, = 7 kHz. j) ;450°C, without ${}^{31}P{}^{1}H{}$ decoupling, v, = 6 kHz. k) ;450°C, with ${}^{31}P{}^{1}H{}$ decoupling, v, = 6 kHz. Bars indicate isotropic peaks.

Figure 5.8. MAS-³¹P-NMR Spectra of Supported Monosodium Phosphates (Continued)

Phosphate Species	osphate Chemical ecies Shift, ppm		Percentage of ³¹ P Signal at Temperature T, %			
	δ	$T = 100^{\circ}C$	300°C	450°C		
NaH ₂ PO ₄ •H ₂ O	2.4	79				
Na ₅ P ₃ O ₁₀ -I	-8.8		44			
Na ₃ P ₃ O ₉	-5.9	21		100		
(NaPO ₃) _n	-19.5		56			

Table 5.14. Conversion of Supported Monosodium Phosphate with Calcination

anhydrous pyrophosphate is observed with a small impurity of hydrated pyrophosphate. Both hydrated pyrophosphates, $Na_4P_2O_7 \cdot 10H_2O$ and $Na_4P_2O_7 \cdot 12H_2O$, have shifts within 0.3 ppm of the observed signal and the peak was too small to measure the anisotropy, so it is impossible to distinguish which hydrated species is present. The spectra of supported disodium orthophosphates are presented in Figure 5.9. and the chemical shifts and anisotropies are tabulated in Table 5.11.

5.3.2.3. Supported Trisodium Orthophosphate

Spectra of Na_3PO_4 supported on silica alumina at 100°C reveal both hydrated and anhydrous trisodium phosphate as well as a small amount of sodium tripolyphosphate, $Na_5P_3O_{10}$ -II, with a shift of 3.9 ppm. Heating to 300°C results in complete dehydration of trisodium phosphate, as well as destruction of the triphosphate and the appearance of a



a) Na,HPO, on Si/Al calcined in air at 100°C, v, = 6 kHz. b) ;300°C, v, = 6 kHz. c) ;450°C, v, = 6 kHz. Bars indicate isotropic peaks.

Figure 5.9. MAS-³¹P-NMR Spectra of Supported Disodium Phosphates

small unknown at 6.6 ppm. Both triphosphate and the unknown contribute less than 4% to the total ³¹P signal. By 450°C, the only species observed is anhydrous trisodium phosphate. Each of the principal values of the chemical shift tensor for anhydrous Na_3PO_4 varied by less than 3 ppm between the neat and supported samples, which is well within the experimental error of 20 ppm. Reproducibility for trisodium phosphate spectra is \pm 0.2 ppm and peakwidths (FWHM) of signals are 4.0-6.6 ppm. NMR spectra of supported trisodium phosphate are presented in Figure 5.10. Chemical shifts and tensors are shown in Table 5.12.

5.3.2.4. Supported Sodium Pyrophosphate

Spectra of supported sodium pyrophosphate show pure pyrophosphate at calcination temperatures of 100, 300 and 450°C. This demonstrates the thermal stability of pyrophosphate. The chemical shift of pyrophosphate agrees with literature results within ± 0.4 ppm. The chemical shift anisotropy of the various samples agrees within ± 2 ppm and peakwidths (FWHM) are 2.0-3.0 ppm. The spectra of neat and supported pyrophosphates are presented in Figure 5.7. and the chemical shifts are tabulated in Table 5.13.

A significant difference between our results and those of literature is our observance of only one peak for pyrophosphate. Several researchers reported two distinct chemical shifts for pyrophosphate, with 0.8-1.4 ppm



a) $Na_3PO_4 \cdot H_2O$ on Si/Al calcined in air at 100°C, $v_r = 6$ kHz. b) ;300°C, $v_r = 6$ kHz. c) ;450°C, $v_r = 6$ kHz. Bars indicate isotropic peaks.

Figure 5.10. MAS-³¹P-NMR Spectra of Supported Trisodium Phosphates

difference between the two signals (63,64,66,68). Our results do not show two distinct peaks, but the lineshapes of many of the spectra suggest that there may be more than one peak. The difference between the two peaks is estimated to be 0.3-0.5 ppm, which is considerably smaller than that reported in literature.

As seen before with pyrophosphate formed from calcined disodium phosphate, the chemical shift anisotropies from our results are self-consistent with other samples containing pyrophosphate. But our results for pyrophosphate chemical shift tensors differ from literature results by typically 23 ppm for both σ_{11} and σ_{33} after accounting for experimental error. A possible explanation for this error is the existence of multiple peaks with almost identical chemical shifts but dissimilar anisotropies. This leads to the possibility that the observed sideband intensities arose from different anisotropies, depending upon which signal gave the largest sideband intensity at that particular sideband. This could lead to an error in the calculated anisotropy, since the method used to calculate the anisotropy assumes that all the spinning sidebands belong to the same signal with an identical anisotropy.

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5.4. Discussion

5.4.1. Thermal Transformations of Sodium Phosphate Salts

Calcium hydroxyapatite forms about 20% pyrophosphate upon heating to 800°C. Neat monosodium orthophosphate monohydrate converts to mostly linear polyphosphate and about 20% trimetaphosphate upon calcination at 450°C while supported monosodium orthophosphate forms exclusively trimetaphosphate under the same conditions. Both neat and supported disodium orthophosphate condense to form >98% pyrophosphate after calcination to only 300°C. Neat trisodium orthophosphate dodecahydrate undergoes a simple dehydration upon calcination to yield the anhydride. Supported trisodium orthophosphate also yields >96% anhydrous trisodium phosphate upon calcination at 300°C. Pyrophosphate appears to be one of the most thermally stable of the phosphates studied with only pure pyrophosphate observed after calcination at 450°C for both supported and neat salts. The transformations of phosphate salts upon calcination are outlined in Figure 5.11.

A review of the thermal transitions in the monosodium phosphate system was reported by Greenfield and Clift (58). Our results agree with theirs for the phosphate species formed upon calcination with the exception of one point. They report the formation of the ring trimetaphosphate, $Na_3P_3O_9$, as opposed to the linear tripolyphosphate, $Na_5P_3O_{10}$.

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<u>Calcium Hy</u>	<u>ydroxyapati</u>	<u>te</u> 100	٩٢		800°	c		
Ca ₁₀ (OH) ₂ (F Hydroxyapa	PO,), → atite	Ca ₁₀ (OH)) ₂ (PO ₄),	→	Ca ₁₀ (OH)	2(PO₄),	+ Ca Pyropl 21	₂ P ₂ O ₇ nosphate 1%
<u>Neat Monos</u>	sodium Phos	phate				450	٦°C	
NaH ₂ PO ₄ •H ₂ O Monosodiur Phosphate	→ (NaPO n Polyphosp 68%) _n + Na hate Trij	a,P,O ₁₀ -I polyphos <u>r</u> 19%	+ NaH phate 1	H_PO4•H_O T1 L3%	→ Na, rimetap 21	P _i O _a + hosphat %	(NaPO₄) _n ce 79%
Supported	Monosodium	Phospha	<u>te</u>					
$100^{\circ}C$ NaH ₂ PO ₄ •H ₂ O Monosodium	+ Na ₃ P n Trimetaph	.0. → osphate	300°C (NaPO) Polyphosp	,) _n + phate I	Na,P,O Tripolypi	₁₀ -I nosphat	→ N e	450°C Ia,P,O,
79%	21%		56%		448			
<u>Neat Disoc</u>	lium Phosph 300	<u>ate</u> °C			45	50°C		
Na ₂ HPO ₄ Disodium	→ Na ₄ Pyrophc	P ₂ O ₇ + sphate	Unknowr	n -	→ Na	4P207 +	- Na ₄ 1	P ₂ O ₇ •nH ₂ O
Phosphate	98.	78	1.3%		97.	.28	2	.88
<u>Supported</u> 100°C Na ₂ HPO ₄	Disodium P + Na_4P_2C	hosphate D ₁ →	300°C Na ₄ P ₂ (⊃ ₇	4 → Na	50°C 4,P207	+ Na	.₄P₂O ₇ •nH₂O
Disodium Phosphate	Pyrophosp	hate						
89%	118				9	918		98
<u>Neat Trisc</u>	dium Phosp	hate	-	200°C				450°C
Na,PO,•12H ₂ O Trisodium Phosphate)	→	N	a,PO4				Na ₃ PO₄
Supported	Trisodium	Phosphat	e	3	0.0.°C			450°C
Na,PO, + Trisodium	Na ₃ PO ₄ •12H ₂ C) + Na ₅) Tripol	P₃O₁₀-II yphosphat	→ N te	00°C Ia,PO₄ +	Unknov	wn →	430°C Na,PO₄
85%	11%		48	9)78	38		
Neat and Supported Pyrophosphate								
Na₄P₂O7 Pyrophosph	.ate		300° Na₄P	2C 207		→		450°C Na₄P₂O7

MAT. I

Figure 5.11. Thermal Transformations of Calcined Phosphate Salts
Chemical analysis was used in the study and the methods used included ion exchange, qualitative analysis using various reagents, colorimetry, solubility and gravimetric analysis. The work appears to be very thorough; there is no reason to believe that tripolyphosphate was misidentified as trimetaphosphate in the study.

Using NMR, we observed a signal which corresponded to one of the two signals reported in literature for tripolyphosphate, Na₅P₃O₁₀-II. This chemical shift matches that for the central phosphate unit. The peak for the terminal phosphate was never seen, although it should be the more intense of the two signals. This points to the conclusion that the central phosphate peak from tripolyphosphate has a chemical shift that is very close to that of trimetaphosphate, since the two phosphorus atoms are in similar environments between two phosphate units. Also, the stoichiometric product of condensation of three monosodium phosphate.

 $3 \text{ NaH}_2\text{PO}_4 \longrightarrow \text{Na}_3\text{P}_3\text{O}_2 + 3 \text{H}_2\text{O}_3$

Since we observe nearly pure product at 450°C for supported monosodium phosphate, it is not possible to form tripolyphosphate without abstracting the required excess sodium ions from another source, either on the support surface, or from another species. These considerations lead us to the conclusion that the observed signal at -5.8 ppm arises from trimetaphosphate rather than tripolyphosphate as we had first thought to be the case.

5.4.2. Effects of Catalyst Support on Thermal Transformations

Only in the case of monosodium phosphate does the support have a major effect on the phosphate species formed after calcination. Neat monosodium phosphate forms mostly polyphosphate while the supported salt forms only trimetaphosphate, $Na_3P_3O_9$.

The role of the support in which product is formed may be explained by several considerations. The support may isolate the phosphate ions, causing it to be more difficult for more than three phosphate units to come into close proximity in order to react. This may be caused by spreading out of the phosphate on the surface, resulting in a physical distance between the phosphate units. This may also be caused by the attraction of the phosphate ions around specific sites on the support surface. The latter explanation is very plausible since we know the support to possess acidic sites, which would conceivably be attractive to the basic phosphate ions. The acidic sites may also be combining with the phosphate ions during reaction, thus changing the mechanism and the product of the reaction. Another explanation may be the fact that the support places the phosphate units on a more or less two dimensional surface with respect to each other. This orientation may make the trimetaphosphate product more attractive either because of the reaction stereochemistry or simply because trimetaphosphate is more stable than polyphosphate on a flat surface.

5.4.3. Comparison of NMR and FTIR Results

Our results using FTIR to characterize phosphate catalysts indicate the formation of polyphosphate upon heating of monosodium phosphate above 250°C, in agreement with our NMR results in Section 6.3.2.1. FTIR spectroscopy demonstrated the conversion of disodium phosphate to tetrasodium pyrophosphate above 250°C, also in agreement with results obtained using NMR. The one difference between the two studies is the fact that FTIR indicated the formation of pyrophosphate from trisodium phosphate above 200°C, whereas NMR showed simple dehydration of the hydrated trisodium phosphate. This difference is explained by noting that the FTIR study was performed on a system in which lactic acid was deposited on the surface of the trisodium phosphate, in contrast to the NMR study in which phosphate was observed with no lactic acid present. The lactic acid abstracts sodium ions from the trisodium phosphate to form sodium lactate and disodium phosphate. The disodium

phosphate then condenses to form pyrophosphate in the FTIR study, while in the NMR study, the trisodium phosphate remains unconverted.

The findings of this study, when combined with results in the presence of lactic acid in the FTIR study, help explain some of the trends observed in the conversion of lactic acid over sodium phosphate catalysts. These trends are covered in detail in Section 6.4.

Chapter 6. Identification of Surface Species on Phosphate Salt Catalysts using Transmission FTIR

6.1. Introduction

In this study, IR-transparent disks were coated with sodium phosphate catalyst salts and then exposed to lactic acid vapors at 25-350°C. The treated disks were then cooled and Fourier Transform Infrared spectroscopy (FTIR) was used to determine the chemical species present on the disk. This study increases our knowledge of the species present on the surface of phosphate salt catalysts when treated with lactic acid at reaction temperatures. This leads to better understanding of why certain trends in conversion and selectivity are observed for actual reactions of lactic acid over phosphate salt catalysts.

6.2. Methods

6.2.1. Materials

6.2.1.1. Chemicals

The origin of materials used is discussed in Section 3.2.1.

6.2.1.2. IR Sample Disks

Silicon IR sample disks were obtained from Spectra Tech Incorporated with the dimensions of 9 mm diameter and 2 mm thickness. Silicon was chosen as the supporting material for these transmission FTIR studies because it is insoluble in water; is mechanically, chemically and thermally stable; and has a wide IR-transparent window from $8300-660 \text{ cm}^{-1}$ (91). Although silicon has considerable IR absorption below about 660 cm⁻¹, our experience shows useful results down to about 550 cm⁻¹. Brittleness is one drawback to use of silicon since the edges of silicon disks tend to chip easily.

6.2.2. Sample Preparation

After exposure to phosphate salts, small IR peaks corresponding to strong phosphate IR bands were observed on the silicon disks even after thorough cleaning with both water and acetone. This indicates that phosphates are impossible to completely remove from the silicon disk surface. For this reason, one sample disk was dedicated to use with samples which contained phosphate species. Another disk was dedicated to use with samples which contained only organics.

Aqueous solutions were prepared by diluting the solute to 3.74×10^{-6} mol/ml with water. To avoid impurities, HPLC grade water with less than 3 ppm evaporation residue was

used in all experiments. Care was taken to clean all glassware used in sample preparation very thoroughly of dust, lint and mineral deposits.

The silicon sample disk was placed in a metal clipstyle sample holder which secures the disk by the edges, leaving both surfaces open. 25 µl of aqueous solution was applied to each face of the silicon sample disk in volumetrically measured amounts using disposable 25 µl glass pipets.

Vacuum drying was used to remove water from sample disks. A disk held in a clip-style holder was placed in a glass vacuum desiccator. Air was evacuated from the desiccator using a rotary vacuum pump. The progress of water evaporation was timed and observed. When the moisture was gone, as determined by visual inspection, air was readmitted to the desiccator immediately and the sample removed. This process was then repeated for a second loading on both sides of the disk. If sample freezing was observed during drying, the sample was immediately exposed to air for a few seconds until the ice melted. The desiccator was evacuated again and drying was resumed. The time under vacuum required to dry a typical sample loaded with a total of 100 µl of solution was 10-13 minutes.

After vacuum drying, the sample disk was removed from the clip-style holder and transferred to a magnetic sample holder (Spectra Tech) which fits into the spectrometer. The

edges of the sample disk were sealed using Teflon tape so infrared light could not leak between the edges of the disk and the magnetic sample holder. The magnetic holder was pressed to fit tightly around the edges of the sample disk. The disk and holder assembly was then held up to the light and visually inspected to check for light "leakage" around the disk edges. The disk and holder assembly was then placed in a glass jar containing a small vial of desiccant to remove moisture while being transported to the spectrometer. Transfer of the sample disk from the vacuum desiccator to the jar was performed as fast as reasonably possible to minimize sample exposure to moist ambient air. The time required for this transfer was typically two to four minutes.

A method of trial and error was used to determine the amount and concentration of solutions required to obtain good results. Too little solute on the sample disk results in little absorption by the sample and obscures small spectral features. Excess solute results in "saturation" or too much absorption and causes peaks with distorted features and flat or rounded apexes (as opposed to pointed ones).

The volume of solution applied to the disk face is also important. Insufficient liquid volume results in incomplete coverage of the disk face while excess liquid results in spillage of liquid from the disk face during handling. A

solution volume of 25 µl was found to be ideal in our experiments.

Since we were required to load each disk twice, double the solute concentration should be used in future experiments to deposit a sufficient amount of solute in only one loading.

The use of heat to evaporate water from sample disks was attempted, but did not work well and was abandoned. Heat tended to "bake on" the phosphates, making them harder to remove from the disks. Heat also made organics evaporate too fast. When organics evaporated quickly along with the water, the reproducibility of amounts deposited during sample preparation was diminished.

6.2.3. Post-reaction Studies

6.2.3.1. Apparatus

An apparatus was designed to expose prepared sample disks to a flow of lactic acid vapor at temperatures of 100-350°C. A diagram of this apparatus is shown in Figure 6.1.

The apparatus consists of a 200 ml three-neck round bottom flask equipped with a thermometer in one neck which extends down into the flask and a dip tube in another neck for a helium carrier gas inlet. The third middle neck connects the flask to a 1.0 inch ID vertical column about 6 inches long with three nibs to support a coarse glass frit halfway up the column. The frit supports the silicon sample disk during runs. The column is connected to a 75°





distilling head with a quartz thermocouple sheath entering from the top and extending down to near the frit. The sidearm is connected to a Liebig condenser with a 105° vacuum adapter on the lower end. The adapter connects with a 250 ml Erlenmeyer flask. The whole apparatus is made of glass except for Teflon adapters with rubber O-ring seals for the thermometer, dip tube, and quartz thermocouple sheath.

The round bottom flask is heated on the bottom by a heating mantel, and by heating tape wrapped around the top and the three necks. Both the mantel and heat tape are controlled by an Omega PI controller connected to a control thermocouple inserted between the flask and the mantel. A thermometer measures the temperature inside the flask independently. The column and distilling head are heated by two heating tapes controlled by another Omega PI controller receiving feedback from the thermocouple near the glass frit inside the column. Use of two separate heating tapes allows the column and head to be disassembled for easy access to the sample.

The exterior plumbing allows helium carrier gas to flow either direction through the apparatus by turning two threeway valves. The effluent flows through a bubblemeter to allow flow measurement.

6.2.3.2. Procedure

The apparatus was prepared by first adding about 100 ml of 85% aqueous lactic acid solution to the round bottom flask, then driving off most of the water present in the solution. This involved heating the contents of the flask to about 140°C under a helium carrier gas flow of 500 ml/min. The column was heated to 160°C to prevent lactic acid condensation in the column. Holding these conditions for about one hour distilled off most of the water in the lactic acid solution.

After water removal, the column was preheated to the temperature at which the subsequent run was to be performed and the apparatus was allowed to come to steady state. At this point, a sample disk was prepared by vacuum drying as described in Section 6.2.2. When the sample disk was ready, the carrier gas flow was turned to the reverse direction (so that no lactic acid is carried through the column), the column heat was turned off and the column was cooled by a fan blowing ambient air across the column.

When the column temperature fell below 100°C, the distilling head was removed from the column, the sample disk was placed on the glass frit inside the column and the head was replaced as quickly as possible. This operation was performed with reverse helium carrier gas flow of about 500 ml/min. The column was then heated to the required temperature of the run. Upon equilibration at the proper

temperature, the carrier gas flow was turned to the forward direction to expose the disk to lactic acid and the timer was started. After exposure to the lactic acid vapor stream for 10 minutes, the carrier gas flow was reversed to avoid further exposure to lactic acid, the column was cooled to less than 100°C and the sample disk removed. The disk was then loaded into the magnetic sample holder and placed in the holding jar, as described in Section 6.2.2. The time required to cool the column from 350°C to less than 100°C is about 17 minutes. Less time is required for lower temperatures.

For samples at 25°C, sample preparation involved vacuum drying of an aqueous solution containing both the phosphate salt and lactic acid without vapor deposition of lactic acid in the heated column. In this respect, the preparation of samples at 25°C and those at all higher temperatures is different: Lactic acid was vacuum dried at 25°C, while it was vapor deposited at temperatures \geq 100°C.

6.2.4. FTIR Spectroscopy

6.2.4.1. IR Spectrometer

Fourier Transform Infrared spectra were collected on a Nicolet IR/42 spectrometer with a broadband helicoil globar source and a deuterated triglycine sulfate (DTGS) pyroelectric detector with a KBr window. The spectrometer used a Michelson interferometer with a KBr beamsplitter. The hardware was operated by Nicolet PC/IR Version 3.00 menudriven software run on a Dell System 200 personal computer. Spectra were collected in the mid-IR region of 400-4800 cm^{-1} with 32 scans and a resolution of 4 cm^{-1} .

6.2.4.2. Collection of Spectral Data

Before collecting data on the spectrometer, the computer was rebooted and the PC/IR program started anew. This set all parameters to their default values to ensure consistency between spectra. After purging the sample compartment with house nitrogen, a background spectrum was taken with no sample holder in the sample holder frame. The magnetic sample holder was then loaded with the clean silicon sample disk. The sample compartment was opened and the magnetic sample holder was inserted into the sample holder frame inside the spectrometer. The sample compartment was closed as soon as possible and purged, before taking a reference spectrum of the clean sample disk. Reference spectra were typically used for about five sample spectra before the baseline drift became large enough to require taking a new reference spectrum. After taking a reference spectrum, the sample disk was prepared with a sample and loaded into the magnetic sample holder, as described above, then placed in the spectrometer. A sample spectrum was taken after purging the sample compartment. The spectrometer sample compartment was purged by house nitrogen for at least

three minutes before collection of all background, reference and sample spectra to assure the absence of water peaks due to atmospheric moisture.

When a background, reference and sample spectrum were acquired, the reference spectrum was then subtracted from the sample spectrum and the baseline of the resulting spectrum was corrected using a third order method. In a few cases the baseline had extreme curvature or error. In most of these cases, the sample was either prepared again after taking a new reference spectrum, or in some cases the baseline was corrected using a fourth order method.

The sample, result and reference spectra were all annotated with information about their preparation and saved on microdisks. The spectra were plotted in two windows, a wide window of 400-4800 cm⁻¹ and a closeup of the fingerprint region of 600-1800 cm⁻¹.

6.2.4.3. Data Reproducibility

The reproducibility of both the sample preparation and spectroscopic techniques was confirmed by comparing repeated runs of samples. The frequencies of the major bands for all repeated runs agreed within the 4 cm⁻¹ resolution of the spectrometer. The ratios of the magnitudes of the major peaks agreed within \pm 23% in the worst case, but typically within \pm 10%.

6.3. Results

6.3.1. FTIR of Pure Substances

Some notable differences are observed between the spectra of lactic acid and sodium lactate. Lactic acid shows a very strong carbonyl stretching band [ν C=0] at 1728 cm⁻¹ which shifts to 1591 cm⁻¹ for sodium lactate. This shift shows a decrease in the calculated force constant from 12.2 N/cm for lactic acid to 10.3 N/cm for sodium lactate. This represents a 16% decrease in the C=O bond strength. Lactic acid has a strong combined stretching and bending band $[U_{AC}CO + \delta_{AC}OH]$ at 1221 cm⁻¹ which does not appear in the sodium lactate spectrum. A clearly defined set of six peaks appears at 1265, 1314, 1364, 1422, 1456, and 1473 cm^{-1} for the lactate salt. Some peaks in this "fingerprint" are present, but less defined, in the lactic acid spectrum. A moderate stretching band [uC-COOH] at 826 cm⁻¹ in the lactic acid spectrum shifts to 855 cm⁻¹ for sodium lactate. Table 6.1. shows an overview of the spectral features and band assignments of the lactic acid and sodium lactate spectra. Lactic acid and sodium lactate spectra are presented in Figure 6.2. All band assignments are based on the results of Cassanas, et al. (92).

Certain features are common to all sodium orthophosphates. Sodium orthophosphates have a strong $v_{as}PO_{3}$ band at 1020-1080 cm⁻¹ and a moderate $\delta_{as}PO_{3}$ band at





Lactic Acid	Sodium Lactate	Band Assignments
(cm ⁻¹)	(cm ⁻¹)	
3600-2300 vs,b	3600-2500 vs,b	H ₂ O
2992 s	2977 s	UCH
2946 s	2934 s	UCH
1728 vs	1591 vs	UC=O
1458 s	1473 m,sh	$\delta_{as}CH_3$
1458 s	1456 m	$\delta_{as}CH_3$
1420 m,sh	1422 s	$[U_{AC}CO + \delta_{AC}OH]$
1375 s	1390 m	$\delta_{AL}OH^{**}$
1375 s	1364 m	$\delta_{sy}CH_3$
1340 m	1314 m	δСН
1275 s,sh	1265 m	δ _{al} OH***
1221 s	-	$[U_{AC}CO + \delta_{AC}OH]$
1127 s	1123 s	δ _{al} co**
1090 m,sh	1088 m	δ _{al} co***
1046 s	1042 m	vC-CH ₃
924 w	925 w	rCH ₃
826 m	855 m	UC-COOH
745 w	779 w	δοςο
652 w	677 w	δС-СОН
530 w	530 w	UOCO
428 w	415 w	δ _{AC} CCO

Table 6.1. IR Frequencies and Band Assignments of Lactic Acid and Sodium Lactate

* based on results of Cassanas, et al. (92)
** intermolecular hydrogen bond
*** solvated
vs = very strong, s = strong, m = moderate, w = weak, b = broad,
sh = shoulder, AC = acid, AL = alcohol,
sy = symmetric, as = asymmetric, u = stretching, δ = bending,
r = rocking

 $470-570 \text{ cm}^{-1}$ (71). Two strong, broad water bands appear at 2000-3700 cm⁻¹ and 1600-1680 cm⁻¹. Our results agree within about 10 cm⁻¹ for the frequencies of the major peaks when compared to literature data (71,93). IR spectra and spectral features of sodium orthophosphates are presented in Figure 6.3. and Table 6.2.

Common features of condensed sodium phosphates are two strong, broad water bands at 2000-3700 cm⁻¹ and 1655-1670 cm⁻¹ and a moderate band at 485-550 cm⁻¹, presumably due to bending vibrations ($\delta_{as}PO_3$). Frequencies of the major peaks of sodium pyrophosphate ($Na_4P_2O_7$) and sodium tripolyphosphate ($Na_5P_3O_{10}$) agree with literature values within about 10 cm⁻¹ (93). Features of some condensed sodium phosphates are shown in Figure 6.4. and Table 6.3.

6.3.2. FTIR Post-reaction Studies

6.3.2.1. Monosodium Phosphate

Lactic acid was deposited on a sample disk loaded with monosodium phosphate (NaH_2PO_4) at temperatures of 25-350°C as described in Section 6.2. Figure 6.5. shows the spectral results of post-reaction studies on monosodium phosphate. Neither sodium lactate (vC=0 at 1590 cm⁻¹) nor phosphoric acid is observed, indicating no significant amount of proton exchange over the temperature range studied. A small, broad shoulder peak appears at 1593 cm⁻¹ but is attributed







Figure 6.4. IR Spectra of Condensed Sodium Phosphates

Phosphoric Acid	Monosodium Phosphate	Disodium Phosphate	Trisodium Phosphate
H ₃ PO ₄	NaH ₂ PO ₄	Na ₂ HPO ₄	Na ₃ PO ₄
(cm ⁻¹)	(cm ⁻¹)	(Cm^{-1})	(cm ⁻¹)
1169 s	1279 m	1080 s	1430-1460 m
1019 s	1165 s	990 m	1028 s
880 w	1049 s	843 w	936 w
803 w	947 s	650-696 w	839 w
702 w	858 m	534 m	708 w
4 71 m	801 w		569 m
	704 w		
	505 m		

Table 6.2. IR Frequencies of Sodium Orthophosphates

s = strong, m = moderate, w = weak

Table 6.3. IR Frequencies of Condensed Sodium Phosph
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Sodium Pyrophosphate	Trisodium Trimeta- phosphate	Sodium Tripoly- phosphate	Sodium Polyphosphate
Na ₄ P ₂ O ₇	Na ₃ P ₃ O ₉	Na ₅ P ₃ O ₁₀	(NaPO ₃)
(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)
1123 s [*]	1289 s	1227 s	1265 s
1024 w	1161 m	1142 s	1154 m
993 w	1100 s	1024 w	1092 s
980 w*	988 s	974 m	1019 s
915 s [*]	760 m	895 m	934 m
893 s ^{**}	687 w	745 w	876 s
710 w	640 w	702 w	779 w
650 w	517 m	548 m	706 w
552 m [*]			486 m

* most notable features, ** likely a water peak, s = strong, m = moderate, w = weak





to a broad water peak at about 1650 cm⁻¹ for monosodium phosphate.

Monosodium phosphate is present at and below 200°C, indicated by the observed bands 1280, 1165, 1057, 992, 874, and 706 cm⁻¹. Lactic acid leaves the surface before 150°C, indicated by the peaks 1744, 1458, 1408, 1377, 1219, 1132, 1096, 1049 and 837 cm⁻¹.

Sodium polyphosphate, $(NaPO_3)_n$, forms at 250-350°C, indicated by peaks at 1242-1273, 1165, 1092, 1046, 938, 856-885 and 706 cm⁻¹. These peaks become stronger and more well-defined as the temperature increases, which possibly indicates an increasing degree of condensation of the phosphate as the temperature increases.

6.3.2.2. Disodium Phosphate

Infrared spectra of post-reaction studies over disodium phosphate are presented in Figure 6.6. Lactic acid converts partly to sodium lactate at 25-100°C. The respective carbonyl bands appear at 1740 and 1609 cm⁻¹, indicating that both sodium lactate and lactic acid are present. Lactic acid peaks include 1740, 1456, 1414, 1372, 1219, 1134, 1090 and 1047 cm⁻¹. Peaks attributed to sodium lactate are 1609, 1456, 1414, 1372, 1134, 1090, 1047, 862 and 530 cm⁻¹. In the acid-base exchange, disodium phosphate is partly converted to monosodium phosphate. Observed disodium phosphate peaks include 988, 835 and 530 cm⁻¹



Transmittance



Figure 6.6. IR Spectra of Lactic Acid on Disodium Phosphate

while monosodium phosphate peaks include 1171, 1047, 943, 882 and 862 cm^{-1} .

Both lactic acid and sodium lactate leave the surface at 150°C and above, indicated by the disappearance of both carbonyl bands at 1740 and 1609 cm^{-1} .

All the phosphates convert to an unidentified species which we believe to be an intermediate to pyrophosphate formation at 150-200°C. This unidentified species has IR bands at 1395, 1358, 1142, 1057, 995-945, 858, 739, 608 and 542 cm⁻¹. These bands do not correspond to any orthophosphates or condensed phosphates which we studied. At 250°C, about 78% of the unknown phosphate has converted to sodium pyrophosphate ($Na_4P_2O_7$), and at 300-350°C, all unidentified phosphate has converted to pyrophosphate. Pyrophosphate IR bands observed were 1146, 1123, 1030, 988, 899, 733, 552 and 490 cm⁻¹.

6.3.2.3. Trisodium Phosphate

Spectra from post-reaction studies of lactic acid on trisodium phosphate are seen in Figure 6.7. These spectra reveal that lactic acid forms sodium lactate and that either lactic acid or sodium lactate is present at 25-350°C. At room temperature, lactic acid and trisodium phosphate undergo a virtually complete proton exchange to form sodium lactate and disodium phosphate. As the temperature increases, the percentage of sodium lactate changes on the





surface, as seen in Table 6.4. The IR bands due to sodium lactate are 1597, 1475, 1460, 1424, 1364, 1316, 1271, 1121, 1050, 853, 779 and 679 cm⁻¹. The disodium phosphate bands observed are 1090, 990, 845 and 650-696 cm⁻¹. As the temperature increases to 200-350°C, disodium phosphate condenses to sodium pyrophosphate, identified by the peaks at 1127, 1034, 1000, 988 and 934 cm⁻¹.

Lactate in Sodium Salt Form (%) Temperature (°C) 25 100 100 65 150 74 85 200 88 250 300 90 350 83

Table 6.4. Percentage of Sodium Lactate on Trisodium Phosphate

6.4. Discussion

6.4.1. Reactions on Catalyst Surfaces

The post-reaction studies show that the more basic is the phosphate salt loaded onto the surface, the more sodium lactate and lactic acid is retained on the surface, especially at elevated temperatures above 150°C. The overall reaction scheme pertaining to lactic acid-sodium phosphate proton exchanges and the subsequent phosphorus-to-phosphorus condensations is outlined in Figure 6.8.

Over Monosodium Phosphate

(gone ≥150°C) (no rxn.)Lactic Acid + NaH₂PO₄ → Sodium Lactate + H₃PO₄ (≥250°C) NaH₂PO₄ → (NaPO₃)_n

Over Disodium Phosphate

 $\begin{array}{cccc} (\texttt{gone } \ge 150^{\circ}\texttt{C}) & (<150^{\circ}\texttt{C}) \\ \texttt{Lactic Acid} & + & \texttt{Na}_2\texttt{HPO}_4 & \longrightarrow & \texttt{Sodium Lactate} & + & \texttt{NaH}_2\texttt{PO}_4 \\ & & (150-200^{\circ}\texttt{C}) & (\ge 250^{\circ}\texttt{C}) \\ \texttt{Na}_2\texttt{HPO}_4 & \longrightarrow & \texttt{Unidentified Phosphate} & \longrightarrow & \texttt{Na}_4\texttt{P}_2\texttt{O}_7 \end{array}$

Over Trisodium Phosphate

Lactic Acid + $Na_3PO_4 \longrightarrow$ Sodium Lactate + Na_2HPO_4 (>200°C) $Na_2HPO_4 \longrightarrow Na_4P_2O_7$

Figure 6.8. Proton Exchange and Condensation Reaction Schemes

6.4.2. Application of Findings to Results of Lactic Acid Conversion

The findings of this study may explain some of the trends observed in conversion of lactic acid over sodium orthophosphate catalysts. We observed that monosodium phosphate condenses to sodium polyphosphate at reaction conditions above 250°C, while both disodium and trisodium phosphates form sodium pyrophosphate above about 250°C. This explains why selectivities to products are similar for disodium and trisodium phosphate catalysts since the actual catalyst is the same.

To explain the increased conversion over trisodium phosphate when compared to disodium phosphate, we employ the following scenario. Excess sodium ions are present on the surface after condensation of trisodium phosphate to pyrophosphate. These ions are present either in the form of sodium lactate or in the form of sodium ions passivated on the surface. The sodium ions shift the equilibrium of lactic acid between the gas phase and the surface. This shift in equilibrium raises the concentration of both sodium lactate and lactic acid on the surface which increases the conversion.

In contrast, few excess sodium ions are left on the surface after condensation of disodium phosphate to pyrophosphate since there are stoichiometric amounts of sodium ions and phosphate ions present. The few sodium ions do not shift the equilibrium between the gas phase and the surface, resulting in lower lactic acid and sodium lactate concentrations on the surface and thus lower conversion.

6.4.3. Equilibrium of Proton Exchange

The equilibrium constants for the first proton exchange between lactic acid and the various phosphate species present at reaction conditions were calculated from acid

dissociation constants obtained from literature (84,86). The only consistent data available was for aqueous solutions at near room temperature, which makes application of these results to surface reactions at reaction conditions (280-350°C) only qualitative, at best.

The equilibrium constants for proton exchange between lactic acid and sodium polyphosphate and also between lactic acid and sodium pyrophosphate are 2×10^4 and 2×10^5 , respectively. The equilibrium for formation of sodium lactate is favorable in both cases, but is an order of magnitude greater for pyrophosphate than for polyphosphate. Since lactic acid is much more volatile than sodium lactate, the greater formation of sodium lactate over pyrophosphate indicates more sodium lactate would be present on the surface of a pyrophosphate catalyst. In other words, the pyrophosphate has a greater ability to "pull down" lactic acid onto the catalyst surface (in the form of sodium lactate) than does polyphosphate. This supports the results of our catalytic studies where higher conversion is observed over disodium phosphate, which forms pyrophosphate at reaction conditions, than over monosodium phosphate, which forms polyphosphate. We conclude that the equilibrium between the gas phase reactant, lactic acid, and the surface phosphate species affects the conversion by altering the concentration of the reactant on the surface.

Chapter 7. Summary and Recommendations

7.1. Summary

Catalytic conversion of lactic acid over zeolites in a batch reactor produced mostly acetaldehyde and ethanol at 30-42% selectivities as well as lesser amounts of propanoic acid, acetic acid and acrylic acid. Conversions based on lactic acid fed were 3.7-5.3% at 240°C.

Lactic acid conversion over supported and neat sodium phosphate catalysts was performed in a downflow differential packed bed reactor. Five major reaction pathways were observed: 1) decarboxylation to form acetaldehyde, CO_2 and H_2 , 2) decarbonylation to form acetaldehyde, CO and H_2O , 3) dehydration to form acrylic acid, 4) direct reduction to propanoic acid and 5) condensation to 2,3-pentanedione. Minor products included ethanol, acetic acid, acetone and acetol. The condensation of lactic acid to 2,3-pentanedione was first observed in our laboratory.

Production of acrylic acid was favored at high temperatures of 350°C and short residence times of 0.4 seconds, while 2,3-pentanedione formation is favored at 280°C and long residence times of 4.0 seconds. Increasing the contact time leads to an increase in decarbonylation to acetaldehyde. Decarboxylation is not strongly affected by contact time. Basic phosphate salts favor acrylic acid and 2,3-pentanedione, while more acidic salts produced greater

amounts of the undesired products propanoic acid, acetaldehyde, acetic acid, acetone and acetol.

A catalyst survey was performed to compare various supported sodium salt catalysts with different central atoms but with oxygen ligands similar to sodium phosphate. The sodium salts studied include tetraborate, carbonate, nitrate, silicate, phosphate, sulfate, chlorate, arsenate, bromate and molybdate. Catalyst salt acidity affects product distribution with basic salts producing higher selectivities to 2,3-pentanedione, relatively acidic salts producing more propanoic acid and moderately basic salts producing more acetaldehyde. Group V salts (nitrate, phosphate and arsenate) exhibit 2,3-pentanedione selectivities up to 64%. Conversion increased strongly with increasing level of occupied molecular orbitals in the central atom of the catalyst salt.

Chemical species present on supported sodium phosphate salt surfaces were determined using MAS-³¹P-NMR. Sodium phosphate salts undergo complex dehydration reactions upon heating to reaction temperatures, so a mixture of condensed sodium phosphate salts was present on the surface of the supported catalysts and was readily analyzed using NMR.

Adsorbed chemical species on catalyst salt surfaces were studied using transmission FTIR after exposure to lactic acid at reaction temperatures. The more basic sodium phosphate salts affect greater conversion by altering the

equilibrium between the gas phase reactants and the surface reactants. A greater surface concentration of lactic acid and sodium lactate is observed over the more basic salts leading to greater conversion and better product selectivity.

Using FTIR and NMR, we show that catalyst salt acidity changes the distribution of chemical species present on a model catalyst surface at reaction conditions. The size of electronic cloud of the central atom of the catalyst salt has a strong effect on the catalyst activity. These considerations were employed to propose reaction mechanisms to acrylic acid and 2,3-pentanedione which both involve the formation of cyclic transition states.

7.2. Recommendations

Our FTIR results suggested that excess sodium ions on a catalyst surface will increase the concentration of reactants on a catalyst surface and produce higher conversions in reactions over real catalysts. Studies may be performed to determine if the concentration of sodium ions on the surface of a catalyst may be manipulated. This may be achieved perhaps by addition of NaOH in increasing concentrations along with a constant phosphate catalyst concentration. From our observations in this work, one would expect this increase in concentration may be correlated with conversion and selectivity over a supported salt catalyst. One may also study supported sodium ions by themselves to determine their catalytic activity and selectivity.

In light of the fact that we know disodium and trisodium phosphate to form pyrophosphate upon heating to reaction conditions, another interesting study may be to synthesize a supported catalyst made of pyrophosphate to simulate condensed disodium phosphate. To simulate trisodium phosphate, equimolar amounts of pyrophosphate and NaOH may be used. A comparison of the performance of these two catalysts may prove an interesting comparison with disodium and trisodium phosphate catalysts.

The catalyst survey results indicate that increasing the number of occupied molecular orbitals in the central atom of the catalyst salt (alternatively, the "size" of the central atom) leads to an increase in the conversion over the salt. We also know Group V salts produce greater selectivities to desirable products. These observations lead to the suggestion that the salts of the "larger" Group V elements antimony and bismuth may prove interesting catalysts. Future studies may determine the catalytic properties of sodium pyroantimonate, Na₂H₂Sb₂O₇•6H₂O, or sodium metaantimonite, NaSbO₂•3H₂O, and sodium metabismuthate, NaBiO₁.

The possibilities of using NMR to make mechanistic determinations are great. Our use of NMR to determine the chemical species present on supported catalyst surfaces only

scratches the surface of the utility of NMR. NMR observation is not obscured by high temperature emissions as FTIR has a tendency to be, so NMR may be used to examine reactions insitu at reaction temperatures. NMR may by used to observe the mechanisms of the reactions by several different, but complimentary approaches. ¹H of the lactic acid reactant on a catalyst surface may be observed perhaps by using a D_2O solvent or by evaporation of H₃O before observation. ¹³C labeled positions of the lactic acid reactant may be observed on a catalyst surface. Lactic-1-13C acid, sodium salt, is available from Aldrich Chemical Company. The central atoms of many catalyst salts may be observed using NMR. The group V elements ¹⁴N, ³¹P, ⁷⁵As, ¹²¹Sb, ¹²³Sb and ²⁰⁹Bi all have substantial natural abundances and may be observed using NMR (84). The feasibility of getting good results using available equipment and methods is unknown, but the possibilities exist.

FTIR studies of reactions in-situ may provide information not available by post-reaction experiments in which the samples have been cooled prior to observation. Insitu reactions may be studied using an infrared transmittance cell in which gas phase reactants are passed over a thin IR-transparent catalyst disk which is observed using FTIR as the reaction proceeds. Several examples and designs for this type of reactor are presented in literature (73-81).
In-situ reactions may also be studied using Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFT). This method analyses infrared radiation reflected from a solid sample and does not require tedious sample or catalyst disk preparation, is not sensitive to sample thickness, may be used to examine non-transmitting samples, and may be used to observe samples in-situ. Spectra Tech markets a diffuse reflectance cell called the Collector which may be configured as an in-situ reactor cell with a temperature range up to 900°C and a pressure range from 10⁻⁵ Torr to 1500 psig (91). Examples of the applications of diffuse reflectance may be found in literature (82-83). APPENDICES

Appendix A Calculation of Macropore Size in Y Zeolites

Mercury porosimetry was performed on Y-82 and Y-62 zeolite samples using a Micromeritics Pore Sizer Model 9310. After mercury intrusion into the catalyst samples, pressure data as a function of intrusion volume was used by dedicated software to produce a plot of incremental pore volume per gram of catalyst as a function of pore diameter, as seen in Figures A.1. and A.2. Incremental pore volumes are tabulated in Tables A.1. and A.2.

The weighted mean pore diameter was calculated from the pore size distribution for each catalyst as follows:

$$\underline{d} = \frac{\sum_{i=1}^{n} w_i d_i}{\sum_{i=1}^{n} w_i}$$

where \underline{d} = weighted mean pore diameter w_i = weight of data point i d_i = pore diameter at data point i n = total number of data points in consideration

MICROMERITICS PORE SIZER 9310 V1.04 PAGE 6 Y-82 Zeolite 7/14/90 GCG 19:00 PENETROMETER NUMBER 161 INCREMENTAL PORE VOLUME PER GRAM % vs. PORE DIAMETER (micrometers) Maximum Incremental Volume = 0.0800 cc/g 201 60I 701 50Z 80Z 0Z 10I 30Z 40Z 90Z 1001 300 -- 300 - 235 - 183 - 183 - 112 - 87.7 - 58.6 - 32.8 - 25.7 - 20.1 - 12.3 - 9.59 - 7.50 - 3.59 - 2.81 - 2.17 - 1.23 - 2.17 - 1.34 235 -1111111 183 -11111111 87.7 -111111111111111 87.7 - 1111111 68.6 - 2111111 53.6 - 111 42.0 - 11 32.8 - 1 25.7 - 11 20.1 - 11 15.7 - 1 12.3 - 1 9 - 9 - 1 9.59 -1 7.50 -11 5.87 -11 4.59 -11 3.59 -111 2.81 -111 2.19 -111 SILE 1.72 -111 1.72 -111 1.34 -111 1.05 -111 0.820 -111 0.642 -111 0.502 -1111 0.392 -1111 0.307 -11111 (um) - 1.05 - 0.820 - 0.642 - 0.502 - 0.372 - 0.307 0.240 -1111111 . 0.188 - 0.147 0.147 - EXERCITE EXECUTE EXECU - 0.115 0.0897 0.0549 - 0.0429 - 0.0336 - 0.9262 - 0.0205 - 0.0160 0.00991 -1111 0.00767 -11111 - 0.0093 - 0.00757 9.00600 -11111111111 0.00600 ...! ſ.... 07 102 201 101 461 50Z 60I 70L 801 907 100I

Figure A.1. Pore Size Distribution in Y-82 Zeolite

203

-62 ZG GCG PENETRI	eolit DMETE	e R NUM	BER	161		v	1.04					PAGS 6 7/14/90 23:40
		INCRE	MENTA Ma	L PORE ximum	VOLUM Increm	E PER ental	GRAM % Volume	∨s. =	PORE D 0.0946	IAMETER cc/g	(micr	romet ers)
		01 [192	201	301	40Z	501 	601	701	801 	90Z	1001
SIZE (um)	300 233 183 143 112 87.7 88.6 53.6 42.0 32.7 20.1 15.7 12.5 7 20.1 15.7 12.5 7 5.87 4.59 7.50 5.87 4.59 7.50 5.87 4.59 7.50 5.87 4.59 0.52 0.52 0.327 0.329 0.329 0.329 0.329 0.307 0.307 0.202 0.0202 0.0242 0.0202 0.0202 0.0242 0.0202 0.00202 0.0002 0.0002 0.0002 0.00000000		8 8888 8888 8988 8988 8988 8988 8988 8									- 300 - 235 - 183 - 143 - 112 - 87.7 - 58.5 - 53.6 - 42.0 - 32.8 - 25.7 - 20.1 - 15.7 - 12.3 - 9.59 - 7.50 - 5.87 - 4.59 - 2.81 - 2.19 - 1.72 - 1.34 - 1.05 - 0.820 - 0.442 - 0.502 - 0.392 - 0.392 - 0.397 - 0.240 - 0.9429 - 0.
		01	IOI	20:	302	497	507	505	701	301	901	1007

Figure A.2. Pore Size Distribution in Y-62 Zeolite

204

MICROMERITICS PORE SIZER 9310

i	d _i (µm)	Wi	w _i d _i (μm)
1	0.188	0.76	0.143
2	0.147	0.93	0.137
3	0.115	0.93	0.107
4	0.0897	0.58	0.0520
5	0.0702	0.31	0.0218
Σ		3.51	0.4608

Table A.1. Incremental Pore Volumes Greater than 20% for Y-82 Zeolite

 $d = 0.4608/3.51 = 0.131 \ \mu m = 1310 \ \text{\AA}$

Table A.2. Incremental Pore Volumes Greater than 10% for Y-62 Zeolite

i	d _i (μm)	w _i	w _i d _i (μm)
1	0.392	0.11	0.0431
2	0.307	0.38	0.1167
3	0.240	0.76	0.1824
4	0.188	0.96	0.1805
5	0.147	0.68	0.1000
6	0.115	0.35	0.0403
7	0.0897	0.25	0.0224
8	0.0702	0.15	0.0105
Σ		3.64	0.6959

 $d = 0.6959/3.64 = 0.191 \ \mu m = 1910 \ \text{\AA}$

Appendix B Calculation of Chemical Shift Anisotropy from Spinning Sideband Intensities

Using Herzfeld and Berger method (88).

Calculate ratios of the intensities of each of the nth order sidebands to the isotropic peak intensity, I_n/I_0 . Using the graphs in the paper by Herzfeld and Berger, plot the contour of each of the intensity ratios. Find the point where the contours intersect and note the values for μ and ρ . Using μ and ρ , solve for the principal values of the chemical shift tensor, σ_{11} , σ_{22} and σ_{33} , as detailed below.

Calculation of Magnetic Field Strength, H_a

$$\begin{array}{l} H_{o} = h \upsilon / g_{I} \mu_{N} \\ H_{o} = \frac{(6.62618 \times 10^{-34} \text{ Js}) (161.903 \times 10^{6} \text{ s}^{-1}) (10^{7} \text{ erg}/\text{J})}{(2.261) (5.0505 \times 10^{-24} \text{ erg}/\text{G}) (10^{4} \text{ G/T})} \\ H_{o} = 9.395 \text{ T} \end{array}$$

Calculation of Principal Values of the Chemical Shift Tensor $\mu = \gamma H_{o}(\sigma_{33} - \sigma_{11}) / 2\pi \omega_{r}$ $(\sigma_{33} - \sigma_{11}) = 2\pi \omega_{r} \mu / \gamma H_{o} = a$ $-\sigma_{11} + 0\sigma_{22} + \sigma_{33} = a \quad (eqn. 1)$ $\rho = (\sigma_{11} + \sigma_{33} - 2\sigma_{22}) / (\sigma_{33} - \sigma_{11}) = (\sigma_{11} + \sigma_{33} - 2\sigma_{22}) / a$ $\sigma_{11} - 2\sigma_{22} + \sigma_{33} = a\rho = b \quad (eqn. 2)$ $-\delta = \sigma_{i} = (\sigma_{11} + \sigma_{22} + \sigma_{33}) / 3$ $\sigma_{11} + \sigma_{22} + \sigma_{33} = -3\delta = c \quad (eqn. 3)$ 3 Equations and 3 Unknowns $-\sigma_{11} + 0\sigma_{22} + \sigma_{33} = a$ $\sigma_{11} - 2\sigma_{22} + \sigma_{33} = b$ $\sigma_{11} + \sigma_{22} + \sigma_{33} = c$ Solve for σ_{11} , σ_{22} and σ_{33} $\begin{bmatrix} -1 & 0 & 1 \\ 1 & -2 & 1 \\ 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \end{bmatrix} = \begin{bmatrix} a \\ b \\ c \end{bmatrix}$ $\underline{\mathbf{A}} \qquad \underline{\boldsymbol{\sigma}} \qquad \underline{\mathbf{a}} \qquad \underline{\mathbf{b}} \qquad \\ \mathbf{\sigma} = \underline{\mathbf{A}}^{-1} \ \underline{\mathbf{b}}$ where $\begin{array}{l} H_{o} = \text{ magnetic field strength, T} \\ h = \text{ Planck constant} = 6.62618 \times 10^{-34} \text{ Js} \\ v = \text{ observe frequency} = 161.903 \text{ MHz} \\ g_{1} = \text{ nuclear g-value} = 2.261 \text{ for } ^{31}\text{ P}, \text{ (ref. 84)} \\ \mu_{N} = \text{ nuclear magneton} = 5.0505 \times 10^{-24} \text{ erg/G} \\ \gamma = \text{ magnetogyric ratio} = 10.8394 \times 10^{7} \text{ rad/sT} \\ \sigma_{i} = \text{ isotropic chemical shift} \\ \sigma_{nn} = \text{ principal values of chemical shift tensor} \\ \omega_{r} = \text{ sample spinning frequency, Hz} \end{array}$

$$\underline{\mathbf{A}}^{-1} = \begin{bmatrix} -1/2 & 1/6 & 1/3 \\ 0 & -1/3 & 1/3 \\ 1/2 & 1/6 & 1/3 \end{bmatrix}$$

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