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PHYSICAL AND CATALYTIC PROPERTIES OF HYDROXY-METAL INTERLAYERED SMECTITE MINERALS

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Ph.D. degree in Chemistry

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PHYSICAL AND CATALYTIC PROPERTIES

OF HYDROXY-METAL INTERLAYERED

SMECTITE MINERALS

Ву

Steven Douglas Landau

A DISSERTATION

Submitted to

Michigan State University

in partial fulfillment of the requirements

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ABSTRACT

PHYSICAL AND CATALYTIC PROPERTIES OF HYDROXY-METAL INTERLAYERED SMECTITE MINERALS

Ву

Steven Douglas Landau

Recent advances in the intercalation of robust polyoxocations into smectite clay minerals has led to the formation of pillared clay catalysts^{1,2}. The interlayer cations are converted to metal-oxide props or "pillars" which then impart high thermal stability, a large N_2 BET surface area, and Bronsted acidity. The pillared clays typically exhibit pore sizes comparable to faujasitic zeolites.

This dissertation will describe the synthesis of a new pillared clay interlayered with hydroxy-chromium polymers³. This new chromium clay is distinguished by a 27 Å lattice expansion, as well as by excellent high temperature stability and novel catalytic activity.

These new chromium interlayered clays possess both hydrogen transfer activity and a weak Bronsted acidity. Cyclohexane dehydrogenation has been used as a model reaction for naphtha reforming whereas dealkylation of β -isopropylnaphthalene has been used to probe Bronsted acidity. The results for the chromia pillared clay will be compared to those for a commercial Cr(III)/Al₂O₃ dehydrogenation catalyst.

Aluminum pillared clay, the subject of several

studies^{4,5}, will also be discussed. Two types of polyoxoaluminum solutions, base-hydrolyzed AlCl₃ and aluminum chlorhydrate (ACH) with OH/Al ratios of 2.00-2.42, and 2.50, respectively, have been used as reagents for the pillaring of Laponite-RD[®], montmorillonite, and fluorohectorite clays. The physical properties of the intercalate depend to a greater degree upon the washing and drying condition than the pillaring solution employed.

The difference in apparent pore size openings and their dependence on drying conditions (air-drying vs. freezedrying) can be explained by use of a clay flocculation model⁵ in which both lamellar (face-face) and delaminated (edge-face, edge-edge) associations of the layers can occur.

 β -isopropylnaphthalene dealkylation⁵ has been used to probe Bronsted acidity and further illustrate the effects of air-drying and freeze-drying upon montmorillonite. Gasoil cracking⁶ was employed to elucidate pore structure facets of laponite, a delaminated catalyst, which were not obtainable from the dealkylation reactions.

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To My Family

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CHAPTER I

INTRODUCTION

Introduction

The production of commercial chemicals involves extensive use of homogeneous and heterogeneous catalysts. Heterogeneous catalysts were used for almost 60% of production capacity in 1983^1 , estimated to be 499 x 10^9 lbs². Zeolites, by far the largest volume commercial catalysts were employed at a rate of 7.5 x 10^6 metric tons per day as cracking catalysts in 1978^3 .

In 1960⁴, zeolites were shown to possess good isomerization ability. The high acidity and regular pore structure of the zeolite family of catalysts enhanced gasoline production over that obtained with amorphous catalysts by increasing selectivity to gasoline along with lower gas and coke yields.

Although a large number of zeolites have been synthesized, only the Faujasitic X and Y types as well as the other zeolites listed in Table 1 have found wide-spread use⁵. Faujasite type zeolites have the largest pores, corresponding to 7.5 Å. Modern cracking catalysts comprise between



Table 1. Physical Properties of Some Commercially Important Zeolites.

Type	Unit Cell Composition	Oxygen Ring	Type of Porosity	Window Opening
x	Na ₈₆ (AlO ₂) 86 (SiO ₂) 106	12	Supercages	7.5 Å
Х	Na ₅₆ (AlO ₂) ₅₆ (SiO ₂) ₁₃₆	12	Supercages	7.5 Å
ZSM-5	Na ₃ (AlO ₂) ₃ (SiO ₂) ₉₀	10	Pores	5.5 Å
Mordenite	Na _{8.7} (AlO ₂)8.7(SiO ₂)39.3	12	Pores	6.7 Å x 7.0 Å
A	Na_{12} (AlO_2) $_{12}$ (SiO_2) $_{12}$	8	Cages	4.2 Å
Erionite	Na ₉ (AlO ₂) ₉ (SiO ₂) ₂₇	8	Pores	3.6 Å x 5.2 Å

10 to 40% of rare earth exchanged HY zeolite dispersed in a matrix of silica-alumina and natural or synthetic $clay^3$.

The framework structure of zeolites is composed of AlO₄ and SiO₄ networks fused together in a high surface area, three dimensional array linked by bridging oxygens as shown in Figure 1 for faujasite. Isomorphic substitution of silicon by aluminum imparts upon the zeolite a net negative charge which is compensated for by exchangeable cations that reside in the cavities formed from linked tetrahedra. A generalized representation of the molecular formula of a zeolite may be written as follows:

$M_{n/2}$ 0.Al₂O₃·xSiO₂·yH₂O

where M is the compensating cation with valence n. As the aluminum content of the crystal lattice increases, the cation exchange capacity, water sorption, and hexane cracking activity all increase in a linear fashion⁶. This is represented in Figure 2 for the zeolite ZSM-5.

Acid sites, especially of the Bronsted type which are necessary for most hydrocarbon conversions, may be generated in a zeolite by two different approaches. Exchange of the naturally occurring sodium or calcium counter ion with a more polarizing one (higher q/r) will increase acidity. Replacement of the native counter ion with ammonium, followed by calcination will generate a delocalized proton⁷ according to Scheme 1. Maximum Bronsted acidity is attained in the 400°C to 550°C range. Above 550°C, Lewis acidity is generated due to the loss of a water molecule









Figure 2. Dependence of the Physical Properties of H-ZSM-5 Upon Aluminum Content⁶.

Scheme 1.



(dehydroxylation) and the formation of tricoordinate aluminum, as shown in Scheme 2.

Scheme 2.





Through the selective substitution of a variety of exchange cations, molecular sieve type compounds may be generated. As early as 1932 it was known that the molecular volume of the sorbate had an influence upon the amount which could be absorbed by the zeolite⁸. Molecular sieving was first demonstrated in a series of papers and patents in the early $1940s^{9-11}$. Eventually zeolites were classified into five distinct types based upon sieving characteristics, as shown in Table 2^{12} .

The sharp delineations in pore size and channel volumes shown in the table were recognized as a very desirable feature for applications of zeolites as Bronsted acid type heterogeneous catalysts. In 1960, Weisz, et al.¹³ published one of the first examples of shape-selective catalysis. Table 2. Classification of Some Molecular Sieves.

•

	He, Ne, Ar, CO H2, O2, N2, NH3, H2O	Kr,Xe CH4 C2H6 C4,OH	C3H8 <i>n</i> -C4H10 <i>n</i> -C7H16	C2F6 CF2Cl2	SF ₆ iso-C4H10 iso-C5H12	(CH ₃) ₃ N (C ₂ H ₅) ₃ N C(CH ₃) ₄	C ₆ H ₆ C ₆ H ₅ CH ₃ C ₆ H ₄ (CH ₃) ₂	Naphthalene Quinoline, 6-decyl-1, 2, 3 4-tetra-	l, 3, 5-triethyl benzene	$(n-C_3\Gamma_0)\Lambda$
	Size limit for Ca- and Ba- mordenites and	CHJCH	n-C ₁₄ H ₃₀ etc. C ₂ H ₅ Cl	CF ₃ CI CHFCI ₂	iso-C ₈ H ₁₈ etc. CHCl ₃	C(CH ₃) ₃ Cl C(CH ₃) ₃ Br C(CH ₃) ₃ OH	Cyclopentane Cyclohexane Thiophen	b, true hydro- naphthalene, 2-butyl-1-	1, 2, 3, 4, 5, 6, 7, 8, 13, 14, 15, 16-decahydro-	
pe 5	here $(\approx 3.8\text{Å})$	CCH CO CS CS Hz	C2H3BF C2H3OH C2H3NH2 CH3Cl2		CHBIJ CHIJ (CHJ)2CHOI (CHJ)2CHCI	CBra CBra H C2F2Cl4	ruran Pyridine Dioxane B ₁₀ H ₁₄	C6F11CF3	ciii ysciic	
	Size limit mordenite sieve 4A ₂ (≈4·0Å)	for Na- and Linde about here	CHF2CI CHF5CI CH5) CH3)2NF	-	<i>n</i> -CyF ₈ <i>n</i> -C4F ₁₀ <i>n</i> -C7F ₁₆ B ₅ H ₉					
		Size limit chabazite, 5A, Ba-i gmelinite (≈4·9Å)	B2H6 for Ca-ric Linde siev zeolite an about hei	ti o di o						A. 447
							Size limit for sieve 10X abou	Linde ut here		
								Size limi sieve 13) (≈ 10Å)	t for Linde Cabout here	

Their work made use of metal exchanged aluminosilicates and the conversion of decane to lower molecular weight olefins and paraffins. The first example of shape-selective catalysis with synthetic crystalline aluminosilicates was demonstrated in 1962 by Weisz and co-workers¹⁴ utilizing Ca A and Ca X (with 4.2 and 7.5 Å pores) for the dehydration of primary and branched alcohols. These results are represented in Figure 3. More sophisticated examples involve the alkylation of toluene to near quantitative yields of para-xylene¹⁵, and methanol dehydration to gasoline¹⁶ in one step.

Shape selectivity can be manifested in several ways¹⁷. Reactant selectivity is observed when reactants within a specific size range have access to the active site because of molecular sieving effects. Product selectivity occurs when only certain products generated within the pores have the correct molecular dimension to diffuse out of the openings leading to the cavities. Restricted transition state selectivity occurs when certain reactions are excluded because the transition state necessary is unattainable due to steric limitations.

Qualitative recognition of any of the selectivity properties mentioned above can be conveniently measured through the use of the constraint index¹⁸. The constraint index approximates the relative cracking rate constant for two hydrocarbons, hexane, and 3-methylpentane: Constraint Index = $\frac{\log_{10}(\text{Fraction of n-hexane remaining})}{\log_{10}(\text{Fraction of 3-Methylpentane remaining})}$



Figure 3. Shape Selective Dehydration of $n-C_4OH$ and $i-C_4OH$ Utilizing Ca A (4.2 Å) vs. the Non-Shape Selective Reaction Utilizing Ca X (7.5 Å).

A shape selective catalyst has a constraint index (C.I.) greater than unity. While the constraint index may have some value, it has been criticized¹⁹ since the test reaction involves the simultaneous diffusion of two reactants into the catalyst structure. Elaborate models²⁰ have been formulated to describe the diffusional characteristics for ZSM-5 in the constraint index reaction.

Regardless of the precise mechanism of diffusion within these intracrystalline environments, the high acidity, large surface area and molecular sieving properties of zeolites make them well suited to perform as heterogeneous catalysts. Their only major disadvantage resides in their rather small largest pore opening, that being 7.5 Å found in faujasitic type X and Y zeolites.

Smectite clay minerals may be used effectively as molecular sieves and catalysts due to their ability to exchange cations and to swell in the appropriate polar solvent. The relationship of various clay minerals is depicted in Figure 4, along with a classification scheme presented in Table 3²¹ and unit cell data in Table 4.

The structure of montmorillonite and other related smectite minerals is shown in Figure 5. The smectite family is comprised of silicate sheets containing four sheets of oxygen atoms²². A center layer of octahedral holes is sandwiched between two layers of tetrahedral holes. The octahedral layer generally contains metal ions suitable for octahedral coordination, i.e. Al³⁺ or Fe³⁺ and Mg²⁺. The tetrahedral layer usually contains Si⁴⁺. The upper



Figure 4. Clay Mineral Classification.

silicate layer has its vertices pointing downward, and the lower sheet has its vertices pointing upward. These three sheets are combined so that the tips of the tetrahedrons of each silica layer and the hydroxyl oxygens of the octahedral layer form a common layer. When Al^{3+} occupies two out of three octahedral positions, the mineral such as montmorillonite is classified as a dioctahedral mineral. When all three octahedral positions are occupied with Mg²⁺, as in saponite, the mineral is said to be trioctahedral.

Type	Charge per Formula Unit	Group	Subgroup		Species
1:1	0	Kaolinite	Dioctahedral Trioctahedral	Kaolinites Serpentines	Kaolinite Chrysotile
2:1	0	Pyrophyllite- talc	Dioctahedral Trioctahedral	Pyrophyllites Talcs	Pyrophyllite Talc
	0.25-0.6	Smectite or Montmorillonite- Saponite	Dioctahedral	Smectites or Montmorillonite	Montmorillonite Beidellite Nontronite
			Trioctahedral	Smectites or Saponites	Saponite, Hectorite Sauconite
	0.6-0.9	Vermiculite	Dioctahedral	Vermiculites	Dioctahedral Vermiculite
			Trioctahedral	Vermiculite	Trioctahedral Vermiculite
	1.0	Mica	Dioctahedral	Micas	Muscovite
			Trioctahedral	Micas	Phlogopite
	2.0	Brittle Mica	Dioctahedral	Brittle Micas	Mangarite
			Trioctahedral	Brittle Micas	Clintonite

Partial Classification Scheme for Phyllosilicates. Table 3. -

Mineral Group	Dioctahedral	Trioctahedral
Pyrophyllite - Talc	Pyrophyllite [Al _{4.0}](Si _{8.0})0 ₂₀ (OH) ₄	Talc [Mg _{6.0}](Si _{8.0}) ₂₀ (OH) ₄
Smectites	Montmorillonite M ⁿ⁺ .YH ₂ O[A1 _{4.0-x}]	Hectorite M ⁿ⁺ .YH ₂ O[Mg _{6.0-x} Li _x]
	(Si _{8.0})0 ₂₀ (OH) ₄ Beidellite	(Si _{8.0})O ₂₀ (OH,F) ₄ Saponite
	$M_{x/n}^{h+} \cdot Y_{H_2}^{h_2} o[a_{1_4}, 0^{1_6}]$ (51).	. M ⁿ⁺ .YH ₂ 0[Mg _{6.0}] (Si. 2 Al)0.2 (OH).
	Nontronite	8.0-X X. 70, 4
	M ⁿ⁺ .yH ₂ O[Fe _{4.0}] (51 _{8.0-x} Al _x)O ₂₀ (OH) ₄	
Micas	Muscovite	Phylogopite
	K2[A14.0 []] (Si6.0 ^{A1} 2.0 ⁾ O20(OH)4	K ₂ [Mg _{6.0}](Si _{6.0} Àl _{2.0}) O ₂₀ (OH) ₄





Figure 5. Representative Structures of Some Related 2:1 Layered Silicates.
Existing between each layer are exchangeable cations. The number of exchangeable cations existing between each layer establishes the Cation-Exchange-Capacity (CEC) of the mineral. The CEC can be measured by saturating a sodium exchanged clay with ammonium or barium ions, and determining the quantity of ammonium or barium incorporated at pH 7.

These exchangeable cations serve to balance the net negative charge distribution for a smectite silicate sheet. The charge distribution for pyrophyllite is as follows:

yielding the theoretical formula $Na_x(OH)_4Si_8(Al_4)O_{20}\cdot nH_2O$ with an average distribution of 66.7% SiO_2 , 28.3% Al_2O_3 and 5% H_2O . As can be seen from the charge distribution, no charge deficiency exists. Isomorphic substitution of Al^{3+} by Mg^{2+} or Fe³⁺ in the octahedral layer will produce a net negative charge in that layer. It is this negative charge that attracts and holds interlayer cations giving rise to the structural integrity of a 2:1 layered silicate. Substitutions within the lattices are also common in the tetrahedral layer where aluminum easily replaces silicon.

This substitution effect accounts for approximately

80% of the observable CEC. Broken bonds within the structure account for approximately 20% of the observable CEC. The contribution of the hydroxyl groups to the CEC is minimal since these groups do not possess exchangeable protons.

With pyrophyllite or talc, where aluminum and magnesium respectively occupy the octahedral layer, there is no net negative charge upon the silicate sheets. These two clays have no intercalation properties.

Smectite clays are characterized by a well ordered structure, exchangeable cations, and an expandable (OOL) interlayer spacing through the use of the appropriate polar solvent. These properties make smectites suitable for the intercalation of molecular props (pillars) between the layered sheets. Pillared clays can act as molecular sieves by limiting the size of the molecule accessible to the interlayer. To make these pillars catalytically active, we can heterogenize previously homogeneous catalysts in the smectite interlayer.

There are advantages to heterogenizing a homogeneous catalyst, among them: (1) easy recovery of the catalyst from the reaction medium; (2) sometimes increased stability to high temperatures and hydrolysis; (3) no solubility limitations and (4) inducement of shape selectivity.

Pinnavaia, et al.²³ have shown that heterogenized dirhodium acetate complexes are useful for alkene and alkyne hydrogenations with total quenching of the isomerization of 1-hexene to 2-hexene. This isomerization accounts for 35%

of the products in the homogeneous systems. Chang and Pinnavaia²⁴, and Farzaneh and Pinnavaia²⁴ have shown that asymmetric hydrogenations and hydroformylation reactions can be carried out on smectite silicates with equivalent or enhanced activity as compared with homogeneous catalysts.

Thomas, et al. 25 have shown that refluxing 1-hexene, 1-heptene, and 1-octene in a hexane solution with a cation exchanged smectite converted these alkenes to their corresponding bis-sec-alkyl ethers. The exchanged cations were Cu²⁺, Fe²⁺, Fe³⁺, Cr³⁺, and Al³⁺. Intercalation of the cation is necessary for reaction, along with a swelled interlayer.

The importance of this synthetic route is apparent when compared to the standard Williamson synthesis of ethers. In the Williamson synthesis

 $R'-X + Na-OR \longrightarrow R'-OR + Nax$

primary alkyl halides work best, whereas secondary and tertiary halides yield the elimination product as well as the substitution product. The synthetic route of Thomas, et al. does not have this rearrangement problem; it allows for the easy production of such ethers as 1-hexyl-2-propyl ether and di-2-hexyl ether.

These examples illustrate that smectite silicates have been recognized as useful supports. In order to utilize these interlayered smectites in industrial processes, high temperature stability must be achieved to allow the catalyst to withstand regeneration procedures. There have been

several successful attempts to construct a swelling resistent, cross-linked smectite which could serve as a backbone for catalysis or act as a molecular sieve.

Barrer and Macleod²⁶; and Barrer and Reay²⁷ in the 1950s replaced the charge balancing cations of montmorillonite with the tetraalkylammonium cations $N(CH_3)_4^+$ and $N(C_2H_5)_4^+$. These pillaring reactions increased the intracrystalline porosity and yielded basal spacings of 13.5 Å and 13.9 Å for the tetramethyl and tetraethyl ammonium intercalates, respectively, as compared with 9.6 Å for a Na⁺-montmorillonite.

At 70 K and 90 K it was shown that the order of sorption for some gases was $O_2 > N_2 > Ar$. At room temperature pentanes were sorbed in the following sequence, $n-C_5H_{12} > iso-C_5H_{12} > neo-C_5H_{12}$. This sorption was in the inverse order of cross-sectional molecular diameter.

Clementz and Mortland²⁸ similarly showed that tetraalkyl ammonium cations can be intercalated into reduced charge montmorillonite. Charge reduction is achieved by exchange with lithium cations before intercalation of the tetraalkyl ammonium cations, with internal surface areas as high as 200 m^2/g being reported.

Several tris-metal chelates have been intercalated into layered silicates, including Cu^{2+} and Fe^{2+} 1,10phenanthroline²⁹; Fe^{2+} , Cu^{2+} and Ru^{2+} tris-bipyridyl³⁰; Co^{3+} and Cr^{3+} tris ethylenediamine³¹; and others³². Intercalation was shown to occur by two methods: (1) cation exchange up to the mineral CEC and (2) intersalation of

excess salt beyond the mineral CEC. Ion exchange proceeds through electrostatic interactions, while intersalation depends on the anion present. Intersalation tends to be favored by the anion's ability to ion pair $(SO_4^{2-} > Br^- > Cl^-)$; and the ability of the M(Chelate)₃ⁿ⁺ to shield the anion from the electrostatic charge of the silicate sheet. Structural stability to 250°C is attainable for some of these tris-chelates. Basal spacings of 18 Å were obtained through CEC-type exchange, and spacings of 29 Å were reported for the intersalation product.

Silica³³ has been intercalated in smectites by two different mechanisms: (1) hydrolysis of Si(acac)₃⁺ exchanged smectite, or by (2) the <u>in situ</u> reaction of SiCl₄ and H(acac) to yield Si(acac)₃⁺, followed by hydrolysis of this product. These two methods yield basal spacings of 12.6 Å, with surface areas from 40 to 240 m²/g and temperature stability to 620°C. This system may have industrial importance for selective adsorption and as a catalyst support.

The protonated dication of 1,4-diazabicyclo(2,2,2,) octane, also known as DABCO^{34,35}, can be intercalated into smectites yielding 14.8 Å basal spacings.

This pillar introduced Bronsted acidity to the interlayer, structural stability to 220°C and shape selectivity caused by an effective interlayer spacing of 5.3 Å and a calculated interpillar distance of 6 Å. These two effects are illustrated in Table 5.

Carboxyile Aci	.us ~	
Acid	H-Montmorillonite	DABCO-M
сн ₃ (сн ₂) ₂ соон	1.65	1.00
(Сн ₃) ₂ Сн соон	1.49	0.48
сн ₃ (сн ₂) 3 соон	2.01	1.24
(CH ₃) ₂ CH CH ₂ COOH	1.95	0.67

Table 5. Relative Rates of Esterification of C₄ and C₅ Carboxylic Acids*

* reacted with n-butanol T = 190°C. LHSV = 6.0 hr^{-1}

As can be seen by the data in Table 5, DABCO-M has greater shape selective properties. As the kinetic diameter increases (normal <u>vs</u>. branched) the relative conversion rate decreases by a greater percentage for DABCO than for montmorillonite. This can be attributed to a rigid pore size for DABCO as opposed to the variable interlayer of a free-swelling smectite.

Several inorganic supports have been synthesized which confer Bronsted acidity and shape selectivity to the smectite interlayer. These pillars can be generated by hydrolysis of a metal chloride solution over a range of OH:M ratios^{36a-e}. The extent of cation oligomerization is controlled through selected experimental conditions (pH, age, and temperature). The mixing of hydrolyzed metal ion solutions with a suspension of fully dispersed sodium exchanged smectite leads to insertion of the polyoxy cation between the negatively charged silicate sheets. The flocculated product is then washed and air dried or freeze dried, followed by calcination which is believed to transform the metal complex into a metal oxide with a smaller hydration sphere^{36d}.

An Al-PILC system has received considerable attention; it is characterized by a d(OOL) basal spacing of over 18 Å at room temperature, and at 600°C the basal spacing is 36a,b,c,d .

The Al pillared species has been probed by ${}^{27}\text{Al-NMR}^{37}$ and appears to be a polyoxy aluminum cation of the family $[\text{Al}_{13}\text{O}_4(\text{OH})_{24-x}\text{H}_2\text{O}_{12}]^{(7-x)+}$ where x = 4. The structure³⁸ (Figure 6) has one central aluminum atom tetrahedrally coordinated to four oxygen atoms, with three aluminum octahedra attached edge on to each vertice of the central aluminum tetrahedron. This ion is consistent with an observed interlayer spacing of approximately 9 Å. Surface areas range as high as 500 m²/g with average pore sizes in the 20 Å range. The mechanism of crosslinking to the silicate sheet has not been fully elucidated. It appears that the first stage of attachment is mainly an electrostatic one.

A plausible mechanism for the observed Bronsted acidity can be related to the degree of hydration of the complex. Mortland and Raman³⁹ showed that the pK of hydrated exchangeable cations decreases with dehydration. As the water content of the metal complex decreases (as caused by calcination), the polarization forces arising from the metal centers become more concentrated on the remaining

water molecules. This causes an increase in hydrolysis, with an increase in proton donating abilities.

Several catalytic systems which proceed through Bronsted acidity have been investigated. Large molecule cracking^{40,41}, esterifications²⁵, and catalytic cracking of gas-oil^{42,43} were the most illustrative reactions employed. It was shown that for a pillared or a delaminated clay, the gas-oil cracking selectivity more nearly resembles a commercial zeolite promoted FCC catalyst than an amorphous aluminosilicate catalyst. In addition, the delaminated clay yields greater amounts of light cycle gas oil (b.p. 221-343°C) and lower amounts of slurry oil (b.p. 343-426°C) than the zeolite based catalyst.

Brindley and Yamanaka⁴⁴ have synthesized a chromium hydroxide montmorillonite which possessed a 17 Å lattice expansion at 200°C. Tzou⁴⁵ recently reported the synthesis of a chromium interlayered clay which was characterized by a 27 Å lattice expansion at room temperature, excellent thermal stability and novel catalytic activity⁴⁶.

Generally there are two distinct methods for the synthesis of an intercalate. The first method involves the modification of an intercalated metal complex to form a hydroxy-metal polymer. The second method involves the exchange of a previously synthesized hydroxy-metal polymer into the layered silicate.

Method one is illustrated in Scheme 3 for the series of reactions utilized to synthesize silica pillared clay³³. Materials generated in this fashion generally contain

Scheme 3.

$$Si(acac)_{3}^{+} + Na^{+} \longrightarrow Si(acac)_{3}^{+} + Na^{+}$$
 (1)

$$\underline{\text{Si}(\text{acac})_{3}^{+}} + \underline{\text{H}}_{2}^{0} \longrightarrow \underline{\text{Si}(\text{OH})}_{4} + \underline{\text{H}}^{+} + \underline{\text{3}}(\text{CH}_{3}^{\text{CO}})_{2}^{2} \underline{\text{CH}}_{2}$$
(2)

monolayer metal-hydroxide polymers. Eventually brucite or chlorite-like structures fill the clay interlayer. This method leads to low surface area materials which are not desirable due to the restricted interlayer.

Method two, direct exchange, is the method of choice for producing well-ordered, high surface area pillared smectites. Cationic hydroxy-metal polymers may be synthesized by the base hydrolysis of almost any desired metal. If the size of the polyoxo-polymer can be regulated, the lattice expansion of the clay can be varied accordingly. As the charge density upon a metal increases, the polarization forces exerted upon the coordination sphere of solvent increases. In aqueous solution, the positive charge upon the metal will cause the loss of a water proton. Upon the addition of base, solu**x**ble polymeric species of high molecular weight will form. This is represented in Scheme 4:

Scheme 4.

$$[M(H_2^{O})_{x-1}^{OH}] \xrightarrow{(y-1)^+} \underbrace{\longrightarrow}_{k=1}^{I} \begin{bmatrix} H_2^{O} \\ H_2^{O} \end{bmatrix} M \underbrace{\longrightarrow}_{H}^{H} M(H_2^{O})_{x-1} \end{bmatrix} \underbrace{\bigoplus}_{k=1}^{Y+1} \begin{bmatrix} H_1^{O} \\ H_2^{O} \\ H_1^{O} \end{bmatrix} M \underbrace{\longrightarrow}_{H}^{I} M \underbrace{\longrightarrow}_{H}^{I$$

This mechanism, termed olation, yields condensation polymers that appear as hydrous gels which are generally more than 99 volume percent water. If the hydrated metal is allowed to react with hydroxide at elevated temperature, or at an artificially adjusted pH, the hydroxy bridged polynuclear species may undergo oxolation reactions as depicted in Scheme 5.

Scheme 5.



As the degree of aggregation increases, high molecular weight polymers will result. If the solution is allowed to age long enough, colloidal particles will result, with eventual precipitation of a metal-hydroxy polymer. A scheme for metal ion hydrolysis aggregation is presented in Figure 7.

Through the appropriate choice of pH, temperature, and aging, the size of the polyoxocation grown may be controlled. In this manner, the synthesis of intercalated clay catalysts with pore openings larger than 7.5 Å may be undertaken.





Objectives of Dissertation Research

A variety of cations have been shown to permanently expand smectite-type layered silicates. The physicochemical properties of clay pillared by polyoxocations are poorly characterized and understood. In general, certain properties of smectite clays are typically overlooked in pillared clay chemistry. The layer charge and partical size are quite heterogeneous. This charge heterogeneity influences the interaction of pillaring species upon the clay surface. It might also serve to promote cluster rearrangement or degradation once the pillaring species is in close approach to the silicate layers. Since the properties of a heterogeneous catalyst are intimately related to its synthesis history, the effects of various washing, drying, and calcination methods are of interest. The history of the hydrolysis reaction itself upon cluster synthesis is also of paramount importance.

In this dissertation, these questions will be addressed by probing the physical and catalytic properties of smectite clay minerals pillared and delaminated by polyoxocations of chromium and aluminum.

CHAPTER II

EXPERIMENTAL METHODS

Clay Preparation

The clay minerals Laponite- $RD^{\textcircled{B}}$ (Laporte Ind. England) and fluorohectorite (Corning Glass, USA) were used as supplied from the manufacturer.

Montmorillonite (Source Clay Minerals Repository) contains impurities which must be removed in order to simplify and standardize the evaluation of clay catalysts. Soluable salts and carbonates are removed from the clay in order to promote flocculation of the clay. Calcium carbonate may act as a cementing agent preventing intercalation of the desired metal oxide species. It may also interfere with CEC determination due to the equilibrium represented in Scheme 6.

Scheme 6.

$$CaCO_3 \longrightarrow Ca^{2+} + CO_3^{2-}$$

The addition of sodium acetate (NaAC), buffered to pH=5 with acetic acid allows for the removal of carbon dioxide upon digestion at 70°C according to Scheme 7. The

Scheme 7.

 $Caco_{3(s)} + 2H^{+} \longrightarrow Ca^{2+} + H_{\Delta}O_{(l)} + CO_{2(g)}$

following procedure, based on a 5 g sample of clay mineral, was employed for the removal of soluable salts and carbonates:

- Add 50 ml of 1 N sodium acetate buffered with NaAC and bring the clay into suspension.
- (2) Digest this suspension for 1 hour at 70°C with occasional stirring.
- (3) Centrifuge the solution, discard the supernatant.
- (4) Repeat the above three steps.

Free (non-lattice) iron oxides which can also cement the clay are removed by treatment with a sodium citrate/ sodium bicarbonate solution and subsequent low temperature (80°C) treatment with sodium thiosulfate.

- (1) Add 40 ml of 0.3 N Na-citrate and 5 ml of 1 N NaHCO₃. The citrate (C.H.0.7) chelates with ferric iron and prevents precipitation of FeS. The bicarbonate maintains neutrality and furnishes hydroxide ion when hydrolyzed.
- (2) Warm the suspension to 75-80°C and slowly add l g of Na.5₂O₄. Do not exceed 80°C or FeS may precipitate. Digest for 15 minutes. This reagent effects reduction of ferric ions to ferrous ions which can then be washed away:

net: 4 $\text{OH}^- + \text{S}_2\text{O}_4^{2-} + 2\text{Fe}^{3+} \rightarrow 2\text{Fe}^{2+} + 2\text{SO}_3^{2-} + 2\text{H}_2\text{O}$

(3) The resulting solution is then cooled and concentrated by centrifugation. The supernatant is discarded.

Hydrogen peroxide is then employed to digest organic matter present in the clay. At this stage the clay is sodium saturated by the addition of sodium chloride. The flocculated particles are then collected, washed until free of chloride ion (as tested with silver nitrate) and air dried.

Pillaring/Delamination Reaction

Two types of polyoxo-aluminum cation solutions were utilized for the aluminum interlayered clay work. One type of solution was a freshly hydrolyzed aluminum trichloride hexahydrate solution which contained between 0.0 and 2.50 mol of hydroxide per mol of aluminum. The other type of solution was the commercially available Chlorhydrol[®] solution (Reheis Chemical Company) of aluminum chlorohydrate, freshly diluted with water to a concentration of 0.23 M. The amount of solution used in the exchange reaction was varied so that the ratio of mmol Al³⁺ to milliequivalents of clay (Q), varied from 0.0 (no Al³⁺ present) to approximately 85. The pillaring solution utilized for the synthesis of chromium interlayered clay was a chromium nitrate solution freshly hydrolyzed with anhydrous sodium carbonate. This hydrolysis mixture was aged at 95°C for 36 hours prior to exchange with clay. The exchange reaction consisted of aqueous suspensions of clay (1 wt. %) slowly added at room temperature to the vigorously stirred pillaring solution. Aluminum reaction mixtures were allowed to age for two hours at room temperature, chromium reaction mixtures for 1.5 hours. The clay intercalates

were then washed free of excess electrolyte with deionized water. Final products were either air- or freeze-dried. Catalysts were dehydroxylated at 350°C in helium for two hours. Use of this procedure enabled clays to be stored indefinately in air without loss of catalytic activity.

X-Ray Powder Diffraction (XRD) Measurements

A Philips or Siemens X-Ray diffractometer with nickel filtered Cu K_a radiation ($\lambda_{\alpha} = 1.5405$ Å) was used to measure basal spacings. For air-dried samples, 1 ml of freshly prepared pillared clay was spread across a 1 inch by 1 inch glass slide and allowed to dry. These slides were then heated to specified temperatures for 2 hours in inert gas. Freeze-dried samples were heated for 2 hours in inert gas at specified temperatures, then slides were prepared before XRD measurements were made. The Bragg angle 20 peak positions were converted to d-spacings by use of a standard Cu K_a radiation d-spacings 20 chart.

Chemical Analysis

Elemental analysis of Al clay samples were carried out at the inorganic laboratory of the Department of Toxicology, Michigan State University, with a Jarrell-Ash 955 Atom-Comp instrument. J.T. Baker instra-analyzed grade standards were used for the analysis of Si, Al, Fe, Mg, Na, and Ca. NBS plastic clay 98a served as a clay standard. Clay samples were prepared for analysis in my laboratory in the following fashion. All clay samples (0.05 g) were fused with lithium borate (0.3 g Gold Label, Aldrich) for 12 minutes

at 1000°C in preignited graphite fusion crucibles. The resultant glass was transferred to 30 ml of 3% HNO₃. This solution was mixed for 10 minutes, or until complete dissolution of the glass was assured, then diluted to 100 ml with deionized water. Galbraith Analytical Laboratory, Inc. analyzed chromium clays for Cr and Si from which unit cell compositions were derived based on the assumption that the Si content of the clay remained constant throughout the pillaring reaction. Carbon analysis on spent catalysts was performed by Galbraith Analytical Laboratory.

BET Surface Area Measurements

Surface area measurements were determined on a Perkin-Elmer-Shell model 212B sorptometer at liquid nitrogen temperature with nitrogen as the adsorbate and helium as the carrier. Nitrogen adsorption capacities were obtained for three partial pressures at -196°C. Approximately 100 mg of sample was used for each measurement. All samples were degassed for 2 hours at 350°C under flowing helium prior to nitrogen adsorption.

Adsorption Uptake Isotherms

The adsorption of organic molecules of various kinetic diameters was measured on a McBain balance equipped with quartz glass springs and buckets. The samples were activated at 350°C under dynamic vacuum for 2 hours prior to measurement. The probe molecules employed were benzene, 1,3,5-triethylbenzene and perfluorotributylamine (PFTBA) whose kinetic diameters are 5.8, 9.2, and 10.2 Å,

respectively. The probe molecules were stirred and equilibrated in a constant temperature bath maintained at 20±1°C, approximately 5°C below room temperature, to insure that capillary condensation did not take place within the sample and yield artificially high readings.

ESR Measurements

ESR spectra were obtained using X-band radiation with a Varian E-4 spectrometer. All spectra recorded at room temperature were obtained at 2000 G field set, and a 4000 G field sweep, as well as a 3600 G field set and a 4000 G field sweep with a 6.3 G modulation amplitude. Diphenylpicyrl hydrazine (DPPH) was used as a reference. Clay samples were subjected to two temperature treatments: (1) They were purged at 350°C for 2 hours in helium as well as (2) heated for 1 hour in helium, 1 hour in hydrogen, and then sealed under helium. The first treatment was part of the standard synthesis procedure. The second temperature treatment represented catalytic pretreatment conditions.

<u>Catalysis</u>

Vertically mounted, fixed bed continuous flow microreactors constructed of 7 mm I.D. quartz tubing were operated in the integral mode. The reactors contained up to 1.5 g of catalyst which was diluted with α -alumina (Norton Chemicals) to yield bed heights of 3 to 7 cm.

The reactors were encased in a tube furnace powered by a three stage temperature controller (Eurotherm, model 919A) fitted with a chromel-alumel thermocouple. Reactant

was introduced with a syringe pump (Sage Instruments, model 341A) at the top of the reactor to a preheater zone. Helium, used as a vector gas, was purified with BASF R3-11 catalyst followed by 4 \mathring{A} molecular sieves. The helium flow rate was controlled through a two-stage regulator followed by a tri-flat flow meter.

All catalysts used in β -isopropylnaphthalene (Alfa Inorganics, 99+%) dealkylations were pretreated at 480°C for 1 hour in purified helium. Dealkylation products were analyzed after they were trapped out of the effluent by an ice bath, and then diluted with approximately 25 ml of benzene. The samples were manually injected onto a 5 foot $\frac{1}{4}$ inch stainless steel column composed of 3% SE-30 supported on diatomite, operated at 160°C. Peak integrations were obtained on a Sargent SR recorder and analyzed with a compensating polar planimeter.

Cyclohexane dehydrogenation catalysts were pretreated at 550°C for 1 hour in helium to remove adsorbed water. This was followed by an additional hydrogen pretreatment (1 hr. 1 atm pressure) which reduced the chromium to the catalytically active +2 oxidation state. Spectrophotometric grade cyclohexane (Fisher) was used as the reagent, products were trapped at the base of the reactor in a liquid nitrogen trap, allowed to warm to room temperature and manually injected onto a 6 foot ½ inch stainless steel column of 10% OV-17 on Chromosorb W. Integrations were obtained with a Disc integrator (model 204) equipped recorder.

CHAPTER III

CHROMIUM INTERLAYERED CLAY CATALYSTS

Introduction

The growth of an oxometal species suitable for intercalation is limited only by the desired metal's hydrolysis chemistry. The properties of the resulting clay intercalate are intimately related to the hydrolysis chemistry and synthesis history of the oxometal species. Table 6 lists the $d_{(OOl)}$ -spacings and surface areas associated with pillared clays. Some metals, such as chromium (III)

Table	6.	Physical	Properties	of	Various	Oxometal	Pillared
		Clays					

 		^d (00l)	Å (a)	Surface Area	
Metal	Ref	25°C	500°C	M ² /g, 500°C	
Ni	47	14.8	12.1		
Zr	48	18.8	16.5	280	
Bi	49	16.6	9.6	35	

(a) d_(OOl) spacings after being heated to the temperature indicated

show extensive hydrolysis chemistry which is highly dependent upon reaction conditions. Brindley and Yamanaka⁵⁰ have produced a chromium interlayered clay characterized by a 16.8 Å spacing and a 250 m²/g surface area at 25°C. The pillaring cluster was generated from a OH/Cr mole ratio solution of 2.00 using sodium hydroxide as a source of base. This pillaring solution was allowed to age for ten days, was mixed with montmorillonite and then allowed to age three additional days. The 16.8 Å spacing is greater than would be expected for a chlorite type structure (14.2 Å). This clay product exhibited low thermal stability in air and collapsed to 9.8 Å at 400°C.

Tzou and Pinnavaia⁵¹ recently synthesized a chromium pillared clay product at a OH/Cr ratio similar to the value used by Brindley for the 16.8 Å clay, but more severe cluster growth conditions were employed. The chromium solution (OH/Cr=2.00) was aged for 36 hours at 95°C. Solid anhydrous sodium carbonate served as the source of base. After high temperature aging, a clay suspension was added according to the procedure outlined in Chapter II. This method produced an expanded intercalate with a 27.6 Å spacing and a 350 m^2/g BET surface area. Results for these two Cr-clay intercalates are presented in Table 7. It is apparent from these results that the hydrolysis of chromium is very sensitive to the experimental conditions utilized to generate the high molecular weight oxocations. Indeed, the hydrolysis chemistry of chromium is very dependent upon the method of base addition.

In 1908, Bjerrum⁵² postulated the existence of the

Clay	mmol Cr ^{3+ (a} MEQ Clay	a) OH/ CR	25°C	(001) <u>Å</u> 350°C	(b) 550°C	SA m ² /g(500)	wt. % Cr in product
I (Brindley)	7.3	2.0	16.8	14.2	13.7	15	13.88
II (Tzou)	62.5	2.0	27.6	23.1	19.6	350	18.44
(a) Ratio of (Cr ³⁺ to clay	used	in react	ion, (b)	Heated	under argon.	

Table 7. Physical Properties of Chromium Pillared Clays.

 $Cr_6(OH)_{12}^{6+}$ and $Cr_{12}(OH)_{30}^{6+}$ ions. He later⁵³ undertook a study of sodium hydroxide hydrolyzed chromium nitrate at 75°C. Products isolated contained OH/Cr ratios of one and two, probably representing the $Cr_2(OH)_2^{4+}$ and $Cr_6(OH)_{12}^{6+}$ ions, respectively. Precipitated crystalline Cr₂O₃ • xH₂O was also observed. This study also showed that equilibrium was generally attained in approximately 110 hours at reflux temperatures. Laswick and Plane⁵⁴ studied chromic perchlorate solutions generated without addition of base under reflux conditions. They showed that the rate of olation is extremely slow under these conditions. The dimeric complex $[Cr_2(H_2O)_4(OH)_2]^{4+}$, attained a maximum concentration within minutes of reaction, which accounted for 11% of the total chromium present. Approximately 74% of the chromium ions remain as unreacted $Cr(H_2O)_6^{3+}$, even after 27 days. The addition of sodium hydroxide at an OH/Cr ratio=1.00 produced an undetermined colloidal polymer after only three hours of reaction that accounted for 13% of the Thirty-eight percent of this base available chromium. hydrolyzed solution remained as the hexaquochromium (III)

species. Several other chromium species, such as a $[Cr_2(H_2O)OH]^{S+} dimer^{55}$ and $[Cr_3O(CH_3CO_2)_6(H_2O)_3]^+ trimer^{56}$ have recently been isolated.

These results suggest that the method used to form chromium polymers (i.e. temperature, pH, and aging conditions) will have a pronounced effect upon the structure of the polyoxochromium intercalated clays. This section concerns itself with the generation of several chromium intercalated clays; including those produced by Brindley's and Tzou's procedure and their characterization with respect to their physical and catalytical properties.

Synthesis of Pillars and Intercalation Procedures

Three distinct types of chromium interlayered clays were used in this study. Those of Brindley (I) and Tzou (II) are summarized in Table 7. Synthesis of high surface area, large pore pillared interlayered clays (PILC) is best achieved by method II, that of Tzou and Pinnavaia.

Tzou's method of hydrolysis was carried out in the following manner, based on 1 g of clay to be pillared. Anhydrous sodium carbonate (5.3 g) is added slowly at room temperature to a 500 ml solution of 0.1 <u>M</u> chromic nitrate. This addition is done slowly enough to prevent loss of solution due to release of carbon dioxide upon dissolution of the carbonate. Typically this addition is complete within five minutes. The resulting solution is then aged for 36 hours at 95°C. Upon completion of this aging period, a 1 wt.% slurry of montmorillonite is added dropwise to the vigorously stirred pillaring solution, and then allowed to further age for 1.5 hours. The resulting solution is washed free of excess electrolyte by repeated centrifugation and dispersion in distilled water, then it is air dried on glass plates.

The addition of solid anhydrous sodium carbonate to a 0.1 \underline{M} chromic nitrate solution at an OH/Cr ratio of 2.00 always produces some precipitate. The amount of precipitate was dramatically decreased after the solution was allowed to age for 36 hours at 95°C. The remaining precipitate was removed by centrifugation prior to the pillaring reaction.

The presence of precipitate after high temperature aging indicates that equilibrium was not attained. This observation strongly suggests that a variety of polymeric species are formed since equilibrium is not attained.

A cluster capable of producing the observed $\Delta d_{(OOl)}$ of 17 Å as well as chromium hydroxide precipitates are among the products. The addition of any solid sodium carbonate at any rate invariably produces localized hydroxide concentrations conducive to chromium hydroxide formation. This precipitation is disasterous to cluster synthesis for several reasons. The hydroxide and chromium concentrations are not easily controlled as chromium hydroxide effectively removes reactant from the solution. Once formed, these hydroxide species can become large, and may facilitate the removal of large amounts of carbonate, and disturb attainment of equilibrium.

Synthesis method III was designed to alleviate the problems associated with solid carbonate addition through the use of dissolved sodium carbonate (solution) as a source of base. A solution of sodium carbonate (0.25 M) was added dropwise to a chromic nitrate solution (0.17 M) to achieve a final OH/Cr ratio of 2.0. Chromium ions were formally present at a 0.05 M concentration. This addition is done very slowly, generally at a rate of 10 ml carbonate per minute while the chromium solution is agitated vigorously. Upon conclusion of this addition, the resulting solution was aged at 95 to 100°C (reflux) for 36 hours. This freshly prepared pillaring solution is now utilized in the direct exchange method of clay intercalation. All chromium clay catalysts (I, II, and III) are then either air-dried or freeze-dried, and purged at 350°C for two hours in either inert gas or vacuum. This procedure allows for long term storage without alteration of physical or catalytic properties, probably due to conversion of the pillaring species to a chromium oxide cluster.

Physical Properties of Chromium Interlayered Clay Catalysts I, II, and III.

Typical unit cell compositions are presented in Table 8, along with chemical formulas derived from analytical results. Variations in chromium hydrolysis conditions leads to a variety of intercalated species. The X-ray diffraction patterns for air-dried and freeze-dried products subjected to various temperature treatments are shown in

	Na ⁺ Mont.	I (a (NaOF	A) II H) (Solid Na ₂ 0	III CO3) (Solution	Na ₂ CO ₃)
sio ₂	53.94	wt.% 45.4	wt.% 32.26 wt	t.% 35.64	wt.8
Al ₂ 03	18.86	16.2	10.71	13.28	
Fe ₂ 03	3.85	3.06	5 2.29	2.71	
MgO	2.18	1.87	7 1.07	1.45	
Na ₂ 0	2.13	0.00	0.02	0.01	
Cr ₂ 0 ₃	0.00	13.8	18.44	6.49	
^{Na} 0.6 [[] I (NaO [Cr(OH	Al _{3.23} F(H)) $^{34}_{2.66}$ (b)	^e 0.42 ^{Mg} 0.47)]1.88 ^{[Al} 3]	7 ^{] (Si} 7.88 ^{Al} 0.13 ⁾ .14 ^{Fe} 0.40 ^{Mg} 0.48 []]	O ₂₀ (OH) ₄ (Si _{7.84} Al _{0.14})	о ₂₀ (он
II (So [Cr(OH	lid Carl).17)2.83 []] 3	bonate) .53 ^{[Al} 3.23	3 ^{Fe} 0.42 ^{Mg} 0.47 ^{](S}	⁵ⁱ 7.88 ^{Al} 0.13 ⁾⁰ 2	20 ^(OH) 4
III (S	olution	Carbonate)	Fe Ma 1(5	SiAl)O	(OH)

Table 8. Unit Cell Compositions of Chromium Pillared Clay Prepared by Hydrolysis of Cr³⁺ with NaOH, Solid Na₂CO₃ and Solution Na₂CO₃.

(a) Taken from Brindley and Yamanaka, <u>Amer. Miner.</u>, 1979, <u>64</u>, 830.

⁽b) This number represents the average charge per Cr atom.

Figures 8 and 9, for catalyst II and III, respectively.

Catalyst (I), synthesized by Brindley's procedure has a chromium content (1.88 Cr per unit cell) near that of catalyst (III) (1.24 Cr per cell) whose pillar was synthesized by hydrolysis with liquid carbonate. The $\Delta d_{(OOL)}$ of 7.3 Å for product I is the smallest lattice expansion of any chromium pillared product. Catalyst II and III have similar $\Delta d_{(OOL)}$ spacings of \sim 16 to 17 Å, but they differ significantly in their chromium content. Catalyst II and III exhibit strong differences in the X-ray intensities. Catalyst III (Figure 9) possesses much stronger and sharper OOL reflections, which could be related to a narrower pillar distribution produced by hydrolysis or selective intercalation into the clays. It is worthwhile to note that all three catalysts (I, II, and TII) generally do not exhibit more than two OOl reflections. This signifies that these catalysts possess good layer order, but that variability in layer spacing exists. As many as 6 orders of OOL reflections are obtainable for some Al-PILC systems indicative of a much greater degree of layer $ordering^{41}$ than is present in this system.

Table 9 lists the surface area results obtained by utilizing the BET Theory of Multilayer Adsorption⁵⁷. All samples were pretreated as described in Chapter II prior to measurement. The clay catalysts generated from high temperature cluster synthesis produce much larger surface area with solution carbonate hydrolysis yielding the highest value of 433 m^2/g for air-dried products.



Figure 8. XRD Patterns for Air-Dried and Freeze-Dried Cr_{3.5}-Montmorillonite Purged at 25°C and 350°C for Two Hours in Argon.



Figure 9. XRD Patterns for Air-Dried and Freeze-Dried $Cr_{1.24}$ -Montmorillonite Purged at 25°C and 350°C for Two Hours in Argon.



Dried Ch	romium Pilla	ared Clays.	•		
	Base		SA (1 (350	n ² /g))°C)	
Catalyst	Hydrolysis	Cr/cell	AD	FD	
I (Brindley)	NaOH	1.88	61	115	
II (Tzou)	Solid Na ₂ CO ₃	3.53	353	368	
III (Landau)	Solution Na ₂ CO ₃	1.24	433	421	

Table 9. N₂ BET Surface Areas for Air-Dried and Freeze-Dried Chromium Pillared Clays.

Hydrocarbon adsorption data for catalyst II and III are presented in Table 10. The molecules used have different kinetic diameters⁵⁸. Catalyst II has a apparent pore volume smaller than that of catalyst III as judged by adsorption data. Catalyst III adsorbs more hydrocarbon per gram of catalyst for all adsorbates employed. Even perfluorotributylamine with a 10.4 Å kinetic diameter is readily adsorbed by both catalysts. As adsorbates increase in size, the freeze-dried clays show small but discernable increases in adsorption capacities. This effect is related to differences in layer aggregation induced by airand freeze-drying. Air-drying facilitates the maximization of long range basal plane-basal plane interactions of clay platelets due to surface tension forces acting upon the clay sheets. Freeze-drying inhibits layer reorganization since the clay is frozen, and excess water is sublimed off. This results in the generation of clays that are somewhat delaminated, a situation in which edge to basal plane and basal plane-basal plane interactions are

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Adsorption	ium Pillared
Hydrocarbon	lvzed Chrom:
able 10.	

			· · c / n · · ·		mmol/g adsorbed	
Sample	Cr/cell	Drying Method	m ² /g (350°C)	Benzene 6.2 Å	1,3,5 Et3 ^{B3} 9.2 A	(C4F9) ₃ N 10.4 A
		Air-dried	353	1.93 (d) (172)	.520 (.107)	.448 (.158)
II	3.53	Freeze-dried	368	1.86	.810	.458
				(.165)	(.152)	(.164)
				2.04	.750	.430
+ + +	- -	Air-dried	433	(.181)	(.141)	(.154)
111	т С4	Freeze-dried	421	2.06	.810	.490
				(.183)	(.152)	(.173)

- All samples were evacuated for 2 hours prior to measurement of organic adsorbates at 20°C. Pressures were as follows: Benzene, 73 torr $(P/P_O=0.77)$; 1,3,5-triethyl-benzene 0.36 torr $(P/P_O=0.65)$; Perfluorotributyl-amine, 0.39 torr $(P/P_O=0.66)$. (a)
- Values in parenthesis represent amount adsorbed in cc/g. (q)

present. This delamination phenomena⁴¹ induces a degree of macroporosity which is available for adsorption above and beyond that attributed soley to the interlamellar region.

The larger pore volume, as well as the lower chromium content of catalyst III implies that the pillaring oxocations are further apart than in catalyst II. This effect is related to the different products formed by solid and solution carbonate hydrolysis. The pillared product formed by solid carbonate hydrolysis is probably like Cr(OH), and the chromium must have a lower positive charge when more is present. The incorporation of colloidal dimers could also account for somewhat smaller pore volumes as well as the higher chromium content in II than in III. It is conceivable that $Cr_{1,24}$ -mont (III) is a "cluster-like" cation, while Cr_{3 53}-mont (II) is a "rod-like" or a two dimensional cation. X-Ray diffraction only tells us that at least one dimension, that which produced the 27 A spacing is similar.

A preliminary ESR study of catalysts I, II, III, and Cr^{3+} -exchanged montmorillonite was undertaken. Instrument settings and sample preparation were described in Chapter II. Figures 10 and 11 represent ESR spectra obtained on purged and reduced clay samples, respectively. Table 11 lists g values and peak-peak widths obtained for low (g₁) and high (g₂) field resonances. The low field resonances for calcined samples all have similar g₁ values of 3.62 to 3.65. Cr^{3+} montmorillonite exhibited the most




Figure 10. ESR Spectra of Purged Chromium Clay Catalysts.





Sample	Conditions (A)	g ₁ (21	.00G)	g ₂ (41	00G)
cr ³⁺	Purged	3.65	(383G) ^(B)	1.98	(599G)
CI	Reduced	3.57	(310)	2.34	(275)
	Purged	3.63	(251)	1.91	(767)
1.88 - MOITE (1)	Reduced	3.52	(226)	1.89	(964)
	Purged	3.63	(237)	1.96	(790)
3.53 - MONE (11)	Reduced	3.54	(165)	1.97	(1929)
	Purged	3.62	(237)	1.96	(766)
1.24 ^{-mont (111)}	Reduced	3.54	(167)	1.92	(1679)

Table 11. ESR g Values of Chromium Clays.

(A) See text, Chapter II, ESR.

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(B) Resonance's peak-peak width.

intense signal at this low field. At higher field strength, the Cr^{3+} -clay exhibited the least intense resonance, with the narrowest peak separation. $Cr_{1.24}$ -mont possessed the broadest peak separation along with the most intense signal. The g values are all between 1.91 and 1.98.

When the samples were reduced as in a catalytic run, the low field resonance (g=3.52-3.57) exhibited a small decrease in g value along with a reduction in peak to peak widths. The high field resonances (g=1.85-2.34) all decreased in intensity and broadened considerably, except Cr^{3+} -montmorillonite which increased in intensity. It should be noted that all reduced chromium pillared clays had a g value (1.85-1.92) upfield of DPPH, while Cr^{3+} -exchange clay had a g value (2.34) downfield of DPPH.

Supported chromium has been characterized by three distinct ESR resonances^{59,60}: Cr^{3+} ions which are electronically decoupled (δ phase), Cr^{3+} ions which are electronically coupled (β phase), and oxidized (Cr^{4+} or Cr^{5+}) chromium (γ phase). These resonances are characterized by a first derivative maximum of 1500 gauss, a broad resonance centered near 3400, and a very sharp resonance near 3400 gauss, respectively. The δ phase resonance⁵⁹ has been assigned to Cr^{3+} ions in a strong axial crystal field distorted to lower symmetry. This phase (1500 gauss) was not observed in this investigation for any catalyst. This indicated that no electronically isolated chromium clumps were present, regardless of the hydrolysis method employed for cluster synthesis.



The absence of large crystal field distortions implies that the chromium polymers do not experience a large degree of internal strain, which would account for their excellent thermal stability. The γ phase, as expected, was not observed for these clay catalysts. The 0 to 1600 gauss region was not shown in Figures 9 or 10. The resonance characterized by g_1 values in Table 11, centered near 2100 gauss, was also observed for Na-montmorillonite. This resonance was caused by iron oxide impurities present in the clay.

The resonances centered near 4100 gauss behave like β_3 resonances characterized by Ellison⁶¹. The g₂ values for the chromium clays (g=1.89-1.97) are similar to those obtained by Ellison (g=1.97) if the Cr³⁺ clay (g=2.34) is not included. The peak to peak width of β_3 (4100 gauss) varied widely (964 to 1929 gauss) for reduced clays, which was also observed by Ellison.

These EPR results show that cyclohexane dehydrogenation activity resides in the β_3 phase. Hydrogen pretreatment produced a mixed-valence phase^{62,63} Cr²⁺/Cr³⁺ cluster. This has also been proposed by Groenveld, et al.⁶⁴ and Wittgen, et al.⁶² as the active site for oxidative addition of an olefin to supported chromia on alumina.

Catalytic Properties of Chromium Catalysts I, II, and III

Chromium based catalysts hold a prominent place in catalytically promoted chemical reactions. Reforming of cracked and virgin naphthas is an important industrial process. This process generally involves several reactions which include the dehydrogenation of cyclohexanes, the

dehydroisomerization of alkylcyclo-pentanes, the isomerization of butenes, and the hydrocracking of paraffins⁶⁵. Chromium catalysts also accounted for 3.08×10^9 Kg of styrene produced in 1978⁶⁶ via ethylbenzene dehydrogenation.

Two major types of catalyst can be utilized for the aforementioned reforming reactions: reduced metals and metal oxides. Other catalytic systems have been developed⁶⁷ but have not achieved wide-spread industrial application. The reduced metals are of group VIIIB, typically nickel, platinum, or palladium, which are deposited on a support of silica or alumina. Metal oxides are typically chromia or molybdena.

In catalytic reforming, the dehydrogenation of naphthenes to aromatics is the chief octane upgrading reaction. In reduced metal catalysis, reaction conditions vary depending upon the catalyst. Supported Pt and Pd reactions take place typically around 250 to 300°C, whereas Ni requires temperatures of 350 to 400°C. Metal oxides operate in the 450 to 600°C temperature range⁶⁶.

The supported metals have a higher dehydrogenation activity than the metal oxide catalysts. To attain comparable levels of activity for metal oxide promoted reactions, one must operate the reaction at a higher temperature, a lower H_2 partial pressure, and a lower reactant space velocity. Perhaps the most important commercial consequence of higher catalyst temperature is that it facilitates the rapid coking⁶⁸ of these metal oxide systems and caused frequent regeneration periods.

The bifunctionality of transition metal oxide catalysts was illustrated by Clark⁶⁹ who utilized several different reactions. Table 12 depicts the hydrogenation and cracking of isobutylene dimers over a chromium oxide gel catalyst.

Table 12. Effect of Alkali-Metal Promotion Upon Chromia Gel Cracking Activity.

	Catalyst	<pre>% Saturation of C₃ Product</pre>	% Cracked
	Chromia gel	99.5	12-15
*NaOH +	Chromia gel	98.5	1.9
Conditions:	390°C, 700 psic *100 ml chromia for 3 hours.	g, 1.0 LHSV H ₂ /HC gel soaked in 30	C = 2. 00 ml 2.5% NaOH

Chromia gel has a hydrogenation and acidic functionality which do not occupy the same active site on the catalyst. This is inferred from the loss of cracking activity upon alkali treatment.

The characterization of Cr-PILC catalyst activity utilized the dehydrogenation of cyclohexane:

and the cracking of β -isopropyl naphthalene:

$$\bigcirc \bigcirc \vdash \longrightarrow \bigcirc \bigcirc + CH_3 - CH = CH_2$$

The reaction pathway of cyclohexane dehydrogenation over metal oxides such as chromia is schematically represented in Scheme 8⁷⁰.



Scheme 8.



where: H,D - Reaction on a dehydrogenation-hydrogenation site. A - Reaction on an acid site.

As Clark⁶⁹ and Bridges, et al.⁷¹ have shown, alkali promoters quench the acid sites in the support and catalyst to inhibit the cyclohexene to methylcyclopentene transition and help reduce coke.

Mechanistically the dehydrogenation of cyclohexane is 1st order with respect to cyclohexane with the rate determining step being the dissociative chemisorption of the hydrocarbon upon the metal⁷², as shown in Scheme 9.

Scheme 9.



The catalysts previously described were used as dehydrogenation catalysts through the procedure outlined in Chapter II. The Weight Hourly Space Velocity (WHSV) reported for each run is reported with respect to the grams of reagent per gram of Cr_2O_3 present in the catalyst per hour. This reporting scheme was selected to enable the catalysts to be compared more accurately since they contained various amounts of metal.

Catalyst I, $Cr_{1.88}$ -mont (I) produced by Brindley's method, showed negligible activity. Catalyst II, $Cr_{3.53}$ mont used as an air-dried catalyst, exhibited an initial conversion of sixty percent that decreased to thirty-four percent after two hours. Catalyst III, $Cr_{1.24}$ -mont, maintained high conversion levels after two hours, quantitatively converting cyclohexane to benzene. These results are shown in Figure 12.

Cyclohexane dehydrogenation is proposed to proceed via dissociative chemisorption of the hydrocarbon upon the metal. The +2 oxidation state, which appears to be the active oxidation state, is first generated by pretreatment of all catalysts in purified hydrogen. Hydrogen pretreatment is a necessary requirement for catalytic activity. This is carried out using hydrogen ($P/P_0 = 1$ atm) at a variety of contact times [volume catalyst bed (ml)/H $_2$ flow rate (ml/ min)]. Figure 13 represents the relationship between initial conversion and post reaction surface areas as a function of hydrogen contact time. As the contact time of hydrogen increases, the ratio mmol $H_2/mmol \ Cr^{3+}$ is reduced. Catalyst III's initial reactivity is optimized between 0.90 and 1.6 sec hydrogen contact time. At short contact times down to 0.90 sec, conversion is quantitative but the catalyst suffers a loss of surface area. The wt % carbon deposited upon the used catalyst also increases away from optimum conversion and maximum surface area



Figure 12. Optimized Cyclohexane Dehydrogenation Activity for Cr_{1.88}-Mont.(I), Cr_{3.53}-Mont.(II) and Cr_{1.24}-Mont.(III) Catalysts.



Figure 13. Initial Cyclohexane Reactivity and Surface Areas After Two Hours on Stream as a Function of Hydrogen Pretreatment.

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retention. The loss of catalytic efficiency and surface area may be attributed to several causes. High contact times correspond to slow movement through the catalyst bed. The reduction of Cr^{3+} to Cr^{2+} liberates water as hydrogen is oxidized. This water could act to re-oxidize the catalyst. Also, steaming the pillaring cluster may cause structural rearrangements leading to loss of catalytic activity. At very short hydrogen contact times, reduction is so complete that structural modifications required upon change in oxidation state might produce a highly strained active site, and cause deactivation. If the active site is a Cr^{3+}/Cr^{2+} composite, then over reduction to all Cr^{2+} would result in loss of activity.

Figure 14 represents conversion over catalyst III after 15 and 75 minutes on stream for a variety of pretreatments. The general shape of the 75 minute conversion curve is similar to that of the initial activity curve.

Figure 15 represents the variability of reactivity with contact time of reagent at a constant WHSV of 3 and a constant H₂ pretreatment time of 1.6 sec. Short (2.7 sec) reactant contact times produce a significant decrease in surface area. In addition, a higher wt. % carbon results than at a 6 sec contact time. Longer contact times (12.8 sec) produce smaller losses of surface area, but greater carbon fouling. The intermediate contact time of 6 sec consistently produced high conversions and low carbon results without any appreciable loss of surface area.

Figure 16 illustrates the WHSV dependence (on a Cr₂O₃





Figure 14. Cyclohexane Dehydrogenation Activity for Cr_{1.24}-Mont.(III) After Fifteen Minutes and Seventy-Five Minutes on Stream.



Figure 15. Cyclohexane Contact Time Dependence Upon Reactivity for Cr_{1.24}-Mont.(III) Catalyst.





Figure 16. Cyclohexane WHSV Dependence Upon Reactivity for Cr_{1.24}-Mont.(III) Catalyst.



basis) for catalyst III at constant hydrogen and cyclohexane contact times. As expected, an increase in WHSV leads to greater carbon deposits, diminished surface areas, and reduced conversion levels. It should be kept in mind that all of the catalysts maintained a ~19.6 Å spacing after reaction. Decreases in conversion at high WHSV values is probably due to the saturation of active sites by the reactant, as well as by carbon deposition.

The dependence of conversion upon pretreatment, WHSV, and reactant contact times for catalyst III are also exhibited by catalyst II. The conversion dependence upon airdrying and freeze-drying was minimal. Freeze-dried catalysts exhibited similar dehydrogenation results, but they were harder to manipulate due to their powdery morphology.

Differences among the three catalysts (Figure 12) may be explained in part by differences in pore structure. Upon completion of reaction at 550°C, catalyst I has a $\Delta d_{(OOL)}$ of only 0.60 Å, while catalysts II and III maintain large $\Delta d_{(OOL)}$ of 10 Å. The pore openings of the latter catalysts is larger than the kinetic diameter of cyclohexane (6.0 Å) and allows for easy diffusion into the intracrystalline pores where reactivity is effected. This is illustrated by the diffusion characteristics of spent air-dried catalysts as shown in Figure 17. Freeze-dried catalysts exhibited similar post reaction adsorption characteristics. Catalyst I, which is collapsed after reaction, exhibits only external adsorption. The differences in the pore sizes of catalysts.





Figure 17. Cyclohexane Uptake by Spent Catalysts for Air-Dried Chromium Catalysts After Two Hours on Stream.

Catalyst III ($Cr_{1.24}$ -mont) was subjected to an 8 hour C_6H_{12} dehydrogenation run. This is shown in Figure 18. Initially the reactivity is constant for 3 hours, followed by diminished conversions with increasing time. Surface area is decreased by 70% accompanied by a large amount of carbon deposited. It appears that deactivation is due to pore blockage or active site coverage by physi-adsorbed carbon. Attempts to regenerate the catalysts by hydrogen treatment proved unsuccessful. Oxygen regeneration was also attempted, but the carbon layer could not be oxidized to CO_2 at the temperatures employed (300°C) and collapse of the Cr interlayer clay to 10.2 Å resulted.

The acidic nature of these chromium catalysts and the dealkylation characteristics were probed using β -isopropylnaphthalene as a substrate. This probe molecule was chosen for two reasons: (1) it is an analog to α -isopropylbenzene (cumene) which is used extensively in the petroleum industry for Bronsted acidity⁷³ characterization, and (II) it is much larger than cumene and illustrates the cracking versatility of a large pore pillared clay versus a faujasitic zeolite. The results of two representative catalytic dealkylation runs are depicted in Figure 19.

Dehydrogenation reaction conditions are most clearly approximated by the reaction at 2.2 WHSV. At a lower temperature of 400°C and a lower WHSV of 2.22 (vs. 550°C and a 3.0 WHSV for dehydrogenations) the catalyst dealkylates quite well. Deactivation is rapid, and attributed to the blockage of active sites as judged by the high wt. % C





Figure 18. Cyclohexane Dehydrogenation Activity of Cr_{1.24}-Mont.(III) Catalyst with Time.



Figure 19. β -isopropylnaphthalene Dealkylation Activity for Cr_{3.53}-Mont.(II) Catalyst as a Function of WHSV.

value of 11.45 %. If this reaction was run at identical dehydrogenation conditions, deactivation and carbon fouling would probably be more rapid and severe.

Catalyst reaction at 1.00 WHSV illustrates the controlling factor in carbon deposition. The relatively long 6 sec contact time produces the same large coke values (~11.00%) at both WHSV employed. This suggests that saturation of the surface occurs readily. Although Bronsted acidity is present in the catalyst, no isomerization products of C_6H_{12} dehydrogenation were produced. It is conceivable that hydrogen pretreatment prior to C_6H_{12} introduction quenches the acidity of the catalysts by reducing the Cr^{3+} to a Cr^{3+}/Cr^{2+} active site which only possessed very weak acidic character.

Chromium catalysts II and III have been compared to commercially available Cr_2O_3 on alumina catalyst obtained from Chemical Dynamics Corporation, USA. The commercial catalyst is approximately 19 wt. Cr_2O_3 with a surface area of 7.7 m²/g. Figure 20 compares the initial reactivity vs. hydrogen pretreatment conditions for catalyst III and the commercial catalyst, designated Cr_2O_3/Al_2O_3 . Two features are worth noting: (1) the commercial catalyst requires almost three times as much hydrogen as catalyst III to achieve maximum activity, and (2) the commercial catalyst is not as effective as $Cr_{1.24}$ -mont (III) in dehydrogenating cyclohexane. Numerous hydrogen pretreatments over a wide range of conditions upon Cr_2O_3/Al_2O_3 were unsuccessful in increasing its overall conversion levels.





 Dependence of Cyclohexane Dehydrogenation Activity on the Contact Time of Hydrogen Reduction for Cr_{1.24}-Mont.(III) and Cr₂O₃/Al₂O₃. The reactivity of $Cr_{1.24}$ -mont (III) and Cr_2O_3/Al_2O_3 are shown for comparison in Figure 21. Analytical results on the spent catalysts and the dependence on reaction parameters are given in Table 13. Catalyst $Cr_{1.24}$ -mont (III) is the most effective catalyst under the conditions employed. This low Cr content clay has better order than catalyst $Cr_{3.53}$ -mont (II) as judged by XRD. This is possible due to the existence of more bridging chromium atoms that have undergone oxolation reactions during cluster synthesis. The $Cr_{3.53}$ -mont (II) prepared by hydrolysis of Cr^{3+} with $Na_2CO_3(s)$ probably has a larger amount of chromium hydroxide like species incorporated into it.

If indeed olation predominates over oxolation in solid carbonate synthesis, the greater amount of chromium in $\operatorname{Cr}_{3.53}$ -mont (II) would be distributed in pillars producing $\operatorname{Ad}_{(OOL)}$ of 17 Å, as well as large islands of monomer and dimer sitting in the pores upon the basal plane or attached to the pillar. This would account for the observed reduction in surface area, the pore volume and the increased Cr content in catalyst II. The presence of these monomers and dimers would also facilitate coke formation by providing the acidic centers necessary for reaction.

Characterization of Cr-Laponite and Cr-Fluorohectorite Interlayered Clay

The work presented in the last section for montmorillonite has been extended to two other smectite type minerals. Laponite-RD[®], which is a synthetic analog of hectorite, has a lath-shaped morphology and a manufacturer specified particle





Figure 21. Cyclohexane Dehydrogenation Activity for Cr_{1.88}-Mont.(I), Cr_{3.53}-Mont.(II), Cr_{1.24}-Mont.(III) and Cr₂O₃/Al₂O₃.



Table 13. Cataly Cataly	tic Paramet sts ^(a)	cers and Physi	ical Charac	terization of Spe	ent Chromium
Catalyst	Wt % Cr	NSHW	Wt % Carbon	doo Å Å	SA m ² /g
Cr _{1.88} -mont(I)	13.9	1.0	1	10.2 (16.9) ^(b)	25.2 (61)
Cr _{3.53} -mont(II)	17.85	3.0	5.13	20.53 (22.6)	170 (353)
Cr _{1.24} -mont(III)	6.49	3.0	1.64	20.05 (23.9)	432 (433)
$\operatorname{cr}_2 \operatorname{O}_3 / \operatorname{Al}_2 \operatorname{O}_3$	19.0	1.0	0.17	ł	5.7 (7.7)
(a) All catalyst Six second c optimum H ₂ p	s were air yclohexane retreatmen	-dried before contact time t (P/P ₀ = 1 at	reaction; , time on s tm).	Reaction temp = tream: 2 hours;	550°C; 1 hour

Numbers in parentheses represent pre-reaction values. (q)
size of a few hundred angstroms. It also possesses a low layer charge. Fluorohectorite possesses a very high layer charge and is characterized by a particle size much larger than Laponite-RD[®] or even montmorillonite. These clay characteristics are presented in Table 14, along with those of the montmorillonite used for generation of clay catalysts I, II, and III.

	Laver Charge	Particle
Clay	per O ₂₀ (OH) ₄ unit	Size
Laponite-RD [®]	0.36	~100 Å
Wyoming-Mont	0.86	~2000
Fluorohectorite	1.6	>>2000

Table 14. Characteristics of Natural and Synthetic Smectites Used for Chromium Interlaying.

Synthesis of the pillaring species was carried out under identical conditions to those described in the previous work and utilized the solution carbonate synthesis method. The concentrations of reactants utilized for cluster growth are summarized in Table 15. The ratio of mmol Cr^{3+}/MEQ clay was maintained at a value of 62.5 for all clay minerals regardless of their cation-exchange-capacity by adjusting the volume of pillaring solution used for each clay on a gram basis. Fluorohectorite was washed free of excess electrolyte by repeated suspension in deionized water, followed by centrifugation. The final product was air-dried. Laponite, because of its small particle size, could not be centrifuged without an appreciable loss of product. The

Table 15. Con	centrations o	f Reactants Utilized	for Chromium Cluster G	3rowth.
Clay	CEC (MEQ/100g)	Formal[CR ³⁺] _{eQ} (moles/liter)	Formal[CO ₃ ²⁻] _{eQ} r (moles/liter) h	mmol Cr ³⁺ MEQ Clay
Laponite-RD [®]	55	0.034	0.03434	62.5
Fluorohectorit	e 187	0.1168	0.1169	62.5
- Initial conc	entration of	cr^{3+} and co_3^{2-} were (0.17 <u>M</u> and 0.25 <u>M</u> , respe	pectively.

small particle leads to low sedimentation coefficients and prevents efficient collection. Dialysis was used to wash laponite, after which it was air-dried and freezedried.

X-Ray diffractograms for Cr intercalated laponite and fluorohectorite are shown in Figures 22 and 23, respectively. Physical properties of the materials are presented in Table 16, along with those of montmorillonite intercalated clay prepared under analogous conditions.

Chromium laponite shows atypical behavior as compared with other chromium interlayered clays. Dialysis of Crlaponite prevented the removal of large hydroxy-metal polymers that were unable to diffuse through the dialysis tubing. The wash water was almost colorless during the entire wash procedure. This indicated that very little Cr³⁺ was washed from the clay during dialysis. This is confirmed by the high chromium content (40 wt. %). The $d_{(00)}$ spacing of 21 to 22 Å is lower than that generally obtained with montmorillonite (~28 Å). This is attributed to hydrolysis of the pillaring agent. As hydrolysis progresses, surface area and d (OOL) spacing decreases. Although the adsorption results are comparable to freezedried Al pillared montmorillonite (~0.3-0.4 mmol/g perfluorotributylamine adsorbed), Al pillared laponite is capable of almost twice the adsorption of Cr exchanged laponite.

The XRD results from Cr-laponite are interesting. Low temperature treatments (25°C) produce discernable, but broad and poorly characterized $d_{(OOL)}$ reflections. At elevated





Degrees 2θ

Figure 22. XRD Patterns for Air-Dried and Freeze-Dried Chromium Laponite Purged at 25°C and 350°C for Two Hours in Argon.





Figure 23. XRD Patterns for Air-Dried Chromium Fluorohectorite Purged at 25°C, 110°C, and 350°C for Two Hours in Argon.

Table 16. P a	hysica nd Mon	<pre>1 Propertie tmorilloni*</pre>	es of Chi te.	romium Iı	nterlayered La	ponite, I	'luorohectorite,
		rying	ں ص	• 4	Wt. %	SA	Benzene
Clay	Ŵ	ethod	25°C	、 350°C	Cr	m ² /g	Ads. mmol/g
-		AD	21.5	(a)	40.28	260	
ыаропіте		FD	22.6	!	40.28	206	1
Fluorohector	ite	AD	19.2	16.1	17.23	144	0.944
Montmorillon	ite	AD	26.8	23.9	6.49	433	2.04

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temperatures, the clay intercalate appears to be delaminated. The amorphous x-ray pattern of the elevated temperature samples may be related to the high Cr content as well. Chromia oxide gel, formed as a condensation polymer of chromium hydroxide, is also x-ray amorphous. It is possible that this new chromium polymer, generated by high temperature base hydrolysis, is also x-ray amorphous when not stabilized by the clay's silicate sheets.

Cyclohexane dehydrogenation was attempted with air dried Cr-laponite, but the experiment proved to be unsuccessful: no benzene was produced. This might be the result of dialysis facilitated hydrolysis of the pillaring agent.

It is very reasonable to speculate that the pillaring agent present after dialysis is different from what would be obtained by removal of excess electrolyte. Hydrolysis rates are markedly different as the ionic strength of the electrolyte changes within the clay interlayer. Differences in dialysis and centrifuge washing may account for the anomolous XRD patterns as well as diminished catalytic activity.

Several interesting features are also exhibited by Cr-fluorohectorite. The $d_{(OOL)}$ of 19.2 Å is considerably lower than the 27.6 Å observed for montmorillonite. The chromium content is similar to solid carbonate-hydrolyzed Cr-montmorillonite, although it was produced by solution carbonate hydrolysis. The surface areas and adsorption capacities are also very low in comparison. The high

chromium content for chromium fluorohectorite is related to the high layer change associated with this clay. A larger number of cations are required to neutralize the higher negative layer charge on fluorohectorite than is required by montmorillonite. The small $d_{(OOL)}$ (~8 Å) and low adsorption capacities and surface areas indicate that the clay picks up an amount of oxocations, which are required for electrical neutrality, then they are degraded by interlayer forces to yield the observed $d_{(OOL)}$ spacing of 19.2 Å. Analogous intercalation procedures using montmorillonite, which possesses a lower layer charge, produced the previously described Cr interlayered montmorillonite. Indeed, this cluster hydrolysis mechanism is operative for many metal hydroxide intercalates.

Catalytic experiments were not attempted due to the low adsorption capacities obtained.

Conclusions

The preceding results have shown that a new class of porous chromium clay intercalates has been generated. This is accomplished by high temperature aging of chromium nitrate and sodium carbonate, followed by intercalation into natural and synthetic smectite minerals. The method of cluster synthesis plays an important role in determining the physical properties of the intercalated clay. Solution carbonate hydrolysis affords a material with lower Cr content, larger pores, and enhanced catalytic activity as compared to that produced by solid carbonate hydrolysis.

These new clay catalysts have been characterized as

traditional metal oxide catalysts which possessed dual catalytic activity affecting both hydrogen transfer and Bronsted acid type reactions. Dehydrogenation activity was shown to be dependent upon chromium content and its reduction to an active site which contains a mixture of Cr^{3+} and Cr^{2+} , the latter produced by a dry reductor. Dehydrogenation upon these clays also illustrated the first use of an intercalated metal-oxide pillar for carrying out catalytic conversions in a pillared clay. These catalysts' Bronsted acidity, which was characterized by β -isopropylnaphthalene dealkylation, is very good, but is not a factor in catalytic reactions when reduced catalysts are used.

The results obtained on the synthetic smectites, laponite and fluorohectorite, suggested that the hydrated oxocations fill the interlayer and hydrolyze to achieve electrical neutrality. This accounts for low surface areas and low adsorption capacities as well as smaller than expected $d_{(OOL)}$ spacings.



CHAPTER IV

ALUMINUM INTERLAYERED CLAY CATALYSTS

Introduction

Zeolites have been used extensively as catalysts and selective adsorbents since the mid-1960s. Their primary uses include catalytic cracking, hydroisomerization, and reforming reactions⁷⁴. Although a large number of zeolites have been synthesized, only a limited number have been extensively utilized. Faujasite zeolites have the largest pore openings corresponding to approximately 8 Å. These pore openings are too small to allow the conversion of heavy oils, present in crude oil, to gasoline due to reactant selectivity. Consequently, it is of interest to synthesize ordered porous materials with pore openings larger than 8 Å.

As noted in the introduction, Barrer and Macleod²⁶, and Barrer and Reay²⁷ were the first to demonstrate that the charge balancing cations of montmorillonite could be replaced with tetraalkylammonium cations. These cations served as molecular props between the clay sheets, imparting a 4 Å free interlayer spacing. In an attempt to further increase the interlayer spacing, several types of tris-metal

chelates, including Cu- and Fe-tris 1,10-phenanthroline²⁹, tris-bipyridyl³⁰ and tris-ethylenediamine cations³¹ have been employed. These cations generally produce a 9 Å $\Delta d_{(OOl)}$ interlayer spacing, but exhibit low thermal stability (<400°C) due to carbon-carbon bond cleavage in the intercalant.

Several inorganic intercalants have been synthesized^{36a-e}. Besides those presented in Chapter III (cf. Table 6), aluminum oxocations have received considerable attention due to their large pore openings and excellent thermal stability. This clay intercalant has been characterized through the microactivity test for cracking catalysts by using gas-oil⁴². The results demonstrate that the catalytic activity is comparable to zeolite-promoted commercial catalysts containing 15 to 20% by weight faujasite type zeolite. Clay catalysts used in these experiments showed a progressive decrease in $\Delta d_{(OOl)}$ spacing between 540°C and 650°C with a corresponding decrease in surface area as well as catalytic activity. At present it appears that clay intercalates suffer from instability to the steam that is typically employed as part of the stripping operation of commercial catalytic cracking procedures⁷⁵.

At present the structure and morphology of aluminum interlayered clay is not fully elucidated. It has been postulated that the polyoxocations undergo dehydroxylation at elevated temperature to form small oxide aggregates which are stable on the interlayer surface⁷⁶. Crosslinking by the pillars to adjacent silicate sheets is another distinct

possibility^{36b}. It has been recognized that by controlling pillar size and distribution it is possible to form intracrystalline materials with pore sizes larger than those of faujasitic zeolites. It is also known that smectite layers may aggregate in an ordered lamellar fashion (basal planebasal plane interaction) or that they may adopt a delaminated or "house-of-cards" structure due to edge-basal plane interactions dependent upon mode of synthesis⁴¹.

The objectives of this present study were to determine the relationship between the OH/Al ratio of the pillaring solution, as well as clay morphology, cation exchange capacity, and history of the clay intercalate reaction with respect to the catalysts' physico-chemical and catalytic properties.

Preparation of Pillaring Reagents

Three different pillaring reagents were employed in this study. Solution #1 was synthesized by the base-hydrolysis of $AlCl_3 \cdot 6H_2O$ with NaOH to yield an OH/Al mole ratio of 2.00. Solution #2 was prepared in an analogous fashion to Solution #1, except the OH/Al mole ratio was 2.42. Solution #3 was the active ingredient of anti-perspirant, 50% w/w chlorhydrol solution obtained from Reheis Chemical Company. The chemical formula as reported by Reheis is $Al_2(OH)_5Cl$, its chemical composition is listed in Table 17. Chlorhydrol is synthesized by the reaction of aluminum trichloride with excess aluminum metal⁷⁷ in an acidic environment as shown by the following equation:

 $5A1 + A1C1_3 + 15H_20 \longrightarrow 3A1_2(OH)_5^+ + 7.5H_2 + 3C1^-$

Solution.	
^{A1} 2 ^O 3	23.7%
Cl	8.21%
Al : Cl (mole/mole)	2.01 : 1
so ₄	<0.025%
Pb	<10 ppm
Fe	42 ppm
рН	4.20
Specific Gravity	1.337

Table 17. Chemical Composition of 50% w/w Chlorhydrol Solution.

The aluminum chlorhydrol (ACH) used in the present work was diluted from a concentration of 6.2 \underline{M} (as supplied by the manufacturer) to a concentration of 0.23 \underline{M} and then utilized in the same fashion as the other pillaring reagents.

The chemical species actually present in solution were probed by 27 Al-NMR by Dr. Ming-Shin Tzou 45 . The 27 Al-NMR spectra are shown in Figure 24. It is apparent from the NMR results that the chemical compositions of these three solutions differ significantly. Solutions #1 and #2, those which are obtained from base-hydrolyzed AlCl₃·6H₂O, are distinguished by a sharp resonance at 62.8 ppm, along with one at 0.0 ppm. Solution #2 has a larger contribution of aluminum giving rise to the 62.8 ppm resonance than does Solution #1. Chlorhydrol (ACH) exhibits resonances at 62.8 ppm, as well as a broad resonance at 10.8 ppm and a sharper one at 0.0 ppm.

²⁷Al-NMR spectra similar to those observed here have



Figure 24. ²⁷Al-NMR of Pillaring Solutions Employed for Interlayering of Smectite Minerals⁴⁵.

been reported by Akitt and Farthing $^{77-79}$ and by Bottero, et al.³⁷ for related base and metal hydrolyzed aluminum solutions. The sharp resonance at 0.0 ppm, based upon data presented by these workers, is attributed to monomeric Al(H_2O)₆³⁺ species. The sharp line at 62.8 ppm is assigned to an Al₁₃ oligomer which possess Keggin ion-like structure³⁸ as shown in Figure 6 (Chapter 1, p. 22). In this structure one aluminum occupies a central AlO_A tetrahedral position while the remaining 12 Al occupy equivalent octahedral positions defined by oxygen, hydroxide, and water ligands. The symmetric AlO_4 unit gives rise to the observed ²⁷Al resonance at 62.8 ppm. The octahedral Al ions probably experience a strong electric field gradient due to quadrupolar relaxation upon the I = 5/2 nucleus and are NMR silent. These assignments are strengthened by the $\begin{array}{c} 27\\ \text{Al resonance of the tetra-}\end{array}$ hedral Al in $AlW_{12}O_{40}^{5-}$ ion which occurs at low field (72) ppm). The octahedral Al of $AlMo_6O_{21}^{3-}$ occurs at 0.0 ppm. The nature of the species giving rise to the broad resonance at 10.8 ppm in Solution #3 is unknown. It has been suggested by Akitt and Farthing⁷⁹ that this resonance is due to aggregates of higher nuclearity than Al₁₃, although they were unable to offer any conclusive proof. Although complete identification of the species present in solution is unobtainable, it is clear that the three pillaring solutions differ significantly for OH/Al ratios in the range of 2.0 to 2.50.

These three different pillaring solutions were utilized to intercalate a variety of smectite clay minerals which may be classified into three distinct subgroups as outlined in Table 18.

Physical Properties of Products Obtained from Laponite and Smectites of Related Layer Charge and Morphology

Laponite-RD[®] was allowed to react with various amounts of aluminum chlorhydrate (ACH) in the range of 0.00 to 10.00 q of ACH per q of laponite. The synthetic procedure de-The ratio mmol $Al^{3+}/$ scribed in Chapter II was utilized. MeQ clay shall be designated as Q. These final products were air-dried on glass plates, as well as freeze-dried. Figures 25 and 26 represent the x-ray diffraction patterns for laponite interlayered with ACH that was freeze-dried and heated at 25°C and 350°C, respectively, for 2 hours in argon. It should be noted that freeze-drying at low Q (0.279) yields a discernable 001 reflection. As the value of Q increases from 0.875 to 84.20, the intercalated minerals all give either no 001 x-ray reflections or very diffuse x-ray reflections. Heating these freeze-dried laponites to 350°C for 2 hours in inert gas produces little variation in the samples ranging from Q=0.875 to 84.20. The Q=0.279 sample shows a decrease and broadening of its 001 reflection. The freeze-dried samples are very different from the air-dried samples shown in Figures 27 and 28. Air-drying leads to materials with distinct 001 reflections in the range Q=0.00to 10.95. Heating these samples to 350°C, as shown in Figure 28 produces broadened 001 reflections, but they remained more pronounced than their freeze-dried counterparts.

Table 19 lists the physical properties for the series

Properties.	large and clay ⁽¹⁾ Layer Charge Particle Size	er charge and/or Laponite-RD [®] (a) 0.36 ~200 Å article size Saponite ^(b) 0.30 ~2000 Å Montmorillonite ^(c) 1.00 ~300 Å	layer charge Montmorillonite ^(d) 0.86 ~2000 Å cicle size	/er charge and Fluorohectorite ^(e) 1.60 >>2000 Å
Pro	ayer Charge a	ow layer char	ypical layer	iigh layer cha
	Morphology	small particle	and particle s	arge particle

Smectite Minerals According to Layer Electrical and Morphological Table 18.

- (1) The unit cell composition of the layer is:
- (a) Li_{0.36}[Mg_{5.64}Li_{0.36}](Si_{8.00})O₂₀(OH)4
- (b) $Na_{0.303}[Mg_{5.03}Al_{0.52}Fe_{0.19}](Si_{7.51}Al_{0.49})O_{20}(OH)_4$
 - (c) $Na_{1.00}[Al_{2.99}Fe_{0.41}Mg_{0.51}](Si_{7.77}Al_{0.23})O_{20}(OH)_4$
- (d) $Na_{0.86}[Al_{2.98}Fe_{0.41}Mg_{0.56}](Si_{7.85}Al_{0.15})O_{20}(OH)_4$
 - (e) $\text{Li}_{1.6} [\text{Mg}_{4.4} \text{Li}_{1.6}] (\text{Si}_8) \text{O}_{20}^{\text{F}}_4$





Figure 25. X-Ray Diffraction Patterns for Freeze-Dried Laponite Interlayered with Aluminum Chlorhydrate, Purged for Two Hours at 25°C in Argon.



Figure 26. X-Ray Diffraction Patterns for Freeze-Dried Laponites Interlayered with Aluminum Chlorhydrate, Purged for Two Hours at 350°C in Argon.



Degrees 20

Figure 27. X-Ray Diffraction Patterns for Air-Dried Laponite Interlayered with Aluminum Chlorhydrate, Purged for Two Hours at 25°C in Argon.



Figure 28. X-Ray Diffraction Patterns for Air-Dried Laponites Interlayered with Aluminum Chlorhydrate, Purged for Two Hours at 350°C in Argon.

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Tabl	e 19. Ph Al	ysica uminu	<pre>l Properties of m Chlorhydrate.</pre>	E Freeze-Dried]	Laponites Interl	ayered with
mmo1 MEQ]	Al ³⁺ Laponite	лб II	ams ACH used n synthesis	Al per Unit Cell(a)	Surface Area m ² /g	PFTBA Adsorbed, mmol per gram
Free: Na -]	ze-Dried Laponite		I		269	0.250
0.27	6		0.0336	0.249	283	0.442
0.84	D		0.1003	0.41	278	0.533
2.75			0.327	1.43	341	0.757
6.75			0.800	3.03	488	0.806
10.9	2		1.30	3.62	438	0.892
21.8	6		2.60	5.00	358	0.654
43.78	8		5.20	8.40	331	0.458
84.21	0		6.99	14.1	264	0.156
Free: ACH	ze-Dried		I	I	I	0.045
(a)	The unit	cell	composition of	f the layers in	[M95.64 ^{Li} 0.36 []] (si _{8.00})0 ₂₀ (OH)4.

Q = 0.00 to 84.20 for freeze-dried laponites.

As the value of Q increased, the aluminum content per unit cell increased as expected. The N_2 BET surface areas and perfluorotributylamine (PFTBA) adsorption capacities both traverse a wide range of values. The PFTBA adsorptions and N_2 surface areas are shown in Figure 29 as a function of the aluminum content per unit cell. Both adsorbates exhibit a maximum at approximately 3 Al per unit cell, then a decrease to values similar to sodium laponite (Q=0.00).

Table 20 presents physical properties of some air-dried

	layered with Alu	minum Chlorhydrate.	
mmol Al ³⁺ MEQ Clay	# Al ^(a) per unit cell	Surface Area (m ² /g)	PFTBA Adsorbed (mmol/g)
0.00		201	.210
2.75	1.43	425	.794
6.75	3.03	451	.825
10.95	3.62	363	.833

Table 20. Physical Properties of Air-Dried Laponites Interlayered with Aluminum Chlorhydrate.

(a) The unit cell composition is $[Mg_{5,64}Li_{0,36}]Si_8O_{10}(OH)_4$.

laponites. Their surface areas and PFTBA adsorption capacities are consistent with those obtained for freeze-dried materials.

The dependence of the apparent pore size of intercalated chromium clays upon drying conditions was explained in terms of a delaminated model in Chapter III, p. 45. This same model, used to explain the differences in adsorption of



Figure 29. Physical Properties of Freeze-Dried Laponite Interlayered with Aluminum Chlorhydrate as a Function of Aluminum Ions Per Unit Cell.

hydrocarbons on air-dried and freeze-dried chromium pillared clays, may now be invoked to explain the observed similarities and differences in air-dried and freeze-dried laponite interlayered clays.

The layer flocculation model previously presented⁴¹ differentiates three distinct modes of layer aggregation: face-to-face, edge-to-edge, and edge-to-face association of platelets. These arrangements are depicted schematically in Figure 30. The central panel represents a flocculated clay product. The stippled regions represent face-to-face pillared aggregates, whereas the unstippled regions represent delaminated aggregates produced by edge-to-face associations of platelets.

If the flocculated clay is freeze-dried, the mixed laminated/delaminated structure tends to be preserved as the solvating water is sublimed. As will be shown later for montmorillonite, this produces a "broad pore" type pillared clay product. If the flocculated clay is allowed to air-dry at ambient room conditions, then the surface tension forces between clay platelets tend to aid in reorganizing the clay platelets as face-to-face aggregates. In this manner the surface tension forces aid in increasing or optimizing the face-to-face aggregation which produces a "narrow pore" type pillared clay.

The behavior of laponite, a small particle, low layer charged synthetic smectite, may be reconciled in terms of the layer flocculation model presented above.

Laponite has a lath-shaped morphology and a layer





Structure of the flocculated clay is largely preserved by freeze drying. Face-to-face layer stacking occurs over > 4 layers. Typically two orders of $00 \not \ x$ -ray reflections are observed. The delaminated fraction is responsible for adsorption of large molecules. Bulk density is low. Surface tension forces of liquid water during air-drying enhances the extent of face-to-face layer ordering. Ordering occurs over tens of layers and essentially all layers are ordered (pillared). Pore structure is regular. Multiple orders of 00 k r-ray reflections are observed. Bulk density is high.

Figure 30. A Layer Aggregation Model for Air-Dried and Freeze-Dried Pillared Clays with a Particle Size $< 2\mu$.

diameter of 10 to 100 Å as specified by the manufacturer. The aspect ratio of laponite (ratio of platelet width to height) is small and does not vary appreciably. Clay layers with a large aspect ratio should tend to aggregate in a face-to-face manner, while a small aspect ratio clay, such as laponite, should facilitate the formation of edge-face and edge-edge interactions⁸⁰. This hypothesis is supported by the XRD pattern of air-dried Na⁺-laponite purged at 350°C (cf. Figure 28). The peak present at ~4 degrees 2θ represents the pillaring of sodium laponite through edgeface or edge-edge interactions as expected on the basis of its small particle size and low aspect ratio. Laponite possesses a low layer charge which also plays an important role in layer ordering. As an intercalated clay product air-dries, it progresses through a wide range of states; from sol state, to gel state, to a fully dried state. Variations in charge distributions accompany these variations in states as described below. Initially the flocculated clay product is characterized by a watery dispersed state. This initial state of the polyoxoaluminum-clay complex is analogous to that of typical alkali metal smectites. The platelets carry a surface negative charge as well as a small positive charge on the edges due to disruption of the lat-In dilute solutions the basal surface charges are tice. much larger than the small edge charges and repulsion occurs. This yields a colloidal dispersion which looks and flows like water. This state is referred to as a sol. As the ionic strength of the solution increases (due to solution

evaporation) the surface negative charge is reduced due to association of the negative clay platelets and the cations in solution. The repulsion between platelets is reduced and the dominating force becomes the face-to-edge interactions, causing the formation of a gel. This is referred to as a "house-of-cards" structure.

As laponite air-dries, clay platelet reorganization resulting from surface tension forces are operative while the solution is still in the sol state. This helps to increase face-to-face interactions over face-to-edge interactions. Laponite undergoes the transformation to a gel state much faster than other large particle or high layer charge smec-This rapid gel formation impedes the quantitative tites. formation of face-to-face aggregates by essentially "locking" the clay platelets into whatever random association they exhibit at the onset of the gel state. This "locking" phenomenom is schematically represented in Figure 31. A clay following this drying track would eventually exhibit OOL reflections which are very broad and poorly characterized, representing a large array of pillaring interactions (cf. Figure 28).

Laponite was also pillared with a freshly prepared basehydrolyzed aluminum chloride solution at r = 2.00. These materials were processed in a similar manner to that of the ACH pillared materials. All samples at r = 2.00 were freezedried. As the following results will show, differences in pillaring solution lead to clay products with different Al contents, but similar physical properties.




Freeze-drying preserves the structure of the flocculated clay. Face-to-face layer association or pillaring is short range (< 4 layers). $00 \pounds$ x-ray reflection is very diffuse to non-existent. Structure is extensively delaminated. Delamination results in formation of macro- and meso-pores. Surface tension forces encountered in airdrying enhance the extent of face-to-face aggregation at the expense of delamination. but the structure is largely delaminated.

Figure 31. A Layer Aggregation Model for Air-Dried and Freeze-Dried Pillared Clays with a Particle Size <500 Å.



Figures 32 and 33 depict XRD patterns for r = 2.00freeze-dried laponite products after being heated at 25°C and 350°C, respectively, for 2 hours in argon. These patterns are similar to those obtained for ACH-laponite. Distinct OOl reflections are present only in Q = 0.283; the remaining series members exhibit very broad, weak, OOl reflections. At 350°C, Q = 0.283 exhibits the "self-pillaring" OOl reflection that is also seen in Na⁺-laponite, as well as ACH-laponite, indicative of edge-plane and edge-edge interactions.

Table 21 presents analytical data, N₂ BET surface areas, and PFTBA adsorption capacities for r = 2.00 aluminum interlayered laponite products. The surface areas and PFTBA uptakes are consistent with those values obtained for ACHlaponite. The aluminum content per unit cell is considerably lower with r = 2.00 than with r = 2.50 (ACH). This is due to the different aluminum species present in each solution. At r = 2.00, tetrahedral aluminum centers (62.8 ppm resonance) as well as octahedral aluminum monomer centers (0.0 ppm resonance) are both present, with the slight excess of the aluminum present being tetrahedral in nature. In ACH (r = 2.5), there is a small tetrahedral aluminum contribution (62.8 ppm), a larger octahedral aluminum monomer contribution (0.0 ppm), and a detectable amount of octahedral aluminum polymer contribution (10.8 ppm) not present in the r = 2.00 solution. It is conceivable that the high molecular weight aluminum polymer (10.8 ppm) is unable to penetrate the dialysis tubing in which the freshly pillared



Figure 32. X-Ray Diffraction Patterns for Freeze-Dried Laponite Interlayered with Base-Hydrolyzed $AlCl_3$ at r = 2.00 and Purged for Two Hours at 25°C Under Argon.



Figure 33. X-Ray Diffraction Patterns for Freeze-Dried Laponite Interlayered with Base-Hydrolyzed AlCl₃ at r = 2.00 and Purged for Two Hours at 350°C in Argon.

Q mmol Al ³⁺ MEQ Clay	Initial Al Conc.	# Al ^(a) per unit cell	Surface Area (m ² /g)	PFTBA Adsorbed (mmol/g)
0.283	0.0494 <u>M</u>	0.17	245	.400
6.75	0.0655	2.18	404	.875
21.89	0.0784	2.72	278	.883
84.20	0.0784	3.16	334	.850

Table 21. Physical Properties of Freeze-Dried Laponites Interlayered with Base-Hydrolyzed AlCl₃ at r=2.00.

(a) Unit cell composition = $[Mg_{5.64}Li_{0.36}]Si_8O_{20}(OH)_4$.

laponite was washed. This would account for the high aluminun content per unit cell for r = 2.50 (ACH), but not for r = 2.00.

In an attempt to better define which factor, particle size or layer charge, is the dominant one operating in the delamination of laponite, two different smectites have been used. A natural saponite, which has a low layer charge (0.30) close to that of laponite, but normal particle size, and high layer charge 0.03µ particle size montmorillonite (gift of Dr. R.H. Raythatha) were pillared by ACH, dialyzed, and freeze-dried.

Figures 34 and 35 show XRD patterns for the synthetic saponite and small particle montmorillonite, respectively. Table 22 lists analytical data, as well as N_2 BET surface areas and hydrocarbon adsorption capacities for the two pillared clays. As shown by XRD data for each pillared clay mineral, both possess discrete $d_{(OOL)}$ reflections. The surface areas obtained are consistent with pillared montmorillonite, much lower than the surface area of a



Figure 34. X-Ray Diffraction Patterns for Freeze-Dried Saponite Interlayered with ACH and Purged at 25°C and 350°C for Two Hours in Argon.

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Figure 35. X-Ray Diffraction Patterns for Freeze-Dried 0.03μ -Montmorillonite Interlayered with ACH and purged at 25°C and 350°C for Two Hours in Argon.

Table 22. Physical Properties of (A) Saponite, and (B) 0.03µ-Montmorillonite Interlayered with Aluminum Chlorhydrate.

 $\frac{\text{Saponite}}{\text{Unit Cell Composition:}}$ $Na_{0.303}^{[Mg}_{5.03}^{AL}_{0.52}^{Fe}_{0.19}^{I}_{(Si}_{7.51}^{A1}_{0.49})_{20}^{OH}_{4}$ $[A1(OH)_{2.86}^{I}_{2.15}^{[Mg}_{5.03}^{A1}_{0.52}^{Fe}_{0.19}^{I}_{(Si}_{7.51}^{A1}_{0.49})_{20}^{OH}_{4}$ Surface Area (FD) = 222 m²/g at 350°C PFTBA Uptake = 0.320 mmol/g $\frac{0.03\mu - \text{Montmorillonite}}{\text{Unit Cell Composition:}}$ $Na_{1.00}^{[A1}_{2.99}^{Fe}_{0.41}^{Mg}_{0.51}^{I}_{(Si}_{7.77}^{A1}_{0.23})_{20}^{OH}_{4}$ $[A1(OH)_{2.83}^{I}_{5.99}^{[A1}_{2.99}^{Fe}_{0.41}^{Mg}_{0.51}^{I}_{(Si}_{7.77}^{A1}_{0.23})_{20}^{O(OH)}_{4}$ Surface Area (FD) = 46 m²/g at 350°C Benzene Uptake = 0.281 mmol/g PFTBA Uptake = 0.031 mmol/g delaminated clay prepared at the same Q value. The hydrocarbon adsorption capacities are also lower than that obtained with delaminated laponite.

Although saponite has a low layer charge on the order of laponites, the larger particle size apparently forces layer organization upon drying as supported by XRD. Even the small particle montmorillonite possesses some layer order with two OOl reflections. The high layer charge of montmorillonite $(1.00 \ \bar{e}/O_{20} (OH)_4 \text{ unit})$, along with the dialysis washing method, leads to a very large number (5.99) of intercalated aluminum ions per unit cell. It may be concluded from these results that a low layer charge along with a small particle size significantly affects the delamination process.

To briefly summarize this section:

(1) A complete or nearly complete delaminated clay structure may be produced by the reaction of polyoxocations with clays possessing a very small particle size as well as a low layer charge. Air-drying tends to reduce the extent of layer delamination, but it does not completely convert the delaminated materials to pillared or laminated clays.

(2) This new class of delaminated clays possesses a high degree of macroporosity, along with a meso- and microporosity. This combination of porosities present imparts novel adsorption characteristics (along with novel catalytic properties to be discussed later) as compared with conventional pillared clays.

Physical Properties of Products Obtained from Montmorillonite, a Typical Smectite

The previous section discussed the inherent nature of a smectite mineral, namely ways in which its layer charge and particle size dramatically influence the physico-chemical properties of the resulting interlayered clay. This section is concerned primarily with montmorillonite, an intermediate layer charged, normal particle size smectite. This section will show how synthesis parameters, including type and concentration of pillaring solution, washing techniques, and drying techniques are intimately related to the physical properties of the pillared species.

Figure 36 shows XRD patterns for three intercalated clays prepared with different pillaring solutions. Table 23 provides the interlayer composition, N₂ BET surface areas, and PFTBA adsorption capacities for each material. All of the polyoxoaluminum clay products contain between 1.99 and 2.59 aluminum ions per unit cell, all are pillared with $\Delta d_{(OOl)}$ expansions between 6 and 10 Å, and all exhibit high surface areas. It should be noted here that all data were obtained for products which were collected and washed by centrifugation and then air-dried. The PFTBA adsorption capacity for samples II and III are similar. Sample I has a larger lattice expansion at 25°C ($\Delta d_{(OOL)} \cong 9$ Å), but collapses at 350°C ($\Delta d_{(OOl)} \cong 6$ Å). This smaller $\Delta d_{(OOl)}$ spacing prevents adsorption of the bulky PFTBA (kinetic diameter = 10.4 Å) molecule into the clay interlayer.

Figure 37 illustrates the XRD patterns obtained when



Figure 36. X-Ray Diffraction Patterns for Air-Dried Montmorillonite Pillared Products (I) r=2.40, (II) 0.80 g ACH/g Clay and (III) 2.6 g ACH/g Clay Purged for Two Hours at 350°C in Argon.

Table	23.	Effect of Pillaring Montmorillonite	Reagent Upon F	hysical Pro	perties c	f Pillared
Sampl	ف	Pillaring Reagent	Al per Unit Cell	^d (00l) Å (350°C)	S.A. (m ² /g)	PFTBA (Ads. mmol/g)
н		AlCl ₃ /NaOH ^(b) (r=2.40, 0=15.1)	2.59	15.49	235	0.000
II		0.80g ACH/g clay (r=2.50, Q=4.6)	1.99	19.19	322	0.401
III		2.60g ACH/g clay (r=2.50, Q=15.1)	2.27	20.07	369	0.415
(a)	Layeı	Composition = [A12.6	98 ^{Fe} 0.41 ^{M9} 0.56 []]	(Si _{7.85} ^{Al} 0.	15)0 ₂₀ (0	I) 4.

Washed by centrifuge and air-dried. (q)



Figure 37. X-Ray Diffraction Patterns for Montmorillonite Pillared Clays (r=2.50, Q=15.1) Subjected to Various Washing Conditions and Purged for Two Hours at 350°C in Argon. a clay product is subjected to different washing procedures. Samples II and IV were washed by centrifugation until the wash water tested free of Cl⁻ ions. Sample III was airdried, while sample IV was allowed to remain as a sol for an additional three days prior to air-drying. It appeared that sample IV was ordered to a greater degree as supported by the OOL reflections. Samples V and VI, which were washed by dialysis exhibited two OOL reflections, and possess the same degree of layer ordering in their XRD patterns.

Table 24 presents physical characteristics of montmorillonite samples III through VI. The unit cell composition ranges from 2.27 to 4.24 aluminum ions per unit cell. Samples III and V clearly illiustrate that dialysis washing of the polyoxoaluminum clay product produces a greater amount of aluminum per unit cell than washing by centrifuge produces. Sample VI was centrifuged 2 times after it was washed free of excess electrolyte. Approximately 0.5 aluminum ions per unit cell were removed, representing ion pairs generated from ACH which were unable to diffuse through the tubing because of their larger size. This implies that all of the aluminum per unit cell was not required to neutralize the negative charge upon the layered sheets. This removal of excess ions dramatically increased the PFTBA adsorption capacity.

Figure 38 illustrates the effect of air-drying versus the effect of freeze-drying upon the XRD pattern of montmorillonite for clays prepared from ACH (r=2.50, Q=15.1), washed by centrifugation with 2.87 Al ions per unit cell.

Tabl	e 24.	Effect of Washing Montmorillonite ^(a)	Method on	the Pnysical	Properties	OF FILLAFEG
Samp	le	Washing Method	Al per Unit Cell	^d (00) Å (350°C)	SA. (m ² /g)	PFTBA, ads. (mmol/g)
III		Cent.	2.27	20.07	369	0.415
IV	t E	Cent. ashed and allowed o age 3 days)	2.30	19.62	265	0.380
Δ		Dialysis (140 h)	4.24	19.13	248	0.037
ΙΛ		Dialysis (Cent. 2x)	3.74	18.39	241	0.247
(a)	Layeı	: Composition: [Al	2.98 ^{Fe} 0.41 ^N	⁴⁹ 0.56 []] (Si _{7.8}	5 ^{A1} 0.15 ⁾⁰²⁰	(OH) 4

All samples pillared with ACH (r=2.50, Q=15.1) and air-dried on glass. (q)

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Figure 38. X-Ray Diffraction Patterns for Air-Dried (Glass) and Freeze-Dried Montmorillonite Clay Purged for Two Hours at 350°C in Argon.

These XRD patterns are a consequence of layer ordering, which is induced by surface tension forces as previously explained by the proposed layer flocculation model. Table 25 lists physical parameters associated with pillared clays that have been dried in a variety of ways. Some samples were washed by centrifugation and dried either on glass (sample III), on plastic (sample VIII), or freeze-dried (sample VII). Other samples were washed by dialysis and either dried on glass (sample IX), on plastic (sample XI), or freeze-dried (sample X). When a polyoxoaluminum clay product is washed by centrifugation, the drying procedure does not influence the N2 BET surface area, or PFTBA adsorption capacity to any appreciable degree. Conversely, dialyzed clay products exhibit striking differences in their properties when dried. Montmorillonite air-dried on glass (sample IX) typically exhibits a PFTBA adsorption capacity in the range of 0.040 to 0.128 mmol/g, whereas plastic or air-dried montmorillonite (sample XI) quantitatively excludes PFTBA. Since the clay sol wets the glass more effectively than the plastic, it may be concluded that the contact angle of the sol is smaller on a glass (hydrophillic) plate than on a plastic (hydrophobic) sheet. The glass plate, composed primarily of SiO₂ units, has a smoother, more regular surface than does the plastic (polyethylene) which is "rougher" on a molecular scale. The hydrophobicity and "roughness" of the polyethylene sheet precipitates the molecular sieving activity of sample XI with respect to PFTBA adsorption.



Table 25.	Effect of Drying Co Montmorillonite.	onditions Upon	Physical	Parameters	of Pillared
Sample ^(a)	Drying Conditions	Al per ^(b) Unit Cell	d _{OOL} Å (350°C)	S _A . (m ² /g)	PFTBA Ads. (mmol/g)
III	Centrifuge, Air- Dried (Glass)	2.27	20.07	369	0.415
NII	Centrifuge, Freeze-Dried	2.27	19.62	326	0.422
VIII	Centrifuge, Air-(c Dried (Plastic)	2.27	18.02	343	0.418
IX	Dialysis, Air- Dried (Glass)	4.24	18.79	170	0.128
X	Dialysis, Freeze-Dried	4.24	21.02	103	0.273
ХI	Dialysis, Air- Dried (Plastic)	4.24	18.39	248	000.0
(a) All	samples reacted with r Formula: [A]F	ACH at Q = 15	.1. iAl_	(HO) - 0 (-	

Ţ 20 7.85.40.15 (c) Polyethylene Plastic.



The preceding results indicate that the pillaring solution employed in the synthesis of polyoxoaluminum clays exerts a minimal effect upon the resulting clay. The only significant difference between base-hydrolyzed AlCl₃ (r = 2.40) and ACH (r = 2.50) is the lower thermal stability of base-hydrolyzed AlCl, pillared clays, and its implications for adsorption of large molecules. The washing procedure used for the removal of excess electrolyte exerts a greater influence over the final product obtained. Centrifugation affords a high surface area, and a large PFTBA adsorption capacity. Dialysis methods produce materials with approximately 33% less $\rm N_{2}$ BET surface area and 40% less PFTBA adsorption capacity when dried in an analogous fashion as centrifuged products. The drying procedure, whether airdried or freeze-dried, is also instrumental in determining adsorptive properties of the final product, as referred to in the layer flocculation model.

Physical Properties of Products Obtained with Fluorohectorite Possessing High Layer Charge and Large Particle Size

Figure 39 presents the XRD patterns of fluorohectorite clay interlayered with ACH (samples XII and XIII) along with base-hydrolyzed AlCl₃ (sample XIV) at r = 2.00. The largest $d_{(OOl)}$ spacing is exhibited by sample XII, which was washed by centrifugation. Dialysis washing produced sample XIII, which possessed a higher degree of layer ordering. Sample XIV, which was washed by centrifugation, produced the smallest $d_{(OOl)}$ spacing, presumably due to the inherent thermal stability of pillared clays prepared from base hydrolyzed



Figure 39. X-Ray Diffraction Patterns for Fluorohectorite Interlayered Clay Synthesized at Various r Values (Q=6.46) and Purged for Two Hours at 350°C in Argon.

solution of low r value (r = 2.00).

Table 26 lists synthesis conditions and physical parameters associated with samples XII through XIV. A larger amount of aluminum ions per unit cell were intercalated in dialysis washing (sample XIII) than in centrifuge washing (sample XII) for ACH pillared clays. The surface area $(14.0 \text{ m}^2/\text{g})$ and benzene adsorption capacity (0.411 mmol/g) are correspondingly lower for the dialyzed material as well. Sample XIV, produced at r = 2.00 and washed by centrifugation had the least amount of aluminum ions per unit cell. Sample XIV also exhibited a lower surface area (66.8 m^2/q) and a diminished benzene adsorption capacity (1.00 mmol/g) than sample XII, which was also washed by centrifugation. The high layer charge of fluorohectorite (1.6 $\bar{e}/O_{20}F_4$ unit) facilitates the incorporation of a greater amount of the pillaring oxocation in sample XII than would be required by montmorillonite (cf. Table 23, sample III). Samples XII and XIII exhibited the effect of centrifugation and dialysis washing with respect to their aluminum contents. Sample XIII possessed a lower surface area and a lower adsorption capacity due to the extra 1.08 aluminum ions per unit cell which occupy internal surface area.

The aforementioned physical properties show that as the smectites' layer charge increased, the clay required a greater amount of aluminum ions per unit cell to satisfy the electrical charge of that cell. The increased number of aluminum oxocations per cell in fluorohectorite occupied more interlayer area, and consequently yielded products

Tanta 2	at Various	r Values.				7
Sample	Pillaring Solution	Washing Procedure	^d ool (350°C)	<pre># Al per (c) Unit Cell</pre>	s.A. (m ² /g)	Adsorption Benzene (mmol/g)
XIIX	ACH (a)	Centrifuge	18.8 Å	3.64	149	1.29
XIII	ACH (a)	Dialysis	18.4 Å	4.72	14.0	0.411
XIV	OH/AlCl ₃ ^(b)	Centrifuge	15.5 Å	2.96	66.8	1.00
(a) r:	= 2.50; (b) r =	2.40; both r	eacted at C	i = 6.46.		
(c) La	yer Formula: (M	g4.4 ^{Li} 1.6)Si8	0_{20} F4.			

Physical Properties of Fluorohectorite Interlayered Clay Synthesized Table 26.

with lower N₂ BET surface areas and adsorption capacities than montmorillonite clays synthesized in an identical fashion.

Catalytic Activity of Aluminum Interlayered Smectites

Several workers have carried out catalytic studies on montmorillonite pillared by aluminum polyoxocations. Vaughan⁷⁶ and his co-workers first demonstrated the zeolitic properties of the materials using spray-dried and oven-dried products. Occelli⁴² has also made use of ovendried pillared clay slurries for the selective cracking of gas oil, while Shabtai, et al.^{81,82} have utilized freezedried pillared clays for the cracking of molecules with kinetic diameters greater than 9.0 Å. The results of these workers demonstrated that polyoxoaluminum pillared clays were effective Bronsted acid catalysts. It was of interest to show how the catalytic properties of an interlayered smectite clay were related to the synthesis parameters of the clay.

Dealkylation reactions with cumene (isopropylbenzene) have been used extensively in the petroleum industry⁷³ as a test for Bronsted acidity. This reaction proceeds in the reverse manner of a Friedel-Craft alkylation. Since pillared clays have pore dimensions larger than faujasitic zeolites, β -isopropylnaphthalene (kinetic diameter 10.2 Å) was chosen to probe Bronsted acidity in pillared clays.

Pillared montmorillonites, along with delaminated laponite, were examined as catalysts for the dealkylation of β -isopropylnaphthalene. The reaction was investigated



over a range of weight hourly space velocities (WHSV, 0.27-2.23), contact times (0.6-6.3 sec), and temperature (300-400°C). Coke formation was especially severe for the air-dried pillared clays at higher space velocities and longer contact times.

Table 27 lists the physical characteristics of the catalysts employed in dealkylation (samples XV through XIX) and gas-oil cracking reactions (sample XIX).

Figure 40 depicts the dealkylation activity of pillared montmorillonite (sample XVII) as a function of the reaction contact time. As the catalyst-substrate contact time decreases, the activity increases, along with a decreased $d_{(OOl)}$ spacing observed after reaction. This decreased spacing was caused by the degradation of the pillar by the free protons present in the reaction. The protonation of bridging oxide units present in the pillar and their migration to the silicate sheets where they were condensed and removed as water, facilitated the observed $d_{(OOl)}$ spacing reduction.

Catalytic activity depended on the WHSV as exhibited in Figure 41. As the WHSV decreased, the longevity of the catalyst increased. This behavior is reasonable to expect. As the WHSV is lowered, the grams of substrate per gram of catalyst per hour is decreased, which prevents the saturation of the active sites and allows more efficient catalysis. A reduction in the WHSV also lowered the % C deposited upon the used catalyst. The reduced % C levels are consistent with a decreased pore blockage mechanism that accounted

ble 27	. Phys Studi	ical Properties ies:	of Smectite	Interlayered	Clays	Used fo	r Catalytic
nple	Ø	Pillaring Agent	Drying Conditions	Al per ^(c) Unit Cell	d_00 <i>k</i> (Å)	S.A. (m ² /g)	PFTBA, Ads. (mmol/g)
	15.1	AlCl ₃ /NaOH ^(a)	AD	2.52	18.5	235	0.00
н	15.1	AlCl ₃ /NaOH	FD	2.52	17.0	210	0.35
II	15.1	ACH (b)	AD	2.87	18.5	378	0.00
III	15.1	ACH	FD	2.87	17.7	284	0.43
×	21.89	ACH	FD	5.00	1	358	0.65
) r =	2.42,	generated from h	base hydroly	zed AlCl ₃ .			
) r =	2.50,	ACH.					
) Com	positio	n of Layers:					
Sam	ples (X	V-XVIII): [Al ₂	$.98^{Fe}0.41^{Mg}o$.56 []] (Si _{7.88} ^{Al}	-0.12)0	₂₀ (он) ₄ .	
Sam	ple (XI	X): [Mg _{5.64} Li ₀	.36 []] (Si _{8.00})	о ₂₀ (он) ₄ .			

•

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% Conversion

 $\beta\text{-}isopropylnaphthalene Dealkylation Conversion Dependence as a Function of Reaction Contact Time.$ Figure 40.

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for increased activity as the WHSV is lowered.

A useful comparison of dealkylation properties for all five catalysts listed in Table 27 could be obtained at a WHSV of 0.27, and a contact time of 0.61 sec.

Figure 42⁴¹ illustrates the results obtained for the dealkylation of β -isopropylnaphthalene at 300°C over airdried and freeze-dried pillared products formed from base hydrolyzed AlCl₃ (Samples XV and XVI) and ACH (Samples XVII and XVIII) as pillaring reagents. Included in the figure are the results obtained for delaminated laponite (Sample XIX). Curves very similar to those in Figure 42 also were observed for the dealkylation reaction at 400°C.

The choice of pillaring reagent has little effect on initial cracking activity, the conversions being in the range 90 to 100% in all cases. However, the method used to dry the products significantly affects catalyst longevity. The two air-dried products exhibit decreasing activity with increasing reaction time, but the freeze-dried pillared products, along with delaminated laponite, are stable over the range of reaction time investigated.

The catalytic instability of the air-dried pillared catalysts may be related to the formation of coke on the reactive surfaces. The wt. % values listed in Figure 42 give the carbon contents of the catalysts following the 105 min. reaction times. Somewhat more carbon is deposited on the air-dried pillared clays than on the corresponding freeze-dried products. Relative to the pillared catalysts, delaminated laponite exhibits the least tendency to form



Figure 42. Catalytic Dealkylation of β-isopropylnaphthalene by Air-Dry (AD) and Freeze-Dry (FD) Forms of Pillared Montmorillonite (Samples XV-XVIII), and by Delaminated Laponite (Sample XIX).


coke.

The results illustrate that dealkylation reactions, due to the nature of the products obtained, do not adequately probe the structure sensitivity of pillared clays. Delaminated laponite, synthesized at Q = 21.89, was probed by the catalytic cracking of gas-oil⁴³ in an attempt to elucidate details of its pore distribution not obtainable from β -isopropylnaphthalene dealkylation.

The lack of long-range layer stacking in a delaminated clay is indicated by the absence of distinct OOl x-ray reflections⁴¹. The absence of such reflections, however, does not preclude the possibility of short-range layer ordering over a few clay sheets. If short-range layer ordering does occur, it should be reflected in zeolite-like catalytic selectivity for the delaminated clay.

Catalyst testing was performed by Dr. M.L. Occelli at the Gulf Research and Development Company, Pittsburgh, PA. Catalyst evaluation was performed using microactivity tests (MAT) similar to the one described by Ciapetta and Anderson⁸³. The following reaction parameters were used: space velocity, 15; contact time 80 sec.; temperature 515°C; catalyst-to-oil ratio, 2.5. The feed stock was a gas-oil with a 260-426°C boiling point range. The same gas-oil was used previously to evaluate the cracking activity of a montmorillonite pillared by aluminum chlorhydrate⁸⁴. The deactivation of the delaminated clay catalyst was accomplished by passing dry air or a mixture of 95% steam - 5% N₂ over the catalyst for 6 hours at temperatures in the 300-600°C range. The

commercial catalysts used as references were treated with steam at a higher temperature or for longer periods of time to obtain the desired conversion level.

The activity of our delaminated clay catalyst for gas oil cracking is similar to the activity of an amorphous AAA-alumina catalyst (78% SiO₂, 22% Al₂O₃). However, the selectivity of the delaminated clay catalyst more nearly resembles the selectivity of a commercial zeolite-promoted FCC catalyst. The zeolite-like activity is indicated by the gasoline yields for conversions in the 54 to 67% range. As shown in Figure 43, the C_5-C_{12} yields for the delaminated catalyst are in the same range as the commercial FCC catalyst and significantly greater than those obtained with amorphous AAA-alumina.

As shown in Figure 44A, the yields of light cycle gas oil (LCGO) obtained with the delaminated clay are higher than those obtained with either the AAA-alumina or the commercial FCC catalyst. The enhanced LCGO yields are accompanied by low slurry oil (SO) yields, as illustrated by the results presented in Figure 44B. Thus, the delaminated clay converts more of the heavier gas oil components to the more desirable LCGO fraction. The selectivity of the delaminated clay toward gasoline and LCGO occurs without increasing the yield of light gases. This result is illustrated by the yields of propane and propylene in Figure 45 and by the

Hydrogen and carbon yields are provided in Figures 47 and 48, respectively. The hydrogen yields for the





Figure 43. Gasoline $(C_5 - C_{12})$ Yields Obtained with Delaminated Clay (\bullet), AAA-Alumina (\blacksquare), and Zeolite-Promoted FCC (Δ) Catalysts.



Figure 44. (A) Light Cycle Gas Oil (LCGO) Yields and (B) Slurry Oil (SO) Yields Obtained with Delaminated Clay (●), AAA-Alumina (■), and Zeolite-Promoted FCC (△) Catalyst.



Figure 45. (A) Propane and (B) Propylene Yields Obtained with Delaminated Clay (●), AAA-Alumina (■), and Zeolite-Promoted FCC (△) Catalyst.



Figure 46. (A) n-Butane, (B) i-Butane, and (C) Butenes Yields Obtained with Delaminated Clay (●), AAA-Alumina (■), and Zeolite-Promoted FCC (△) Catalysts.



Figure 47. H₂ Yields Obtained with Delaminated Clay
 (●), AAA-Alumina (■), and Zeolite-Pro moted FCC (△) Catalysts.



Figure 48. Carbon Yields Obtained with Delaminated Clay (●), AAA-Alumina (■), and Zeolite-Promoted FCC (△) Catalysts.

delaminated clay are in the range typically observed for both zeolitic and amorphous cracking catalysts. The carbon yields, however, are significantly larger than is typical for a zeolite-type catalyst. In fact, the carbon yields for the delaminated clay are even higher than those for the amorphous AAA-alumina catalyst. The tendency for the delaminated clay to form coke may be related to the macroporosity of this catalyst. Certainly, aromatic molecules can readily adsorb in the macroporous structure. The interactions of the adsorbed aromatics with Lewis acid sites on the dehydroxylated oxocations could facilitate polycondensation of the aromatic centers and the formation of coke.

The selectivity described above for the delaminated clay catalyst is very similar to the selectivity exhibited by a conventional pillared clay for the cracking of the same gas-oil sample under analogous reaction conditions⁸⁴. The pillared clay gave a somewhat lower gasoline yield and somewhat higher light gas and carbon yields than the delaminated clay, but the relative LCGO and SO yields are very similar to those for the delaminated clay. The tendency for the pillared clay to give less gasoline, more light gas and more coke than the delaminated clay is probably related in part to the iron contents of the two catalysts. The pillared clay used to prepare the previously reported pillared catalyst⁸⁴ was a natural montmorillonite with an appreciable structural iron content. In contrast, our delaminated clay is prepared from a synthetic smectite which contains only trace amounts of iron⁴¹. Structural iron in

aluminosilicate catalysts can facilitate the cracking of heavier hydrocarbons to light gases and promote coke formation.

The similar cracking selectivities for delaminated and pillared clay catalysts suggests that the delaminated clay possesses significant two-dimensional zeolitic character. Zeolite-like catalytic properties persist for the delaminated clay despite the presence of macroporosity and the lack of x-ray evidence for long-range layer stacking. The previously proposed "house-of-cards" model⁴¹ for a delaminated clay is consistent with the presence of zeolitelike microporosity, as well as macroporosity. The "houseof-cards" model is shown in Figure 49. Included in the Figure is a model for the structure of a well-ordered pillared clay.

In the delaminated clay model shown in Figure 49A, the extensive edge-to-basal plane interactions lead to the formation of macropores. In addition, some basal plane to basal plane layer stacking takes place, in accord with the zeolite-like cracking selectivity found in the present work. However, the layer stacking is short-range, occurring only over a few (2 to 3) layers (40-60 Å), thus accounting for the absence of discrete OOL x-ray reflections. It should be noted, however, that the intercalated oxocations in these short-range stacked layers may not be as regularly spaced as in a well-ordered pillared clay. Evidence supporting a distribution of micropores in a delaminated clay has been provided previously by Pinnavaia and co-workers⁴¹



B



Figure 49. (A) House-of-Cards Structure for a Delaminated Clay Catalyst. (B) The Long-Range Layer Stacking in a Well-Ordered Pillared Clay. on the basis of physical adsorption data for molecules of different kinetic diameters.

In contrast to the short-range layer ordering which occurs for a delaminated clay, the layer stacking in a wellordered pillared clay occurs over a much longer range (cf. Figure 49B). Also, the spacing of pillars is quite regular. Thus, a pillared clay exhibits several OOL x-ray reflections, along with well-defined molecular sieving properties. However, well-ordered pillared clays lack the macroporosity and facile diffusion properties⁴¹ of a delaminated clay.

Conclusions

Two types of polyoxoaluminum solutions, base-hydrolyzed AlCl₃ (r=2.00-2.42), and ACH (r=2.50) have been used as reagents for pillaring Laponite-RD[®], montmorillonite, and fluorohectorite. ACH imparts larger d_(OOL) spacings and greater thermal stability to these smectites than to pillared clays formed from base-hydrolyzed AlCl₃. Selective adsorption studies demonstrate that the method used to wash the exchanged smectite sol, as well as to dry the flocculated clay layers, has a pronounced effect on the resulting pillared products' physico-chemical properties. For montmorillonite and fluorohectorite, centrifuge washing of the reactant sol removes large intercalated species. This leads to final products with a lower # Al bound per unit cell, larger d_(OOl) spacings, larger surface areas, and larger PFTBA adsorption capacities than obtained for dialyzed materials, regardless of the drying conditions employed.

Laponite, which was dialyzed free of excess electrolyte, exhibited two distinct XRD patterns depending upon the drying method employed. Air-dring afforded a material with discernable, sharp XRD patterns, whereas the freeze-dried materials possessed no d (OOL) reflections. The surface areas and PFTBA adsorption capacities were similar for both materials. A clay flocculation model is presented in which both lamellar (face-to-face) and delaminated (edge-face, edge-edge) associations of the layers can occur, depending in part on the morphology and charge of the layers. Layer delamination also has important catalytic consequences, as demonstrated by differences in the sensitivity of air-dried and freeze-dried pillared clays to coke formation in β -isopropylnaphthalene dealkylation. Gas-oil cracking was used to probe the layer orientation in laponite, and showed that short-range order $(40-60 \text{ \AA})$ does exist. This is reflected in zeolite-like cracking selectivities.

APPENDIX

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APPENDIX

Washing Procedures

As was shown by the data presented in Table 24 (cf. p. 115), the method used to wash a pillared clay sol free of excess electrolyte greatly influences the physical properties of the resulting pillared clay. In an attempt to standardize this critical step of the synthetic procedure, a detailed description of dialysis and centrifuge washing, as well as air- and freeze-drying techniques employed in this study are outlined below.

Dialysis washing is accomplished in the following manner. After the appropriate aging period is completed, the pillaring solution-clay sol is transferred to standard cellulose dialysis tubing. The dialysis tubing employed in the preceding studies was supplied by VWR Scientific, Inc., (45 mm x 100 ft.) with a 12,000-14,000 molecular weight cut-off. The filled dialysis tubing was placed in deionized water which was repeatedly changed approximately every two hours during the course of a normal working day. This procedure was continued until all excess chlorine was removed, as checked by the silver nitrate test for chloride.

Centrifuge washing can be accomplished in several ways.

The procedure given below must be followed exactly if one wishes to reproduce any material presented in this dissertation. The centrifuge must be set to maintain its internal temperature at 25°C. The intercalated clay is first separated from the bulk pillaring solution mixture by centrifugation at 5500 RPM for 15 minutes. After the first 1500 ml aliquot is centrifuged, the mother liquid is decanted. Additional pillaring solution-clay sol is added to the tubes without redispersion of the previously sedimented clay. The tubes are again centrifuged for 15 minutes at 5500 RPM. This procedure was continued until all the interlayered clay was collected.

The clay present in the centrifuge tubes was dispersed before removal from the tubes by the addition of 100 ml of distilled water, along with two small stir bars, which were used to break up the sedimented clay through agitation. It should be noted that the sedimented clay must not be resuspended upon a stir plate since this action facilitates pillar hydrolysis causing structural rearrangement. After dispersion, stir bars were removed and the clay suspension was transferred to a 2.0 1 Erlenmeyer flask. The clay was then shaken in a minimum of water to further break up any small clay aggregates remaining. After all the lumps were removed, the solution was diluted to the volume necessary to fill the centrifuge tubes (1500 ml), shaken quickly to produce a homogeneous dispersion, and then transferred to the centrifuge tubes and centrifuged for 15 minutes.

After the centrifuge stopped, the mother liquid was decanted and the clay was again redispersed according to the previous directions. The sequence of centrifugation speeds employed are as follows:

2x at 5500 RPM for 15 minutes
1x at 5000
1x at 4500
1x at 4000
nx at 3500

Once the 3500 RPM speed was reached, the clay was washed at this speed until the decanted liquid yielded a negative silver nitrate test for chloride.

Flocculated clay particles appeared in aluminum systems after four washings, but still contained a considerbale excess of chloride. Typically it took 8 to 10 washings before the silver nitrate was negative. The chromium system generally takes 7 to 8 washings before flocculated particles are noticeable. Since no chlorine was used in chromium cluster synthesis, this system was washed in an identical fashion as the aluminum pillared clays, with the following exception: after flocculated chromium clay particles were present (~7 washings), the clay was washed an additional two times at 3500 RPM.

Drying Techniques

Clay samples were either air-dried on glass sheets or polyethylene film, or freeze-dried. Air-drying was accomplished by dispersion of the washed clay in distilled water at approximately 1 wt. %, which was then spread on the desired drying surface.

Freeze-drying was accomplished in the following manner. The clay suspension (~1 wt. %, 200 ml) was placed in a freeze-drying flask and immersed in liquid nitrogen. Initially, while the solution was cooling down, the flask was swirled to prevent settling of the clay. Once the solution started to freeze, the flask was removed from the liquid nitrogen and rotated at a 45° angle. This action coated the walls of the flask with a thin film of clay. This procedure of immersion and rotation was continued until the remaining clay was frozen.

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