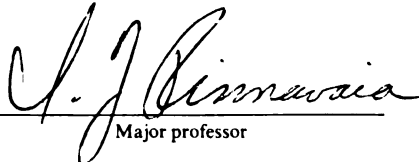




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**ALUMINA PILLARED CLAYS: AN INVESTIGATION OF THE
CATALYTIC PROPERTIES FOR BIPHENYL ALKYLATION**

By

Jean-Rémi Butruille

A DISSERTATION

**Submitted to
Michigan State University
in partial fulfillment of the requirements
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ABSTRACT

ALUMINA PILLARED CLAYS: AN INVESTIGATION OF THE CATALYTIC PROPERTIES FOR BIPHENYL ALKYLATION

By

Jean-Rémi Butruille

Alumina pillared clays are a relatively new class of microporous solid acids. Their catalytic activity has been studied for a variety of chemical conversions, however, the molecular sieving properties of these materials have not been demonstrated as clearly as with zeolites. We have selected the isopropylation of biphenyl as a test reaction for pillared clay catalysts. The study included clays of various charge densities, charge localization and extent of layer stacking. For comparison purposes, the performance of an acid washed montmorillonite and two zeolites were also investigated. Under liquid phase conditions at 250 °C, the reaction was under diffusion control. Thus, the activities and selectivities of the catalysts were mainly dependent on their pore structure. In particular, the mesoporous volume was a critical factor of catalytic activity. This was demonstrated by the study of a series of highly mesoporous pillared clays with similar acidity, obtained by surfactant modification. When isopropanol was used as an alkylating agent instead of propene, hydrophobic alumina pillared montmorillonites were the most efficient catalysts. Catalytic activity was strongly correlated to acidity for alumina pillared clays of similar pore structure. Thus, when calcined at 350

°C, alumina pillared fluorohectorite exhibited greatly enhanced catalytic activity and acidity, whereas calcination at 500 °C resulted in a relatively inactive clay with greatly diminished base chemisorption properties. The effect of the calcination process on the clay layer was studied by ^{27}Al , ^{29}Si and ^{19}F MAS-NMR, FTIR spectroscopy and by mass spectrometric analysis of volatile by-products. It was shown that between 30 °C and 500 °C, specific lattice fluorine atoms adjacent to charged sites in the octahedral layers are replaced by hydroxyl groups. The Brønsted acidity of hydroxyl groups is enhanced by the near-neighbor fluorine at neutral sites in the octahedral sheet. Between 350 °C and 500 °C, a second process occurs that causes dehydroxylation of the layers, and this results in a sharp decrease in the acidity and catalytic activity of the pillared clay. A computational study showed that the thermodynamic orientation was meta, para, whereas the kinetic orientation favored the ortho isomer. Very microporous catalysts, for which diffusion control was strong, favored the thermodynamic distribution whereas mesoporous catalysts favored the kinetic distribution.

**To Astrid,
To my family,**

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INTRODUCTION

Acid catalysis is a field of considerable practical importance. It is involved in many chemical processes worldwide and, in 1989, 44 million tons of sulfuric acid and 12 million tons of phosphoric acid were used industrially, albeit not all for catalysis. Yet, such homogeneous acid catalysts have drawbacks including corrosion, toxicity and effluent pollution. The growing concern for safety and environment has motivated a strong effort to find alternative acid catalysts. Solid acids hold their acidity internally and are thus easy to handle. Their acid strength can nevertheless be very strong, exceeding in some cases by ten times that of concentrated sulfuric acid. Moreover, most solid acids are derived from silicon oxides and can thus be discarded easily. On the whole, solid acids are the environmentally friendly catalysts that are needed.

Several classes of solid acids can be distinguished. Sulfonated resins have been called solid superacids, which emphasize their exceptional acid strength. However, such catalysts are thermally unstable and cannot be used above 200 °C. Heteropoly acids are another class of attractive solid acids.

In these solids, the negative charge of polyoxometalate ions like $\text{PW}_{12}\text{O}_{40}^{3-}$ is compensated by hydronium ions, which provide them with a very strong acidity. However, these structures are mainly accessible to slightly polar molecules which limits their potential use. Zeolites are aluminosilicates with highly ordered crystalline structures. Cavities of a definite size are formed as part of a rigid three dimensional network typically composed of SiO_4 and AlO_4 tetrahedra. The central atom of the tetrahedra in the zeolite lattice can also be occupied by a large number of other atoms such as B, Fe, Ga, Ti and even P. Since the beginning of the 1960s, zeolites have been used extensively as cracking catalysts. They replaced catalysts based on amorphous aluminosilicates and clays, which had been used industrially since 1938. Until recently, the applications of zeolites were limited by their relatively small pore opening. However, recent progress in zeolite synthesis have overcome this limitation. Zeolites with pores in the nanoporous range (1-10 nm) are now currently synthesized and are promised to a wide range of applications.

Owing to their facile synthesis and structural adaptability, pillared clays are also an attractive class of acidic microporous solids for a variety of chemical conversions. The first Chapter of this dissertation is a review of the literature on the physical and catalytic properties of alumina pillared clays. The shape selectivity of pillared clays has been recognized in gas oil cracking and certain alkylation reactions of aromatic compounds. However, the molecular sieving properties of these materials have not been demonstrated as clearly as for zeolites. We have selected the isopropyl alkylation of biphenyl as a test reaction for pillared clay catalysts. Our study included clays of various charge densities, charge localization and extent of layer stacking. For comparison purposes, the performance of an

acid washed montmorillonite and two zeolites were also investigated. Chapter 3 presents the relationships between the catalytic activities of these materials and their physical properties like porosity and acidity. The effect of mesoporosity on catalytic activity is more specifically addressed in Chapter 4. Thus, pillared clays of various mesopore volumes were obtained by surfactant modification and tested for the propene alkylation of biphenyl. A special behavior was observed for alumina pillared fluorohectorite. The acidity and catalytic activity of this pillared clay are dramatically affected by the calcination temperature. We elucidate the structural modifications related to this behavior in Chapter 5. The selectivity of the different catalysts towards the monoalkyl isomers of isopropylbiphenyl is presented in Chapter 6. A computational study of the alkylation reaction shows the favored isomers under kinetic or thermodynamic control. The selectivity of the catalyst can, then, be understood in terms of pore structure.

CHAPTER ONE
ALUMINA PILLARED CLAYS CATALYSTS, A REVIEW

A. Introduction

Pillared clays are a relatively new class of microporous solid acids.¹ They are extensively studied as catalysts for different types of reactions, especially acid catalyzed reactions such as cracking, alkylation or isomerization.²

The term "pillared" has a specific meaning.³ Pillared lamellar solids are intercalation compounds that meet two important criteria. Firstly, the gallery species are sufficiently robust to prevent gallery collapse upon dehydration. Secondly, the pillars are laterally spaced to allow for interpillar access by molecules at least as large as nitrogen.

Clays are two-dimensional aluminosilicates of particle size $<2\mu\text{m}$. The sheet silicates of principal interest in catalysis have edge sharing layers of octahedra ($\text{M}(\text{O},\text{OH})_6$) where M is typically Al, Fe, Mg, Li ... flanked on either sides by corner sharing tetrahedral (SiO_4 or occasionally $(\text{Si},\text{Al})\text{O}_4$) layers. This structure is represented in Figure 1. The 2:1 clays (two layers of tetrahedra for one layer of octahedra) can be further classified as trioctahedral and dioctahedral in which, respectively, 3 and 2 octahedral sites are occupied for one unit cell ($\text{O}_{10}(\text{OH})_2$). A typical neutral formula for a 2:1 dioctahedral clay would be $\text{Al}_4\text{Si}_8\text{O}_{20}(\text{OH})_4$ and for a trioctahedral clay $\text{Mg}_6\text{Si}_8\text{O}_{20}(\text{OH})_4$. However, substitution of atoms within these lattices by atoms of lower valency (Si by Al, Al by Mg and Fe, Mg by Li) usually imparts a net charge to the clay layer. Some idealized formula for typical 2:1 layered silicates are given in Table 1.

Table 1. Unit Cell Formulas for 2:1 Layered silicates.

Mineral group	Dioctahedral	Trioctahedral
Pyrophyllite Talc	Pyrophyllite $\text{Al}_4 \text{Si}_8 \text{O}_{20} (\text{OH})_4$	Talc $\text{Mg}_6 \text{Si}_8 \text{O}_{20} (\text{OH})_4$
Smectites	Montmorillonite $\text{M}_{x/n}^{n+} y\text{H}_2\text{O}$. $[\text{Al}_{4-x}\text{Mg}_x] \text{Si}_8 \text{O}_{20} (\text{OH})_4$ Beidellite $\text{M}_{x/n}^{n+} y\text{H}_2\text{O}$. $\text{Al}_4 [\text{Si}_{8-x}\text{Al}_x] \text{O}_{20} (\text{OH})_4$	Hectorite $\text{M}_{x/n}^{n+} y\text{H}_2\text{O}$. $[\text{Mg}_{6-x}\text{Li}_x] \text{Si}_8 \text{O}_{20} (\text{OH},\text{F})_4$ Saponite $\text{M}_{x/n}^{n+} y\text{H}_2\text{O}$. $\text{Mg}_6 [\text{Si}_{8-x}\text{Al}_x] \text{O}_{20} (\text{OH})_4$
Micas	Muscovite $\text{K}_2 \text{Al}_4 [\text{Si}_6\text{Al}_2] \text{O}_{20} (\text{OH})_4$	Phlogopite $\text{K}_2 \text{Mg}_6 [\text{Si}_6\text{Al}_2] \text{O}_{20} (\text{OH})_4$

In order to achieve electroneutrality, the layer charge is compensated by interlayer cations such as Na^+ or Ca^{2+} . In polar solvents, the layers can be swelled and the interlayer cations become accessible and exchangeable. In 1955 Barrer and McLeod⁴ discovered that the exchange of the smectite counter ions by highly charged, large cations yielded materials with a substantial internal microporous volume. The large cations function as pillars and prevent the collapse of the structure during outgassing (see Figure 2).

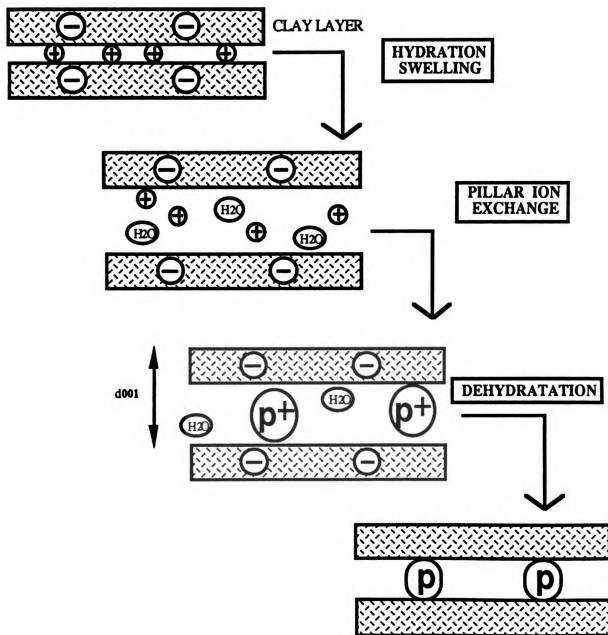


Figure 2. General scheme for synthesis of pillared clays.

This early work utilized organic cations such as tetraalkylammoniums ions which suffered the disadvantage of being unstable above 300°C. The introduction of inorganic pillars in the late 1970s^{5,6,7} afforded much more robust intercalated products, some of which were stable above 500°C. The most effective pillars proved to be metal oxide aggregates derived from polycations of aluminum⁵⁻⁷, zirconium⁸, chromium⁹, iron^{10,11} and titanium¹². The nature of the polycation and the host clay gave rise to different catalytic properties.

We focus here on the most commonly used polycation pillaring agent, the Keggin-like ion $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$, generated by base hydrolysis of an aluminum chloride solution. The hydrolysis chemistry of aluminum has been thoroughly explored and the existence of the " Al_{13}^{7+} " cation was shown unambiguously by such techniques as ^{27}Al NMR and SAXS (Small Angle Xray Scattering).^{13,14,15} Recently, it was shown that upon aging Al_{13} solutions at about 80 °C, dimerization could occur to yield an hypothetical Al_{25} oligomer.^{16,17}

The physical properties of pillared clays that most significantly affect their catalytic behavior are porosity and acidity. These properties are essential to catalytic performance and are best characterized by adsorption and desorption techniques. Several other physical techniques, including X-ray diffraction, elemental analysis, electron microscopy and MAS-NMR spectroscopy are also useful tools for the characterization of pillared clays.

B. Synthesis and characterization of alumina pillared clays

1. Synthesis methods

As with many other heterogeneous catalysts, the synthesis method can greatly affect the catalytic properties of alumina pillared clays.

Differences in porosity or acidity are observed depending on the method used to form the pillaring agent, the method used to dry the products and other processing variables.

The first step in a pillared clay synthesis is the preparation of the pillaring agent. Essentially two methods have been used to prepare the " Al_{13}^{7+} " cation. The first one is the base hydrolysis of an Al^{3+} solution at a OH/Al^{3+} molar ratio approximately between 2.0 and 2.4,¹⁸ with a value of 2.4 preferred. The second method utilizes a commercially available aluminum chlorohydrate solution such as the Chlorohydrol® solutions provided by Reheis Chemical Co of Berkeley Heights, NJ 07922, USA. These latter solutions are formed by the dissolution of Al metal in a solution of AlCl_3 . In addition to the Al_{13}^{7+} cation, they usually contain oligomers with a higher degree of polymerization.¹⁶ The dilution level and aging of the pillaring solution determine the properties of the pillared product.¹⁹ An optimum dilution level of 0.06M has been established for Chlorohydrol®. Lower dilutions levels do not allow sufficient depolymerization, whereas higher dilution levels cause excess depolymerization. In order to obtain optimum pillared clay properties, an aging time of 10 days has been recommended for the diluted Chlorohydrol® pillaring solution.

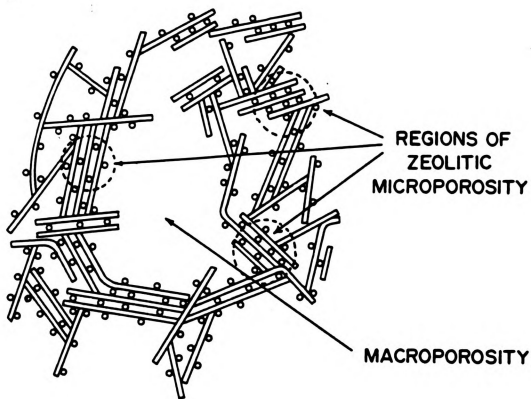
A suspension of the Na^+ clay in water and a solution of the pillaring agent are then mixed, for example, by adding dropwise the clay suspension to the pillaring agent solution. It is usual to use an excess of pillaring agent with regard to the cationic exchange capacity of the clay (approximately 15 mmol Al^{3+} /meq of clay). The excess chloride salt is then removed from the clay by repeatedly suspending the clay in deionized water and centrifuging.

The washing process frees the clay of excess electrolyte, and this results in the flocculation of the clay layers.

The product can then either be freeze-dried or air-dried. Air drying favors face-to-face orientation of the layers, whereas freeze drying tends to preserve the structure of the flocculated clay which exhibits substantial edge-to-face orientations.²⁰ The morphology of the clay layers also plays a decisive role in the layer ordering. Layers with a small aspect ratio like Laponite, a synthetic clay produced by Laporte Industries Ltd, tend to organize by edge-to-face interactions, which results in a card-house structure. On the other hand, typical smectites like montmorillonite have large platelet diameters and organize face-to-face (Figure 3). When no long range face-face order can be observed by X-ray diffraction, the material is said to be delaminated. Delaminated clays and pillared clays have very different pore structures.

Calcination of the air-dried Al_{13} -smectite reaction product at 350°C converts the material to a stable metal oxide pillared derivative. If the product is not calcined soon after preparation, the pillared structure will eventually collapse. Depending on the conditions of humidity and temperature, the decomposition may occur over periods of weeks to months, owing to intracrystalline hydrolysis of the aluminum polycation. Thus, calcination is an important step in producing an alumina pillared clay that is stable toward storage over long periods at ambient conditions. This latter point has, however, been contested recently by Chevalier et al. who found that uncalcined pillared saponite was more stable over a period of 5 months than calcined ones.²¹ This controversy emphasizes the difficulty of comparing pillared clays obtained from different methods. The term alumina pillared clay really covers a wide range of different materials.

a.



b.

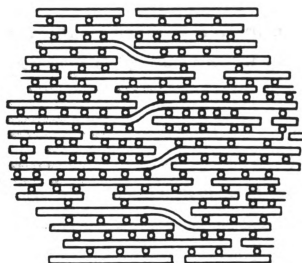


Figure 3. A schematic representaion of
a. Delaminated clay
b. Pillared clay

2 Characterization of pillared clays

a) X-ray diffraction pattern

The quickest way to determine whether pillar intercalation was successful is to record an X-ray diffraction pattern of an oriented film of the product. Such films are formed by allowing a suspension of the product to evaporate on a glass microscope slide. A basal spacing around 18Å indicates right away that pillaring occurred since the layer thickness of a smectite is 9.5Å and the size of the Al_{13}^{7+} Keggin-like ion is about 9.0Å. Oriented film samples favor 00l Bragg reflections. The width at half maximum of the X-ray diffraction peaks can be an indication of the crystallinity of the pillared clay. There are different sources of line broadening.²² Particle-size broadening arises as a consequence of the small size of clay crystallites. The diffraction peak width can be used to estimate quantitatively the particle size, or more precisely, the size of the scattering domain, by the Scherrer equation:

$$L = \frac{\lambda K}{\beta \cos \Theta}$$

where L is the mean crystallite dimension in Ångstroms along the c-axis, K is a constant very near unity and β is the width of a 2Θ reflection at half-height expressed in radians.

There are other sources of X-ray line broadening. Smectite clays exhibit a turbostratic stacking, which means that the layers stack flat (face-face) on each other, but without alignment of the ab planes. This defect can contribute to variations in basal spacing and increase the line-broadening of the 00l reflection. Also, since hydrated pillars prop the layers apart, differences in pillar density or hydration can lead to a distribution of basal-spacings. This distribution may be correlated to the density of the pillars and thus to the cationic exchange capacity (CEC) of the clay. Charge

localization on the layer can also be an important factor in determining pillar distribution. For example, the uncalcined pillared form of a fluorohectorite with a relatively large and localized charge density of 140 meq/100 g exhibits much sharper XRD peaks than an analogous Wyoming montmorillonite with a low and delocalized layer charge of 75 meq/100 g (see Figure 4).

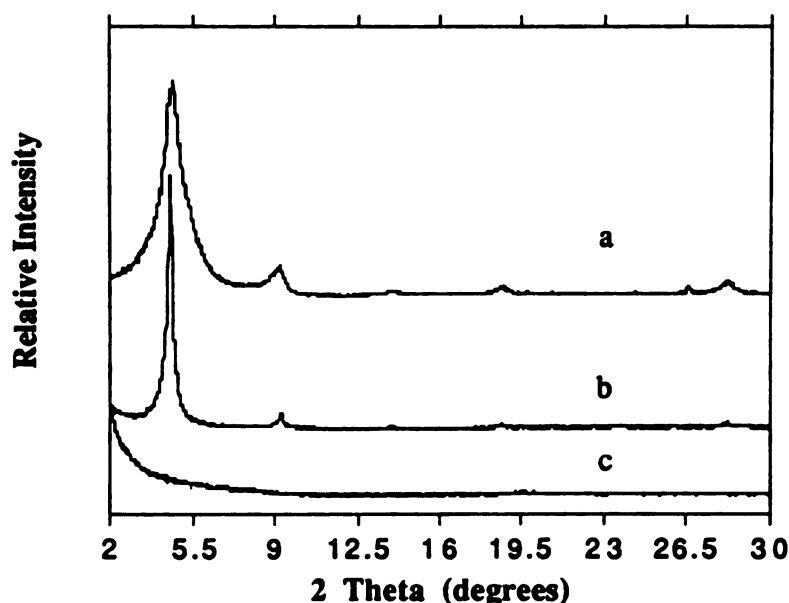


Figure 4. XRD of:
a: uncalcined Al_{13} pillared Wyoming montmorillonite
b: uncalcined Al_{13} pillared fluorohectorite
c: delaminated Al_{13} Laponite

It is also shown in Figure 4 that the Al_{13} reaction products of clays with very small particle sizes (eg., Laponite) can exhibit an amorphous X-ray diffraction pattern. As previously discussed, the absence of X-ray diffraction peaks shows that no long range face-face layer aggregation is present and that the material is an edge-face delaminated clay.²³

b) Elemental analysis

Elemental analysis enables one to determine the amount of aluminum per unit cell that has been incorporated in the clay by pillaring. The first step in this determination is to obtain a satisfactory analysis of the starting clay.²⁴ Several techniques can be used to solubilize the sample for chemical analysis such as fusion with lithium metaborate (LiBO_2) or dissolution in an $\text{HF}/\text{HCl}/\text{HNO}_3$ mixture with a microwave digester. The composition is then analyzed by ICP emission or atomic absorption. It is beyond the scope of this contribution to explain how to obtain a unit cell formula from the elemental analysis. However, this procedure is explained by Newman and Brown.²⁴ Difficulties in determining the unit cell composition can arise from the presence of mineral impurities such as quartz, kaolin, and other fine grain materials, and from inaccurate subtraction of such impurities from the bulk analysis. However, if the clay is carefully purified before use, the impurity phases are usually low and their contribution can usually be disregarded. It is not necessary to obtain a complete unit cell formula to obtain the amount of aluminum incorporated for one $\text{O}_{20}(\text{OH})_4$ unit. This amount can be obtained from the difference in the aluminum content before and after the pillaring reaction. It is given by the following simple formula:

$$N_{\text{Al}} = N_{\text{Si}} \cdot \left(\left(\frac{\text{Al}_A}{\text{Si}_A} \right) - \left(\frac{\text{Al}_B}{\text{Si}_B} \right) \right)$$

where N_{Al} and N_{Si} are, respectively, the number of incorporated aluminum atoms and the number of layer silicon atoms for one $\text{O}_{20}(\text{OH})_4$ unit of the host clay and Al_A , Al_B , Si_A and Si_B are, respectively, the relative molar amounts of aluminum and silicon after and before the pillaring reaction.

c) Electron Microscopy

The structure of pillared clays can be confirmed by lattice imaging using high resolution Transmission Electron Microscopy (TEM), but this is not a routine technique. Basal-spacings observed by TEM are in agreement with XRD results.²⁵ The TEM images can provide information on the long range ordering of the layers and on the defects of these materials. For delaminated clays, TEM is particularly useful, since XRD provides limited information on structure. For example, it was shown by TEM that very small pillared regions containing only a few face-face layers are present in delaminated Laponite. Poorly crystallized alumina can be observed as well.²⁶

d) Pore structure by adsorption-desorption techniques

Adsorption-desorption isotherms of probe molecules can provide quantitative information on the pore structure of pillared clays. The main information obtained from N₂ adsorption is the specific surface area of the sample. Usually, a non-pillared clay exhibits a surface area of less than 50 m²/g whereas a pillared clay has a surface area in the 200-400 m²/g range. The surface area is typically obtained from the adsorption branch by applying the BET equation. However, for microporous solids like pillared clays, the BET equation does not apply over the usual partial pressure range between 0.05 and 0.25, and the Langmuir treatment has then been used by some authors. The Langmuir equation is derived from a very simple model of monolayer adsorption which does not take into account lateral interactions between the adsorbate molecules. This equation usually fits surprisingly well to the adsorption isotherm of microporous solids. However, this does not mean that the Langmuir model actually describes

the adsorption process in the micropores. Since the Langmuir model is very different from the BET model of multilayer adsorption, there is no utility in comparing surface area values derived from these two models. As many workers typically report BET surface areas of solids, it is customary to report BET surface areas for microporous solids like pillared clays. However, one should ensure applying the BET equation in the pressure range where it is valid, *ie.*, where the correlation coefficient is near one. For pillared clays, the range of validity of the BET equation is usually between $P/P_0 = 0.01$ and 0.1 .

The validity of the Langmuir equation is an indication of the presence of micropores. However, it is much more useful to use the t-plot or the α_s -plot methods, which not only indicate the presence of micropores, but also allow one to quantify them.²⁷ The main idea of the t-plot and α_s -plot methods is to compare the adsorption isotherm of a porous solid with a standard adsorption isotherm for the same adsorbate on a non-porous solid. The t-plot is a plot of the adsorbed volume on a sample versus the statistical thickness of the adsorbed layer on the non-porous reference. The values of the standard adsorbate layer statistical thickness, t , are obtained with the help of the BET theory. In the α_s -plot method, the BET theory is not used. The α_s values are the ratios of the number of adsorbed molecules per unit area at P/P_0 to the the number of adsorbed molecules per unit area at $P/P_0 = 0.4$. For a non microporous solid, a plot of the adsorbed volume versus t or α_s will be a straight line passing through the origin. The slope of this resulting straight line is proportional to the surface area. For microporous solids like pillared clays, the t-plot exhibits two regions.

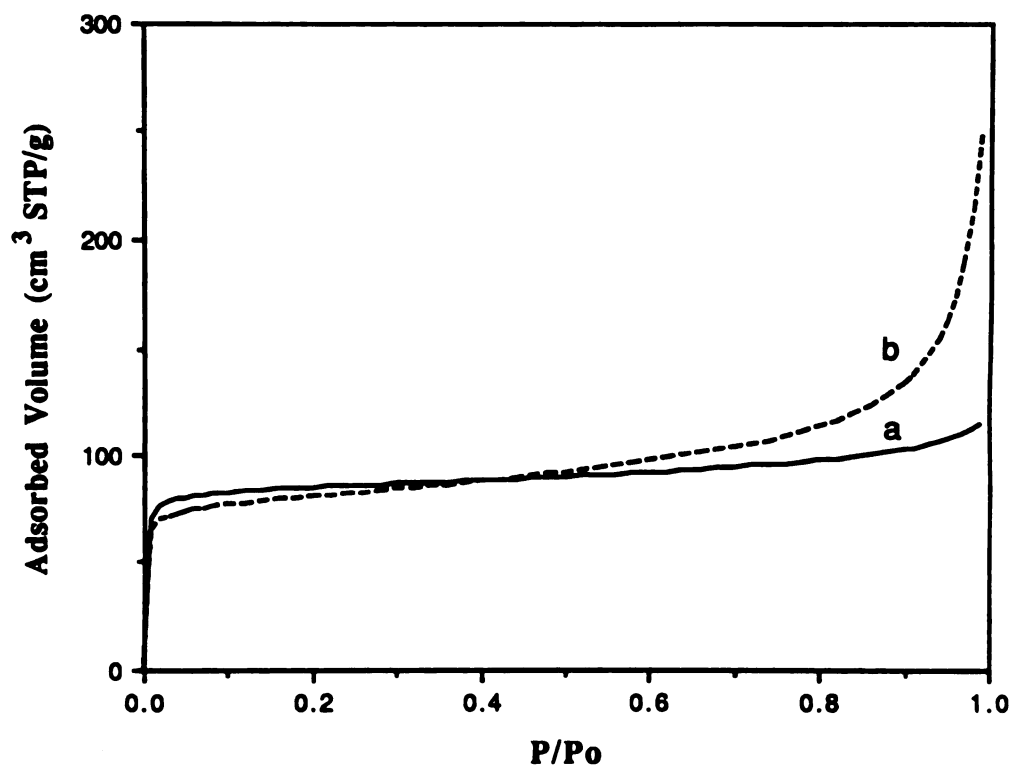


Figure 5: N₂ adsorption isotherms:
a: Calcined (350°C) Alumina Pillared Wyoming Montmorillonite prepared from base hydrolyzed Al³⁺ (OH/Al=2.4).
b: Calcined (350°C) Alumina Pillared Beidellite prepared from aluminum chlorohydrate.

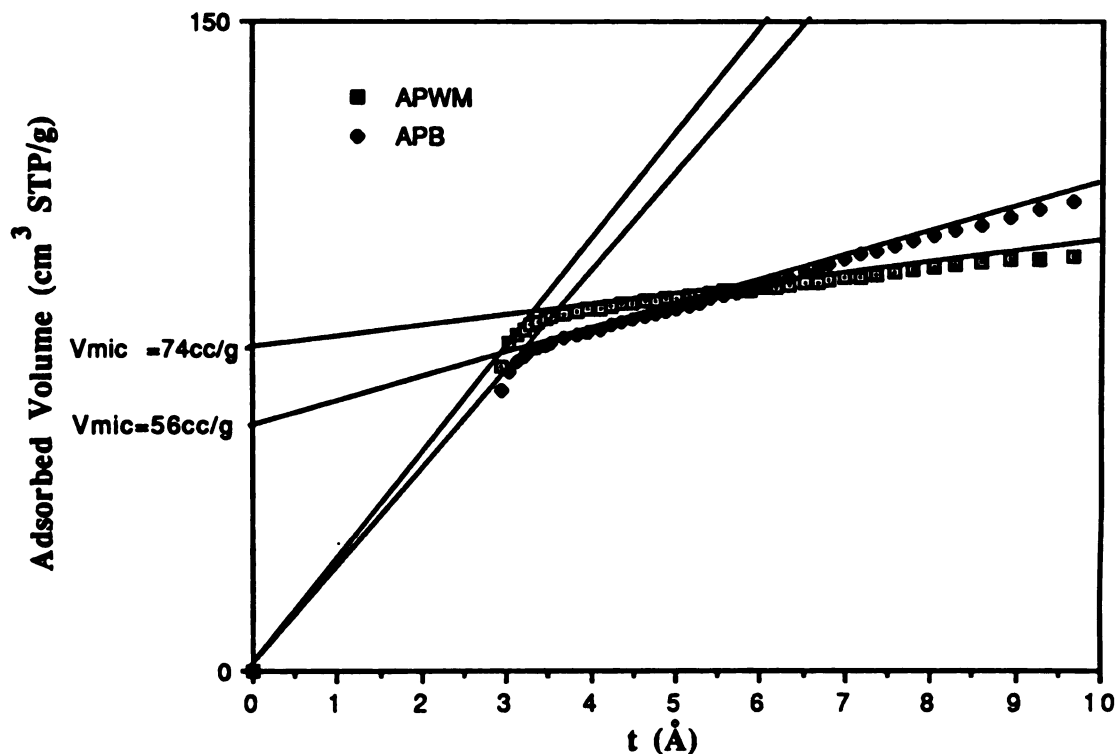


Figure 6: t-plots of N₂ adsorption on:
 Calcined (350°C) Alumina Pillared Wyoming Montmorillonite (APWM) prepared from base hydrolyzed Al³⁺ (OH/Al = 2.4)
 Calcined (350°C) Alumina Pillared Beidellite (APB) prepared from aluminum chlorohydrate.

Figures 5 and 6 display two N₂ adsorption-desorption isotherms and their treatment by the t-plot method. In the first region of the t-plot, the first few data points are fitted to a straight line passing through the origin. The slope of this line yields an equivalent surface area. If the adsorption data are reported in cm³ STP, the surface area is given by:

$$S = \sigma K b_{t_0}$$

where S is the specific surface area, σ is the thickness of a single molecular layer of N_2 molecules ($\sigma = 3.54 \text{ \AA}$), $K = \frac{N_A}{V_{N_2\text{gas}}} \cdot \sigma_{N_2\text{gas}}$ is a constant equal to $4.37 \text{ m}^2/\text{cm}^3$ (N_A is the Avogadro's number, $V_{N_2\text{gas}}$ is the molar volume of a gas, and $\sigma_{N_2\text{gas}}$ is the average area occupied by a molecule of nitrogen in the completed monolayer, $16.2 \cdot 10^{-20} \text{ m}^2/\text{molecule}$) and b_{t0} is the slope of the line passing through the origin of the t -plot (cf., Figure 6).

A second domain of data points below $t=6$ are fitted to another straight line. The intercept of this line gives the microporous STP volume (V_{STP}) which can be converted to a microporous liquid volume ($V_{\text{liq}} = 0.00154 V_{\text{STP}}$) and to an equivalent microporous surface area ($S_{\text{mic}} = K V_{\text{STP}}$). The slope of this second line (b_{t1}) provides the mesopore plus macropore surface area ($S_{\text{meso} + \text{macro}} = \sigma K b_{t1}$)

The sizes of micropores in zeolitic materials have been estimated by adsorption of probe molecules of various kinetic diameters.^{7,20,28} This method can also provide information on diffusion limitations in the catalysts.²⁹ Pillared clays usually exhibit a broader pore size distribution than zeolites. With reliable data for argon or nitrogen adsorption in the low pressure range, one also can estimate the micropore size distribution from the isotherm.³⁰ Vaughan³¹ has reported a micropore distribution centered near $9\text{-}10 \text{ \AA}$ for an alumina pillared clay prepared from Chlorohydrol® as a pillaring agent. The value obtained is close to the gallery height measured by XRD, but it may not be related to the lateral interpillar spacing. A differential plot of the isotherm on a logarithmic scale is also useful to determine pore sizes in the range of large micropores and small mesopores.³²

Most workers favor the desorption branch of an adsorption/desorption isotherm to evaluate the mesopore size distribution.

With pillared clays, a slit-shaped or parallel pore model is appropriate.³³ The mesopore plus external surface areas obtained from this method should be in agreement with the t-plot results.

There is a growing interest in using ^{129}Xe NMR to characterize micropores of solid acids. Some initial work has been reported for alumina pillared clays.³⁴ The apparent pore size ($\sim 10\text{\AA}$) was near the gallery height measured by XRD.

e) Surface acidity

Temperature programmed ammonia desorption has been used to characterize the acidity of solid acids.³⁵ The basics of this technique are simple. After adsorption of ammonia on a sample at about 100°C , the temperature is raised and the amount of ammonia desorbed is recorded by a TCD cell. There is, however, a difficulty. For pillared clays, layer dehydroxylation can occur between 450°C and 500°C . Consequently, the peak for desorbed water can be superimposed upon the desorption peak for strongly adsorbed ammonia. Pre-heating the sample to the dehydroxylation temperature might modify the acidity of the solid. To overcome this problem, it is possible to run a blank experiment for each sample and subtract it from the TPD spectrum.³⁶ Alternatively the desorbed ammonia can be trapped in H_2SO_4 and titrated.³⁷ These methods, however, can be ambiguous, and there is some disagreement among authors about acidity measured in this way. Moreover, NH_3 is a small molecule and might access sites inaccessible to bulkier organic molecules.

Thermodesorption of pyridine observed by IR spectroscopy is a powerful method to study surface acidity of solids because it allows Lewis and Brönsted acidities to be distinguished.³⁸ Pyridine adsorbed on Lewis

acid sites exhibits absorption bands at 1450, 1490, 1577 and 1620 cm^{-1} , whereas for Brönsted sites absorption occurs at 1490, 1545, 1620 and 1638 cm^{-1} .³⁹ Acid strength is estimated by the desorption temperature of the probe. Several methods have been proposed to quantify the Lewis to Brönsted acidity ratio.^{40,41} In order to obtain quantitative amounts of chemisorbed pyridine, it is necessary to know the extinction coefficient for the different absorption bands. Extinction coefficients can be obtained by IR measurements at different levels of measured portions of pyridine. The extinction coefficients determined by Datka⁴² were $\epsilon=0.059\pm0.004 \text{ cm}^2 \mu\text{mol}^{-1}$ for the 1545 cm^{-1} band of PyH^+ and $\epsilon=0.084\pm0.003 \text{ cm}^2 \mu\text{mol}^{-1}$ for the 1457 cm^{-1} of Lewis bonded pyridine. This suggests a 1.4 ratio of the Brönsted to Lewis extinction coefficients, which does not agree very well with the value of 1.1 proposed by Ward.⁴¹

f) ^{29}Si , ^{27}Al and ^{19}F MAS-NMR

The growing use of MAS-NMR of minerals for the last 15 years has enabled a better comprehension of their structure.^{43,44} As noted by Fripiat⁴⁵ in his excellent review of the topic, MAS-NMR is especially useful for characterizing poorly crystallized materials like pillared clays because it is sensitive to short range order. Owing to the MAS-NMR of ^{29}Si and ^{27}Al nuclei, the nature of the pillaring species and their interaction with the clay layer was better understood.⁴⁶ Studies of the transformations occurring during calcination, e.g., crosslinking of the pillar to the layer in the case of beidellite⁴⁶ and fluorohectorite⁴⁷ or proton migration from the pillars⁴⁸ were also greatly facilitated by MAS-NMR.

There are, however, several inherent difficulties associated with the MAS-NMR of clay minerals. First of all, ^{29}Si MAS-NMR is often

preferred to ^{27}Al MAS-NMR because the nuclear electric quadrupole interaction in the latter case can produce very broad NMR peaks for powder samples.⁴³ Also, studies have often been restricted to clays with low iron content because of the line broadening arising from the relaxation effects of paramagnetic centers.⁴⁹

^{29}Si chemical shifts are affected mainly by the nature of the neighboring atoms of its oxygen tetrahedron and the Si-O-Si bond angle. In phyllosilicates where each Si site is linked to three other tetrahedral sites (i.e. Q³ environments), Si atoms with no aluminum atoms as nearest neighbors in the tetrahedral layer exhibit shifts between -99 and -93 ppm, whereas the resonance appears between -85 and -90 ppm when one aluminum atom is a nearest neighbor. This difference in chemical shifts allows one to differentiate beidellite from most other clays since aluminum is present in the tetrahedral layer of this clay. A relationship has also been demonstrated between the ^{29}Si chemical shift and the clay layer charge.⁵⁰ A change in chemical shift towards negative values (higher field) upon calcination of the pillared clay has been attributed to a lowering of layer charge caused by proton migration from the gallery to the layer.⁴⁷

^{27}Al MAS-NMR shows unambiguously the distinction between tetrahedrally and octahedrally coordinated aluminum. Thus, octahedral aluminum appears between 0 and 10 ppm, whereas tetrahedral aluminum appears between 60 and 70 ppm. Relative intensities are, however, very difficult to analyze because the peak shape is very sensitive to the symmetry of the coordination shell. The tetrahedral aluminum atom at the center of the Al_{13} oligomer is observed at 62.3 ppm in uncalcined pillared beidellite.⁴⁶ This strongly supports the hypothesis that Al_{13} is indeed the intercalated species.

^{19}F MAS-NMR has been used more recently has a new tool to investigate fluorinated clays.⁵¹ Due to the high ^{19}F homonuclear dipolar interaction which typically dominates static spectra or spectra obtained at low spinning speed, the use of this spectroscopy was limited until recently. The new development of probes able to spin routinely between 8 and 12 kHz has considerably increased the power of ^{19}F MAS-NMR, which will certainly be very useful.⁵² The range of ^{19}F NMR chemical shifts is very large and enables one to distinguish easily between fluorine atoms in dioctahedral clay and trioctahedral clays, and also between different fluorine sites in a clay layer.

C. Acidity of alumina pillared clays

Alumina pillared clays have been essentially used as acid catalysts. A general knowledge of the nature, strength and stability of their acid sites is thus of critical importance for any catalytic application. The study of surface acidity remains a difficult task because many different factors contribute to acid behavior. Also, there is not any standard parameter which could be used to compare all the solid acids. On the contrary, each technique used to investigate acidity has its own peculiarities, and is often not normalized between different authors. Reviews of analytical methods to determine the acidity of solids, often zeolites, are numerous, reflecting the ever growing interest in this field.^{53,54} They include thermodynamic measurements such as calorimetric methods and temperature programmed desorption methods, spectroscopic methods such as solid state NMR and FT-IR, and theoretical studies. Application of many of these methods to alumina pillared clays have revealed the presence of both Lewis (or

aprotic) and Brönsted (or protonic) acidity in these materials. However, the nature of the acid sites still requires elucidation and further investigation. In his review, Figueras² pointed out that several types of acidity probably coexist in pillared clays, thus complicating the catalytic properties of these materials. Indeed, it is clear that the acidity can originate from the clay layer, from the intercalated species or from an interaction between both of them. We will detail several approaches to study the acidity. First of all, it is very fruitful to study the evolution of acidity with the pillared clay calcination temperature. The acidity originating from the clay can be further studied by varying the nature of the host smectite. Also, varying the pillars density helps in the understanding of the pillar acidity.

1. Evolution of alumina pillared montmorillonite acidity with calcination temperature.

Alumina pillared montmorillonite has been the most studied among pillared clays, it is thus a natural choice to start an investigation of pillared clay acidity. It has been shown by FT-IR spectroscopy of chemisorbed pyridine^{2,36,55,56,57} and NH₃ TPD³⁵ that the acidity of alumina pillared montmorillonite decreases when the calcination temperature is increased from 300 °C to 700 °C. NH₃ TPD indicates that the decrease is mainly due to the loss of strong acid sites. Thus, a remarkable decrease in ammonia adsorption above 400 °C is observed for a sample calcined at 550 °C.³⁶ FT-IR spectroscopy of chemisorbed pyridine or NH₃⁵⁵ allows one to distinguish between the loss in Brönsted and Lewis acid sites. Brönsted acidity decreases much faster than Lewis acidity with increasing calcination temperature. According to some authors^{55,56,58}, Brönsted acidity has virtually disappeared on a sample calcined at about 500 °C, but this is not

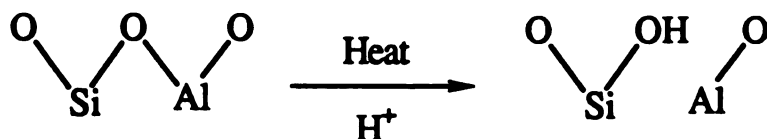
always observed.² He et al.⁵⁵ showed a correlation between the amount of structural hydroxyl groups, as observed from the intensity of the IR absorption band at 3630-3650 cm^{-1} , and the amount of Brönsted acidity, as observed from the IR spectra of adsorbed NH_3 . Indeed, the dehydroxylation temperature of alumina pillared montmorillonite is surprisingly low, typically between 400 °C and 500 °C,^{48,55,58} as compared to the dehydroxylation temperature of montmorillonite, which is between 500 °C and 700 °C. Both dehydroxylation and Brönsted acidity loss occur between 400 °C and 500 °C. This correlation suggests that the structural hydroxyl groups of montmorillonite are the source of Brönsted acidity. The exchange of seven sodium cations by one Al_{13} could probably increase the accessibility of these protons which are usually blocked by interlayer cations. However, a direct evidence for this hypothesis is missing: one should be able to observe a decrease in the intensity of the hydroxyl groups IR band by adsorption of a base, as was demonstrated in zeolites, and this has never been reported. In contrast with Brönsted acidity, Lewis acidity decreases linearly and relatively slowly with increasing calcination temperature⁵⁵.

At a given calcination temperature, the relative strength of Lewis and Brönsted acidity has been studied by pyridine thermodesorption.^{2,36,56} Usually, there is no Brönsted bonded pyridine left at a degassing temperature of about 300 °C. On the contrary, Lewis bonded pyridine is still present after degassing at 400 °C. The Brönsted acidity in an alumina pillared montmorillonite is, thus, relatively weak. The relative weakness of Brönsted sites is compatible with the hypothesis that structural hydroxyl groups are the main source of Brönsted acidity.

The Brönsted acidity of alumina pillared montmorillonite might, however, be very dependent on the catalyst water content. Giannelis et al.⁵⁹ reported that vacuum-dried alumina pillared montmorillonite, which retains 4.5% of water, readily protonates $M_3(CO)_{12}$ ($M=Os, Ru$) clusters. This suggests that alumina pillared montmorillonite is as strong an acid as trifluoroacetic acid or 98% sulfuric acid in these conditions. The adsorbed water undoubtedly plays a role in the clay Brönsted acidity. Upon addition of excess water, the protonation reaction was reversed, demonstrating the leveling effect of physisorbed water on the gallery acidity.

2. Evolution of alumina pillared clay acidity with the nature of the clay.

The acid properties of alumina pillared beidellite and alumina pillared montmorillonite are different, as observed from pyridine thermodesorption. Indeed, the Brönsted acidity of alumina pillared beidellite does not decrease significantly with increasing calcination temperature, in contrast with that of alumina pillared montmorillonite.^{57,58} Also, increasing the calcination temperature to 500 °C yields stronger Brönsted acid sites on pillared beidellite, as observed from the outgassing temperature of pyridine. This stronger and thermally generated Brönsted acidity was correlated with an O-H IR absorption band at 3440 cm^{-1} . In particular, it was shown that as pyridine is introduced on alumina pillared beidellite, the absorption band at 3440 cm^{-1} decreases in intensity whereas the pyridinium absorption band intensity at 1540 cm^{-1} increases simultaneously.¹⁸ Beidellite contains tetrahedrally substituted aluminum like acidic zeolites. It was, thus, suggested that, like in zeolites, a silanol group could be formed by breaking an Si-O-Al bond.



Moreover, based upon ^{27}Al MAS-NMR evidence of the formation of new Al^{IV} site, it was suggested that an inversion of the tetrahedral aluminum site and its cross-linking with the pillar might occur.⁴⁶

A related observation concerning the Brönsted acidity was made by Matsuda et al.⁶⁰ in the comparative study of alumina pillared montmorillonite, saponite and laponite. Alumina pillared saponite exhibited a stronger Brönsted acidity than both of the other pillared clays. Indeed, like with beidellite, the outgassing temperature of Brönsted bonded pyridine was higher than 400 °C on alumina pillared saponite. The effect of calcination temperature was also studied and showed very little change in acidity between alumina pillared saponite calcined at 300 °C and 600 °C.⁶¹ Urabe et al. also reported the presence of stronger acid sites on alumina pillared saponite than on alumina pillared montmorillonite, from NH_3 TPD evidence.⁶² In saponite, there is some substitution of Al^{3+} for Si^{4+} in the tetrahedral layer. Therefore, the interpretation of Brönsted acidity was made by analogy with pillared beidellite, namely that formation of silanol groups by rupture of $\text{Si-O-Al}^{\text{IV}}$ linkages was the main source of Brönsted acidity. It was suggested that tetrahedral substitution in rectorite might originate the same kind of behavior.⁶³

On the contrary, alumina pillared laponite (preferably called alumina delaminated laponite) exhibits at the most very few Brönsted acid sites.^{23,59} It was proposed that the acidity originates from unsaturated aluminum centers on the surface bound alumina. Also, the Lewis acidity in alumina delaminated laponite appeared weaker than that in alumina pillared

montmorillonite. Most of the Lewis bonded pyridine is thus lost at an outgassing temperature of 400 °C with this catalyst. However, it should be emphasized that alumina delaminated laponite is essentially a mesoporous material in which pyridine is not trapped in micropores and might escape more readily from the surface.

3. Evolution of alumina pillared clay acidity with pillars density

Several reports converge to the conclusion that alumina pillared clay acidity increases with increasing pillars density. Three different methods have been used to modify the pillar density. The first one is to use a pillar to clay ratio less than the stoichiometric value. The stoichiometric ratio, assuming Al_{13}^{7+} as a pillaring species, is about 2 mmol of Al for 1 meq of clay. This ratio is quite accurate, since it was reported that the amount of aluminum incorporated in montmorillonite and beidellite reaches a plateau when the initial aluminum content in the pillaring solution is greater than 2 mmol/meq of clay.⁶⁴ Surprisingly, it appears that the clay can be pillared successfully, as evidenced by x-ray and surface area measurements, at ratios below stoichiometry, typically around 1.5 mmol/meq of clay.^{55,65} At this lower ratio, the alumina pillared clay exhibits a high surface area but a lower acidity, according to pyridine desorption or n-butylamine titration. Moreover, pyridine thermodesorption showed that when fewer pillars are present, the acidity loss is mainly due to a decrease in Lewis acid sites.⁶⁵ This suggests that the pillars are the main source of Lewis acidity. A second way to vary the pillar density is to use clays of different layer charge. Clays of different CEC can be obtained by charge reduction using the irreversible fixation of Ni^{2+} cations⁶⁶ or by direct synthesis⁶². In both cases it was evidenced that increasing the clay layer charge helped

increasing the resulting alumina pillared clay acidity, as measured by NH_3 desorption⁶² or pyridine irreversible adsorption⁶⁶. Finally, it was suggested that pillared clays could be reexchanged with Al_{13}^{7+} after their CEC has been increased by ammonia treatment. In this case as well, the acidity increased with the number of pillars.⁶⁷

4. Conclusion

After ionic exchange with the clay counter ions, the Al_{13} pillars have about the same structure as in solution, as evidenced by ^{27}Al MAS-NMR.⁴⁶ It has been suggested⁷ that during calcination of a pillared clay, the pillars dehydrate by the following reaction:



When the tetrahedral layer is not substituted, like in montmorillonite, the protons liberated can diffuse into the octahedral layer. This hypothesis was supported by the upfield shift of the ^{29}Si MAS-NMR signal upon calcination, which is indicative of a layer charge reduction.⁴⁸ These protons do not, apparently, play a significant role in the pillared clay acidity, but they can be brought back by ammonia.^{48,67} The activated pillars are then the main source of acidity which is of the Lewis type. A weak Brönsted acidity is also present arising probably from structural hydroxyl groups. When aluminum substitutes for silicon in the tetrahedral layer, like in beidellite or saponite, the protons liberated react with $\text{Si-O-Al}^{\text{IV}}$ linkages to generate silanol groups which are relatively strong Brönsted sites. Overall, it must be emphasized that the calcination temperature of a pillared clay is a decisive factor for its acidity. The chemistry occurring during the calcination process strongly depends on the nature of the clay layer.

D. Porosity of alumina pillared clays

The goal of pillaring layered materials is to introduce microporosity and to enable permanent access to the layers. The porous properties of alumina pillared clays are thus of primary importance. N₂ surface areas of more than 300 m²/g are currently observed for alumina pillared clays. The contribution of microporous surface area to the total surface area, as calculated from the t-plot, is usually higher than 75%. As we noted earlier, the drying conditions influence surface area and pore structure. Air-dried materials usually exhibit substantially higher surface area than freeze-dried materials, the difference being attributed to the extent of face-to-face arrangement of the layers.²⁰ The particle size of the clay is also an important factor for the pore structure of the pillared product. Thus, clays with small particle size like laponite²³ or certain saponite^{60,62} tend to yield delaminated rather than truly pillared products upon reaction with Al₁₃. This behavior is related to the aggregation mechanism of clay tactoids. Computer simulation showed that the aggregation mechanism produces irregularly shaped particles.⁶⁸

The size of the micropores is relatively difficult to estimate. The height of the micropores, around 9 Å is easily obtained from x-ray diffraction. However, the interpillar distance is difficult to evaluate because pillared clays are non crystalline materials. Adsorption of molecules of various diameters shows that alumina pillared clays exhibit a molecular sieving effect for molecules in the range 8 to 10 Å.⁵⁰ However, this effect might be mainly directed by the intergallery height. N₂ adsorption³¹ and Xe NMR³⁴ can also provide a pore size, but it is again in the range of the

pore height and might not reflect the interpillar distance. X-ray diffraction peaks (in transmission mode) corresponding to the lateral free distance between cations in clays pillared with organometallic complexes were resolved by Tsvetkov and White. This analysis provided an interpillar distance in the range of 12.7-15 Å for montmorillonite and 9.5-10.8 Å for a highly charged fluorohectorite.⁶⁹ In an x-ray diffraction and thermodynamic study of Xe and Kr adsorption in pillared montmorillonite, an interpillar distance of 18 Å was calculated.⁷⁰

E. Catalysis with alumina pillared clays

1. Application to oil refining

The problem of oil refining is a very sensitive one in the modern world. The present refining catalysts (faujasites) are designed for light crude oil. However, since reserves in light crude oil are decreasing and since prices are unstable, there is considerable interest in developing efficient catalysts for heavy crude oil. Pore openings of commercial zeolites have been limited to 8 Å for a long time. More recent developments by Mobil Research have resulted in regularly mesoporous zeolites which may find increased utility for heavy oil cracking, provided they have suitable steam stability.³² The fast development of pillared clays was closely related to this problem: pore openings larger than those of zeolites were expected with this new catalysts (see Vaughan in ref.1). The first results of catalytic cracking with alumina pillared clays were reported by Vaughan et al.⁷¹ and were quite encouraging since the conversion and gasoline yields obtained with pillared clays were competitive with those of faujasite and higher than those of silica alumina. These results,⁷² with similar results obtained by Occelli and Tindwa⁷³ are gathered in Table 2.

Also, Occelli noted that alumina pillared clays yielded more light cycle gas oil than conventional cracking catalysts.⁷⁴ However, as noted in two reviews of the topic,^{2,56} two major problems have been encountered and have up to now deferred any commercialization of these materials. Most pillared clays are selective for coke formation and their hydrothermal stability is low.

Table 2. Catalytic cracking performances of alumina pillared clays.

Conditions		Alumina Pillared Clay	Amorphous Silica-aluminas	REY (commercial cracking catalyst)*	Reference
Heavy oil 510°C	Conversion, vol%	71.0	55.5	73.5	72
	C5 gasoline, vol%	51.5	38.0	58.0	
Light oil 480°C	Conversion, vol%	74.2		70.6*	73
	C5 gasoline, vol%	44.0		47.7*	

a) Coke formation

As noted by Figueras,² several explanations have been proposed for the high coke selectivity of alumina pillared clays. Coke formation might be related to the large pore size of these materials. Horio et al.⁶⁶ reported some evidence that coke formation increases with decreasing pillars density. However, this hypothesis seems to be ruled out by results showing that large pore freeze-dried pillared clays coke slower than small pore air-

dried pillared clays.²⁰ It was also suggested that coking might be related to the relatively high iron content of some alumina pillared clays. Lussier et al.⁷² showed that a H₂SO₄ treatment used for iron removal improved coke selectivity. However, as noted by Occelli et al.⁷⁵ a H₂SO₄ treatment can have many other consequences than iron removal. Tichit et al. noted that coke formation was iron dependent for the cracking of sulfur rich heavy oil.⁷⁶ However, Occelli and Finseth⁷⁷ reported that pillared clay containing 0.3% of iron were generating as much coke as those containing 3 to 5% of iron. It can be argued that this difference originates in the type of oil processed.² Heavy oil is probably more sensitive to the presence of iron because of its high sulfur content. Occelli et al. proposed that the high coke selectivity is related to the strong Lewis acidity of pillared clays, which favors retention of aromatic compounds. A careful study of the relationship between coke formation and iron localization supported this hypothesis.⁷⁵ Thus, it was demonstrated that iron influences coke formation only when located next to the pillars.

b) Hydrothermal stability of alumina pillared clay

Surprisingly, little work was done to understand why the structure of most pillared clay collapse around 700 °C. It is not clear especially if it is due to an intrinsic instability of the pillars in acidic medium, as proposed by Occelli and Tindwa.⁷³ Tichit et al.⁷⁸ studied the sintering of alumina pillared clays. The authors observed that upon calcination above 600 °C, the 060 X-ray diffraction line of montmorillonite shifted from 8.988 to 9.017Å, whereas the same line shifted from 8.988 to 8.928Å in pillared montmorillonite. They suggested that the clay layer is less stable for a pillared clay because protons are introduced into the lattice upon

calcination. This conclusion can be related to the NMR evidence that protons are migrating into the clay layer presented earlier.⁴⁸

The nature of the clay layer is an important factor of the pillared clay thermal stability. Thus, using an interstratified clay, rectorite, Guan et al.⁷⁹ synthesized an alumina pillared product which kept 3/4 of its surface area even after 17 hours of steaming at 800 °C. The authors reported that the cracking activity for heavy crude oil of pillared rectorite was significantly higher than that of REY zeolite (68 vs. 59% conversion). These results were confirmed by Occelli⁶³ who reports that 90% of pillared rectorite initial surface area as well as cracking activity are maintained after 5 hours of steaming at 800 °C. Brody and Johnson⁸⁰ also reported an "extraordinary stability" for alumina pillared rectorite. The stability was very dependent on the rectorite sample, the best result being obtained with a relatively rare rectorite from Jeffrey Quarry, Arkansas. However, Occelli showed that coke formation was still a problem with pillared rectorite. Finally, it was observed that the low particle density of pillared rectorite could be a problem for its commercial application. The enhanced stability of these materials shows that pillars hydrolysis might not be a limiting factor for the stability of pillared clays. Guan et al.⁷⁹ suggested that the more rigid layer structure (two 2:1 layers of oxygen are present in rectorite instead of one in smectites) enhances the pillared clay stability. However, Sterte tried without success to reproduce this result with different illites.⁸¹ Illites exhibit a similar thickness than rectorite but the smectite layer has less beidellitic character. The enhanced stability would thus be a consequence of beidellitic character and increased layer thickness.

Alternatively, it is possible to increase the pillared clay thermal stability by introducing new pillars compositions. Many elements have been used successfully as pillaring agents and it would be beyond the scope of this work to review them thoroughly. We will limit ourselves to examples close to the genuine Al_13 pillar and showing a real improvement in thermostability. Hydrothermal treatment of aluminum chlorohydrate yields positively charged bohemite particles. Porous materials presenting significant cracking activity and thermal stability were prepared by interaction of these particles with montmorillonite.^{82,83} McCauley used hydrothermally treated pillaring solutions containing aluminum chlorohydrate and a cerium salt.⁸⁴ Pillared clays obtained with this procedure exhibit a large basal spacing, typically between 25 and 28 Å. Similar results were obtained by Sterte with lanthanum.⁸⁵ The Ce/Al pillared clays showed a high cracking activity even after steam deactivation at 760 °C. The hydrothermal treatment is critical to obtain stable pillars of large size. González et al.⁸⁶ were not able to obtain a thermally stable Ce/Al pillared clay when they prepared the pillars by base hydrolysis at room temperature of a solution containing Ce^{3+} and Al^{3+} by sodium hydroxide. They nevertheless reported a high activity of their material for the cracking of n-heptane.

Rare earth elements have also been used by a different method to modify the pillared clays. Tichit et al. proposed to exchange a base treated pillared clay with a CeCl_3 .⁷⁶ The base treatment of the pillared clay by K_2CO_3 ⁷¹ or NH_3 ⁶⁶ regenerates partially the clay cationic exchange capacity and allows for a cationic exchange with a rare earth. The modified pillared clays exhibited a surface area of 150 m²/g but no observable d₀₀₁ X-ray diffraction line after thermal treatment at 800 °C.⁷⁶ Similar

observations were made by using lanthanum instead of cerium.^{87,88} The use of calcium or zinc was unsuccessful.⁸⁷ Competitive ion exchange between Al_{13} and NH_4^+ during pillaring also increases the thermal stability of alumina pillared clays according to Figueras et al.⁸⁹

The Ga/Al pillar has been well characterized by NMR.⁹⁰ It consists of a Keggin-like ion in which the tetrahedral position is occupied by gallium and has thus the stoichiometry GaAl_{12} . The GaAl_{12}^{7+} cation is more stable than the Al_{13}^{7+} cation, probably because of an improved size match between the Ga^{3+} cation and the tetrahedral cavity.⁹¹ The pillared clays obtained with GaAl_{12}^{7+} pillars exhibit an increased thermal stability.^{92,93} The surface area obtained after calcination at 700 °C was around 200 m²/g, compared to 110 m²/g for an alumina pillared clay in similar conditions.⁹²

2. Shape selective reactions with alumina pillared clays

Shape selectivity can occur in a porous catalyst when the reactants, transition state, intermediates or products and the pores are of similar size. Several types of interaction can be distinguished, as represented in Figure 7. There is a cage effect when the relative energies of the transition state yielding different isomers are affected by the pore size (Figure 7a). In other cases, different isomers are formed inside the catalyst, but molecular sieving properties of the catalyst favors one isomer (Figure 7b). In this latter situation, the shape selectivity is related to diffusion limitations inside the catalyst particle. These concepts have to be used carefully because shape selective effects can easily be mistaken for diffusion or electronic effects where the micropore size does not really orient the reaction.

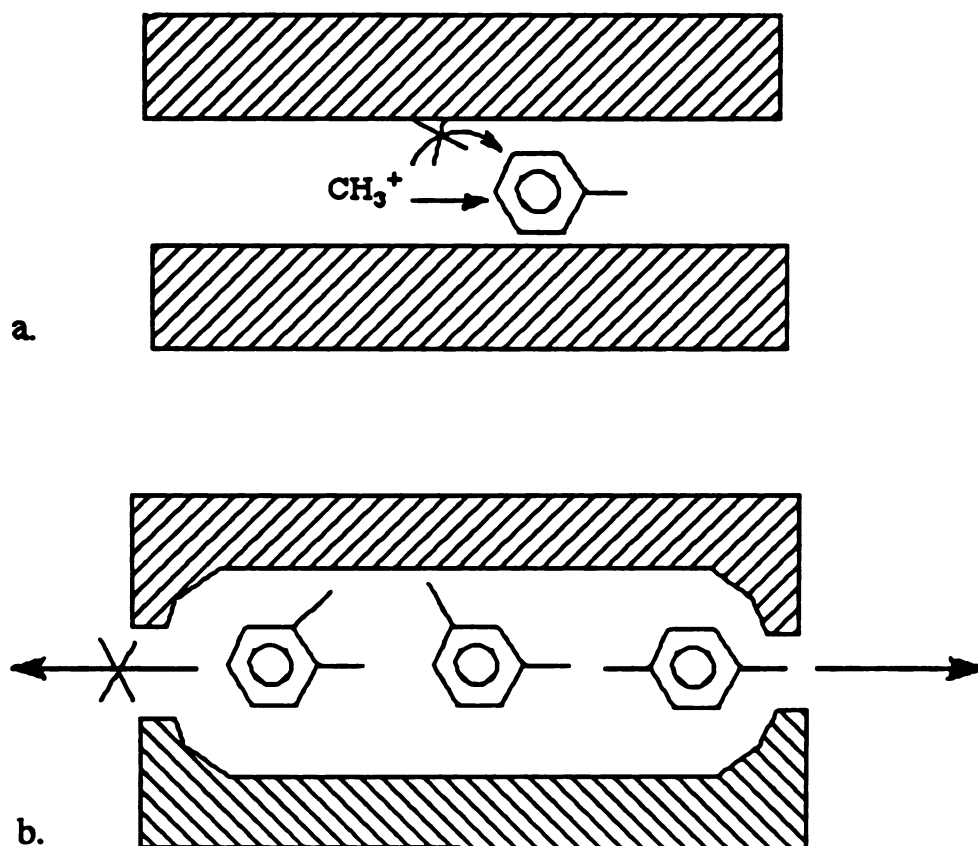


Figure 7. Shape selectivity in porous catalysts

a. Cage effect

b. Molecular sieving effect.

Because of their crystalline pore structure, zeolites are very suitable materials for shape selective catalysis. There is some controversy on whether shape selective reactions really occur in the zeolite channels or at the external surfaces of the zeolite in so called "half-cavities".^{94,95} As observed by Weitkamp⁹⁶, there have been in recent years a renewed interest for shape selectivity. Although in the past most of the shape selective reactions involved mononuclear aromatics and the zeolite H-ZSM5, recent examples of shape selective reactions involving larger molecules and zeolites of larger pore size like mordenite have been demonstrated. Thus, the shape selective formation of 4,4'-

diisopropylbiphenyl over dealuminated mordenite probably evidences a cage effect.⁹⁷

The ca 9 Å gallery height of pillared clays makes them suitable materials to consider shape selective effects on relatively large molecules. Kikuchi and Matsuda have reviewed different reactions for which shape selectivity have been proposed as an explanation of products distribution.⁹⁸ Reactions like oligomerization, esterification or cracking have been used to test shape selectivity. These systems are, however, often chemically complicated and do not usually give solid evidence for shape selective effects. On the other hand, reactions involving aromatic compounds are specially favorable to investigate shape selectivity because they involve mechanistically similar pathways yielding isomers of different sizes.

The 1,2,4-trimethyl benzene disproportionation has been used as a test reaction for alumina pillared clays.

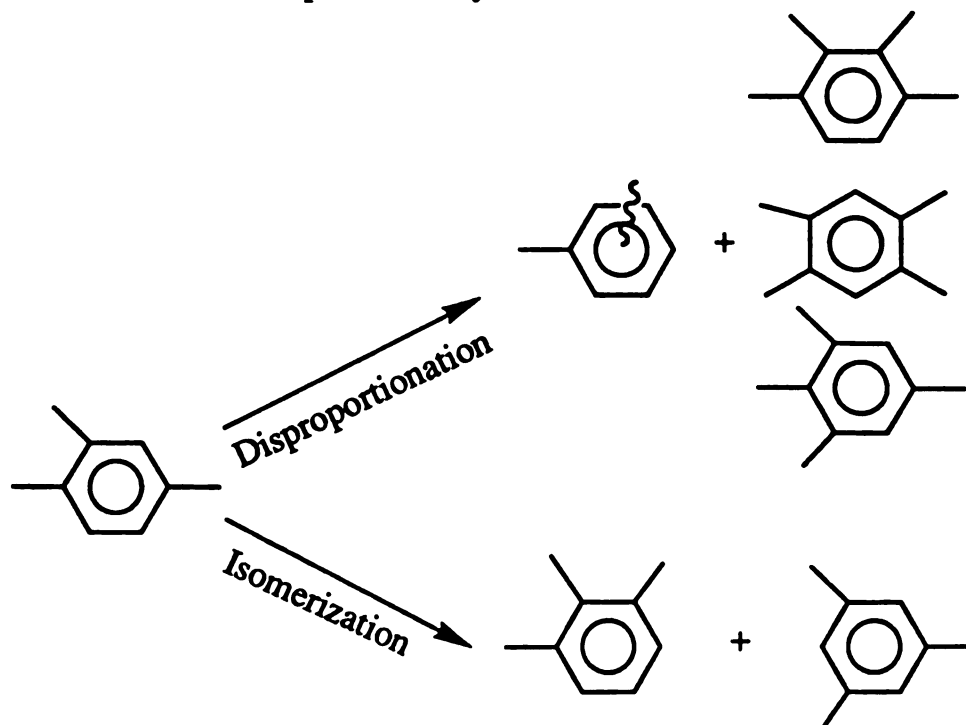


Figure 8. Reaction paths for 1,2,4 trimethylbenzene.

As shown in Figure 8, 1,2,4-trimethylbenzene can undergo two reactions over an acid catalyst: disproportionation and isomerization. Kikuchi et al.⁹⁹ observed that 1,2,4,5-tetramethylbenzene and ortho xylene were formed in excess of thermodynamical levels over alumina pillared montmorillonite. They proposed that a cage effect in favor of the smaller bimolecular transition state leading to 1,2,4,5-TMB was occurring in the micropores. The authors also showed that the selectivity for 1,2,4,5-TMB was enhanced when the gallery height of the pillared clays was decreased.¹⁰⁰ The interpretation proposed by Kikuchi et al. was criticized by Kojima et al.³⁷ who showed that certain non pillared clays gave higher 1,2,4,5-TMB selectivity than pillared clays, ruling out any shape selective effect. They noticed that increased selectivity in 1,2,4,5-TMB was always correlated with decreased selectivity for isomerization and proposed that 1,2,4,5-TMB selectivity is mainly governed by the isomerization to disproportionation ratio, and not by pore size. Indeed, Matsuda et al.³⁶ observed that increasing the calcination temperature of alumina pillared montmorillonite resulted in increased 1,2,4,5-TMB selectivity and decreased isomerization/disproportionation ratio. As we noted earlier, higher calcination temperature mainly affects the Brönsted acidity, which is known to catalyze isomerization reactions. Thus, the 1,2,4,5-TMB selectivity might be in fact mainly governed by the Brönsted to Lewis acidity ratio. Two other examples can be explained by either way. A lower selectivity is observed with delaminated saponite as compared to pillared montmorillonite.⁶⁰ This might be the consequence of the large pores of the delaminated clay or of its higher Brönsted to Lewis acidity ratio. Similarly, the higher selectivity observed with increasing number of pillars⁶⁷ might

be a consequence of the smaller pores or of the higher Lewis acidity in the clay enriched in pillars.

Shape selective effects with alumina pillared montmorillonite were also reported by Mori and Suzuki.¹⁰¹ In this work, the catalytic properties for m-xylene conversion of pillared clays with different lateral distances were studied. The conversion of m-xylene as well as the isomerization to disproportionation ratio increased with increasing pillar density. The authors suggested that isomerization, being a monomolecular process, can occur in smaller pores than disproportionation which is a bimolecular process. However, as we have seen in the previous example, several factors other than pore size can affect the isomerization to disproportionation ratio. Also, the authors compared selectivities at very different levels of conversion which is usually not recommended.

Finally, alkylation of toluene by methanol was also used as a test reaction for pillared clays. Urabe et al.¹⁰² reported that the yield of para-xylene was significantly higher than the thermodynamic equilibrium with alumina pillared saponite. Alumina pillared montmorillonite gave even higher para-xylene yields and this selectivity enhancement was explained by a pore size effect, alumina pillared montmorillonite having a more regular microporous structure.⁶² However, as noted by Horio et al.⁶⁶, differences from thermodynamical equilibrium in this reaction might only reflect a kinetic control of the alkylation reaction in the pillared clay.

It appears from the discussion of the previous papers that no unquestionable example of shape selective reaction with alumina pillared clay has yet appeared. This is not really surprising for two main reasons. First, shape selective effects are difficult to prove even with crystalline zeolites. The pore distribution is broader in pillared clays than in zeolites,

and it will certainly be even more difficult to evidence shape selectivity with them. Also, pillared clays exhibit relatively large micropores and the examples presented deal with mononuclear aromatics which are probably too small to undergo any cage effect in these pores. The use of larger molecules might lead to shape selectivity evidences with pillared clays.

3. Bifunctional catalysis with alumina pillared clays

A lot of chemical transformations involve several steps which need different kinds of catalysis. For example, it is very frequent to need an acid-base step and a redox step in a transformation. The great versatility of pillared clays enable one to design materials in which the properties of the pillars and of the layers are complementary, or where the pillared clay is used as a support for other catalytic centers. As this chapter deals with alumina pillared clays, we will not discuss here the very interesting developments in bifunctional catalysis with chromia, iron or titania pillared clays. However, the incorporation of transition metals in pillared clays is also a very attractive way to combine acidity and redox activity in the same catalyst. We will discuss advances made to use modified alumina pillared clays as hydrotreating or Fisher-Tropsch catalysts.

a) Hydrocracking, hydroisomerization with alumina pillared clays.

The hydrocracking and hydroisomerization of saturated alkanes involve a dehydrogenation step of alkanes on metal center, a cracking/isomerization step of the resulting olefins on acid centers and finally an hydrogenation step of olefins on metal sites. It is thus of interest to design catalysts in which acid centers and metal centers are next to each

other. In order to obtain a bifunctional catalyst, Parulekar and Hightower¹⁰³ used conventional impregnation methods to achieve metal dispersion on a pillared clay. They observed that platinum was poorly dispersed whereas rhenium was highly dispersed by this method. The transition metal accelerated the thermal reduction of the lattice Fe^{3+} to Fe^{2+} , increasing the layer charge. An excess amount of H^+ was present in the galleries to compensate the excess charge, resulting in an increased Brønsted acidity, as observed by pyridine adsorption. The resulting material was an active hydroisomerization catalyst.²⁹ The n-C₆ and n-C₇ hydroisomerization was satisfactorily described by a bifunctional mechanism in which the rate limiting step is the rearrangement of the carbocation, as demonstrated by poisoning experiments. Thus, poisoning of the metal sites by dimethyl sulfide affected the selectivity between cracking and isomerization whereas poisoning of the acid sites by pyridine did not, as expected from this mechanism. Metal impregnated alumina pillared montmorillonite proved to be a very selective catalyst for the formation of single branched isomers. A similar observation was made independently by Schutz et al.¹⁰⁴, who compared Pt loaded pillared montmorillonite and beidellite with USY and H-ZSM5 for n-decane hydrotreatment. The observed sequence for increasing dibranched products was H-ZSM5 < pillared montmorillonite < USY < pillared beidellite. A combination between pore size and acidity effects was suggested to explain this trend. Selectivity for hydroisomerization was very high with pillared beidellite, with a maximum of 70% vs less than 40% with USY.

In industry, however, hydrotreating catalysts are often a combination of two components. The cracking component is classically an acid zeolite and the hydrogenation-dehydrogenation component an alumina hydrate

loaded with a transition metal. Pillared clays have been tested as cracking component and also as metal support.¹⁰⁵ Alumina pillared bentonite was significantly less active than HY zeolite as cracking component. Fast deactivation due to coking was probably responsible for this behavior. When used as metal supports, pillared clays were very efficient components of hydrocracking catalysts in association with zeolites. Deactivation due to coking disappeared and selectivity for light furnace oil was observed. The Ce/Al pillared montmorillonite was also claimed to be an excellent component for midbarrel hydrocracking catalysts ¹⁰⁶

b) Modified alumina pillared clays as Fischer-Tropsch catalysts

The synthesis of hydrocarbons by hydrogenation of carbon monoxide in the presence of acid is an attractive alternative for fuel production. Alumina pillared clays were used as metal supports for Fischer-Tropsch catalysts. Mori et al.¹⁰⁷ used a conventional ion-exchange method to introduce ruthenium in alumina pillared montmorillonite. The resulting catalyst exhibited a relatively poor catalytic activity, but was remarkably selective for the production of C₄-C₁₀ hydrocarbons, compared to silica supported ruthenium. The branched to normal ratio was relatively high, suggesting that the acid sites of alumina pillared montmorillonite were participating in the reaction. In an attempt to molecularly introduce transition metals in the galleries of the pillared clays, Giannelis et al.⁵⁹ reacted M₃(CO)₁₂ (M=Os,Ru) clusters with alumina pillared montmorillonite. The protonation of the cluster by the pillared clay was evidenced by IR spectroscopy. Upon aging, the chemisorbed clusters were converted to the pillar-grafted complex [M(CO)_x(OAl≡)₂]_n. Conversion of the pillar-grafted ruthenium to metallic

crystallite was accomplished at 673K under hydrogen. Electron microscopy studies showed that the ruthenium crystallites were embedded in the pillared clay structure, although they were too large to penetrate the galleries. The Ru/pillared clay material was studied as a Fischer-Tropsch catalyst. The distribution of hydrocarbons followed the Anderson-Shultz-Flory plot. In agreement with Mori et al.¹⁰⁷, the authors observed a high isomerization to normal ratio. The dispersion of the metallic particles in the clay network forced the hydrogenated products to interact with the acid sites of the pillared clay. A comparison of this catalyst with a catalyst derived from ruthenium clusters on a layered double hydroxide support confirmed this hypothesis.¹⁰⁸ Thus, this latter material afforded high yields of oxygenates, specially methanol. The absence of acid sites prevented the conversion of methanol to hydrocarbons. A similar observation was made by Bartley and Burch¹⁰⁹ in their comparison of Cu/ZnO with a Cu impregnated zirconia pillared clay. The Cu/ZnO catalyst produced methanol in high yield. On the Cu supported pillared clay, alkenes and alkanes were formed.

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CHAPTER TWO EXPERIMENTAL METHODS

A. Catalysts preparation

1. Clay preparation

Natural Wyoming and Arizona montmorillonites were obtained from the Source Clay Minerals Repository at the University of Missouri, Columbia, Mo. These naturally occurring smectite clays were first treated with 1.0 N NaCl to ensure complete conversion to the swellable Na⁺ exchanged form. The major impurities (quartz, carbonates, iron oxides) were removed by sedimentation. Typically a 1-2 wt % suspension of the Na⁺ form of the clay was poured into a graduated cylinder and allowed to stand overnight before siphoning-off the fraction of clay remaining in the upper three-quarters of the suspension. Natural beidellite was lithium exchanged to improve its swelling properties and then purified by sedimentation. The synthetic clays Laponite RD, Laponite B (Laporte Industries Ltd.) and fluorohectorite (Corning) were used as obtained from the manufacturer.

2. Pillaring/Delamination reactions

a) Alumina pillared clays

A sodium hydroxide hydrolyzed AlCl₃ solution (0.11M AlCl₃, OH/Al=2.4) aged from one day to several weeks was used as a pillaring agent. The pillaring procedure described by Pinnavaia et al.¹ was used. Aqueous suspensions of clays (1 wt.%) were added slowly at room temperature to the vigorously stirred pillaring solution. Aluminum was present in large excess (15 mmol Al/mequiv clay). The reaction mixture was aged 12 hours at room temperature. The clay usually flocculated. The clay intercalates were then washed free of chloride ion (as observed by

AgNO₃ test) by repeatedly placing the clay in suspension in de ionized water and then centrifuging. The final products were air-dried on glass plates and then calcined 12 hours in air at 350 °C, unless otherwise specified. The heating rate was 10 °C/min. The resulting pillared clays were ground in a mortar and sieved to the desired particle size.

b) Surfactant modified pillared clays

The C₁₂₋₁₄ E₅ non-ionic surfactant, Tergitol 15S-5, was provided by the Union Carbide Corporation. This surfactant, which is a derivative of a secondary alcohol containing 5 ethylene oxide units with the general chemical formula C₁₂₋₁₄-H₂₅₋₂₉-O-(CH₂CH₂O)₅-H, has an average molecular formula of 420 and a specific gravity of 0.961. A quantity of C₁₂₋₁₄E₅ surfactant between 0 and 1000 mg in 500 ml of de ionized water was added to 200 ml of the Al₁₃ solution previously described. The surfactant modified Al₁₃ clay was then prepared by adding dropwise to the pillaring solution 330 ml of a 0.60 wt.% of sodium montmorillonite (1g of clay) under vigorous stirring. The suspension was allowed to age overnight and the product was collected by centrifugation, washed and dried in air. The final alumina pillared products were calcined in a programmable oven at 500 °C for 12 hours in air. At this calcination temperature, the combustion of the surfactant was complete, as observed from C,H analysis. A heating rate of 1 °C/min. was used to reach the calcination temperature. The surfactant-modified pillared clays are referred to, in the text, according to their initial loading of surfactant (S = 0, 200, 400, 800, 1000 mg of surfactant/ g of clay).

c) Al/Ce pillared clay

The Al/Ce pillaring solution was prepared according to the procedure described by McCauley.² A 2.4 molar Ce^{3+} solution was obtained by dissolution of 10.42g of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich) in 10 ml of water. 15.6 g of Chlorohydrol® (23.4 wt. % of Al_2O_3 , 72 mmol Al) and 0.825 g of the Ce^{3+} solution (1.4 mmol Al, Al/Ce mol ratio: 52) were mixed and then refluxed for 96 hours. A precipitate appeared after the third day of refluxing and a gel was formed upon cooling the mixture to room temperature. The gel was dissolved in 276 ml of water and the resulting solution was used for the pillaring reaction. 5g of Li-fluorohectorite (1 wt. % suspension) were added to the Al/Ce solution. The suspension was allowed to age overnight and the product was collected by centrifugation, washed and dried in air. It is worth noting that washing was unusually difficult, 15 washings being necessary instead of 5 or 6 classically.

In another experiment an Al/Ce ratio of 5 was used. With this ratio, no gel formation was observed upon refluxing. However, no significant difference was observed on the pillared product except, possibly, a somewhat larger pore distribution. In the results described in this work, the Al/Ce ratio of 52 is used.

3. Reference catalysts

K10 montmorillonite is a sulfuric acid leached montmorillonite supplied by Aldrich. It was used without further modification. An X-ray diffraction of this material is reported in Figure 9. Two zeolites were obtained from UOP. The acid leached mordenite M8(48) (Si/Al molar ratio of 48) was used without modification but the Y zeolite LZ-Y-84 was

inactive under our reaction conditions. Y zeolites crystallize in the cubic system. The unit cell parameter a_0 was obtained from the d_{533} X-ray diffraction line, by the formula $a_0 = d_{hkl} \sqrt{h^2 + k^2 + l^2} = d_{533} \sqrt{43}$. For LZ-Y-84, $d_{533} = 3.74 \text{ \AA}$, and consequently $a_0 = 24.52 \text{ \AA}$. The range of a_0 for USY is 24.2-24.4.³ Thus, LZ-Y-84 was ammonium exchanged and steamed 3 hours at 750 °C. The resulting catalyst ($a_0 = 24.35 \text{ \AA}$) can be referred to as USY.

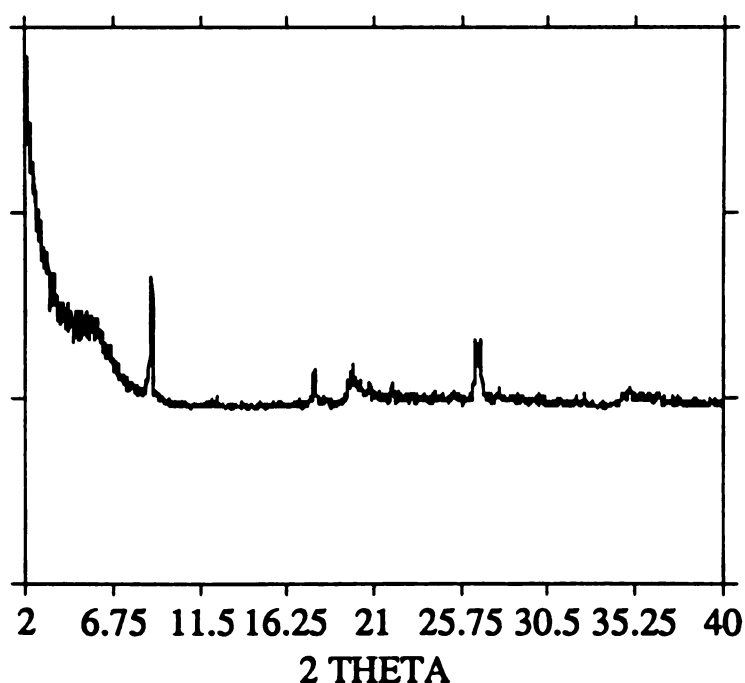


Figure 9. X-ray diffraction pattern of K10 montmorillonite.

B. Catalysts characterization

1. Chemical analyses

Cationic exchange capacities (CEC) were measured according to the procedure described by Busenberg and Clemency.⁴ The clays were ammonium exchanged with ammonium acetate. The amount of ammonia

liberated under strong basic treatment was then measured with an ammonia electrode.

Elemental analyses were performed as described by Pinnavaia et al..¹ A 50 mg quantity of sample was mixed with 300 mg of lithium metaborate and heated for 10 minutes at 1000 °C. The fused product was then dissolved in 3% HNO₃. The resulting solution was analyzed by ICP emission spectroscopy by the MSU Toxicology Laboratory. Carbon analyses were performed by MBI, Lansing, MI or by Galbraith Laboratories, Knoxville, TN.

2. Physical measurements

X-ray diffraction patterns (Cu-K α) of oriented films were obtained with a Rigaku X-ray diffractometer equipped with a rotating anode.

The thermogravimetric curves were obtained on a Cahn TG system 121 analyzer. The starting temperature was held at 30°C for 5 min.. The sample was then heated to 800°C at 5 °C/min..

Continuous flow N₂ adsorption-desorption isotherms at 77K were obtained on a Coulter Omnisorb 360 CX sorptometer. The samples were outgassed at 150 °C for 12 hours under 10⁻⁴ torr.

Temperature programmed ammonia desorption (TPD) curves were obtained for 200-mg samples of pillared clay. The catalysts were outgassed at 350 °C prior to NH₃ adsorption at 100 °C. The catalysts were then heated at 10 °/min. and the molecules desorbed were detected by a thermal conductivity detector.

The FTIR spectrum for chemisorbed pyridine was obtained on an IBM IR44 spectrometer. 25mg self-supported pellets of the catalyst were outgassed one hour at 300 °C prior to pyridine adsorption at 150 °C. A

minimum outgassing time of 16 hours at 150 °C was necessary to remove most of the physically absorbed pyridine. Chemisorbed pyridine was then further desorbed by evacuation at 250 °C and 350° for 45 min. All spectra were recorded at 150 °C. The quantitative results were obtained with the extinction coefficients reported by Datka⁵, from the following formula.

$$c = \frac{A S}{\epsilon w}$$

where c is the pyridine concentration in $\mu\text{mol.mg}^{-1}$, A is the measured absorbance, ϵ is the extinction coefficient ($\epsilon=0.059\pm0.004 \text{ cm}^2 \mu\text{mol}^{-1}$ for the 1545 cm^{-1} band of PyH^+ and $\epsilon=0.084\pm0.003 \text{ cm}^2 \mu\text{mol}^{-1}$ for the 1457 cm^{-1} of Lewis bonded pyridine), S is the area of the pellet ($S = 1.3 \text{ cm}^2$) and w is the weight of the pellet ($w = 25\text{mg}$).

^{29}Si , ^{27}Al and ^{19}F MAS-NMR spectra were obtained on a Varian VXR 400 spectrometer. A Bruker probe was used to spin the samples at 4 kHz for ^{29}Si and ^{27}Al MAS-NMR. A delay time of 480 s allowed full relaxation of the Si nucleus. The chemical shifts for ^{29}Si and ^{27}Al respectively, are reported relative to tetramethylsilane and $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$. ^{19}F MAS-NMR spectra were obtained using a Doty probe with 35 s delay time and a spinning rate of 9 kHz. The ^{19}F chemical shifts are relative to hexafluorobenzene ($\delta(\text{CFCl}_3) = 164.9 \text{ ppm}$ relative to hexafluorobenzene).

The IR-MS results were obtained on a Bruker IFS 88 Fourier transform spectrometer coupled to a Balzers QMG 420 C quadrupole mass spectrometer. This instrument is capable of discriminating masses between 0 and 200. KBr pellets of the solid sample (2.5 wt%) were mounted in a special cell where both the temperature ($-20 \text{ }^\circ\text{C}$ to $1000 \text{ }^\circ\text{C}$) and pressure (10^{-7} torr to atmospheric pressure) could be controlled. The cell windows were polished KBr.

C. Catalysis

1. Alkylation of biphenyl by propene

The alkylation of biphenyl by propene was carried out in a 300-ml batch reactor (n°4561 Parr instruments). Propene was CP grade (Matheson Company), and biphenyl was practical grade (Baker company). The catalysts were used without pre-activation except for the zeolites, which were pre-heated 3 hours at 360 °C under vacuum.

Biphenyl (30g, 0.194 mole) and 0.05g to 0.6g of catalyst were heated to 90 °C. The system was then purged with propene under stirring until the temperature reached 150 °C. The temperature and propene pressure were then carefully increased until they reach the final conditions of 250 °C and 140 psi (9.5 bar). A temperature ramp of 3°/min. was used. The reaction was carried out for 20 hours, unless otherwise specified. The reactor was then allowed to cool and the pressure was slowly released. Eventually, the reaction mixture was dissolved in 300 ml toluene, the catalyst was filtered, and the products were analyzed by gas chromatography.

The gas chromatographic analysis was performed on a HP5890 chromatograph with a 60 m SPB1 column (SUPELCO) and a FID detector. Injection temperature was 290 °C, and the detection temperature was 250 °C. The column was heated from 100 °C to 230 °C at 4°/min. A typical example is shown on Figure 10.

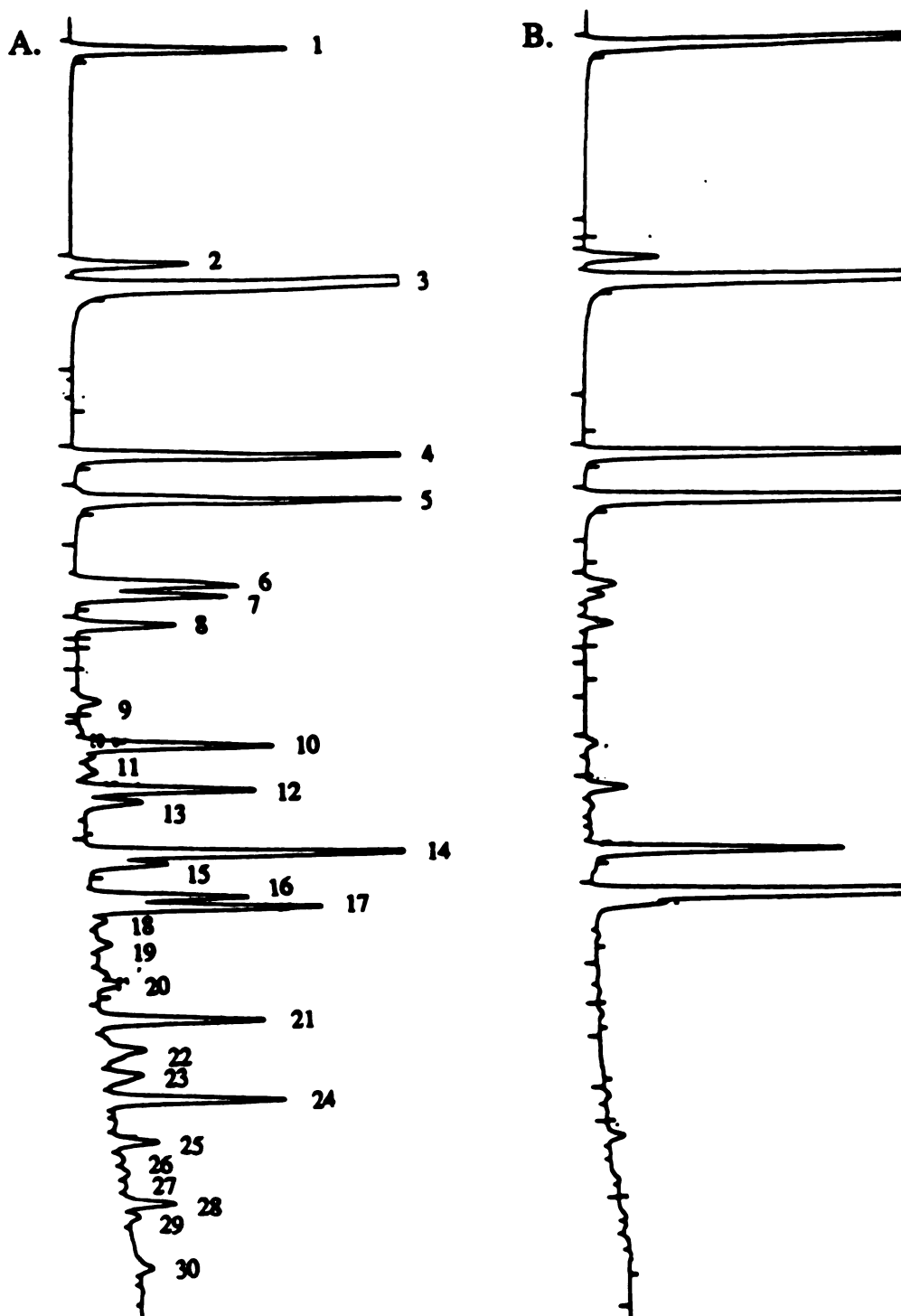


Figure 10. Typical gas chromatograms of the products obtained by propene alkylation of biphenyl. The peak n° 3 corresponds to bibenzyl, which was used as an internal reference. The catalyst used was

A: Alumina Pillared Wyoming Montmorillonite.

B: mordenite M8(48).

The conversion was calculated from the following equation:

$$\text{Conversion (\%)} = \frac{(\text{Biphenyl})_{\text{converted}}}{(\text{Biphenyl})_{\text{unreacted}} + (\text{Biphenyl})_{\text{converted}}} \cdot 100$$

Where $(\text{Biphenyl})_{\text{unreacted}}$ refers to the area of the biphenyl peak in the GC chromatogram and $(\text{Biphenyl})_{\text{converted}}$ was calculated as follows:

$$(\text{Biphenyl})_{\text{converted}} = \sum \left((\text{area alkylbiphenyl}) \cdot \frac{12}{x} \right)$$

where x is the carbon atom number of the alkylbiphenyl considered.

The degree of alkylation was determined by GC-MS (Figure 11). The monoalkyl isomers were identified according to the literature^{6,7} on the basis of their retention times. An attempt to identify the dialkyl isomers was conducted. The propene alkylation of biphenyl by mordenite M8(48) as a catalyst is known for the selective production of the p-p' isomer⁸. The product obtained with mordenite allowed us to identify this isomer (Figure 10). The assignments of the p-p' and m-p' isomers were confirmed by analysis of the pure p-p' and m-p' isomers kindly supplied by the Dow Chemical Company. The retention times of the monochloro and monoalkyl biphenyls are in the same range. We thus used the retention times of the dichlorobiphenyls⁹ to assist in the assignment of the seven dialkylbiphenyl peaks. The proposed assignments are given in Table 3.

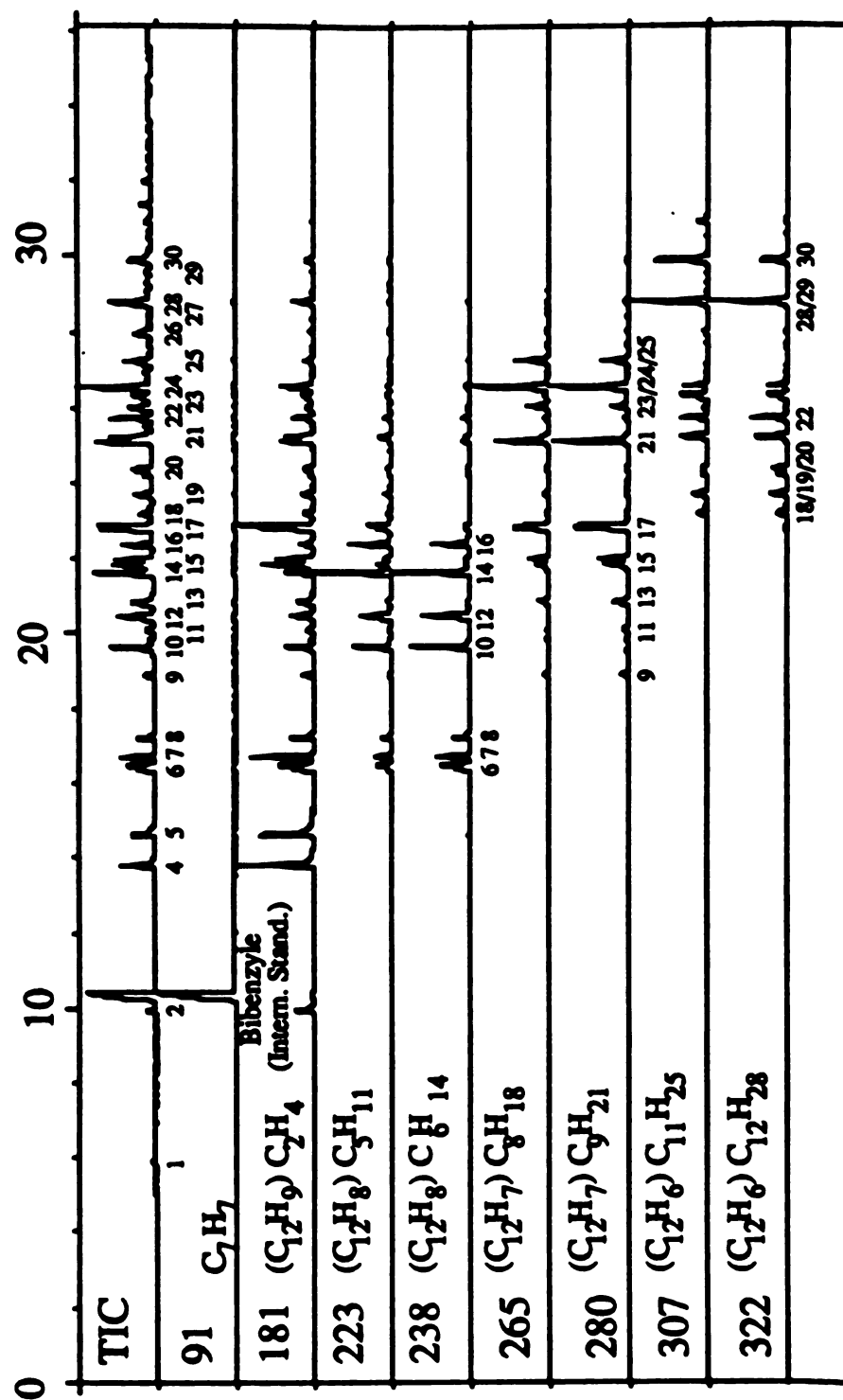
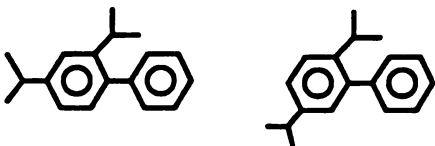
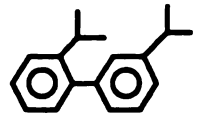
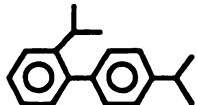
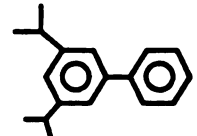
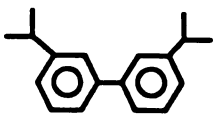
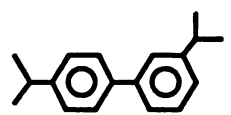
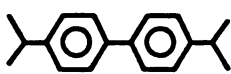


Figure 11. GC-MS analysis of the products, for the masses 91, 181, 223, 238, 265, 280, 307, 322.

Table 3. Assignments proposed for dialkyl biphenyl peaks.

PEAK	ISOMER	FORMULA
6	o-p + o-m	
7	o-m'	
8	o-p'	
10	m-m	
12	m-m'	
14	m-p'	
16	p-p'	

2 Alkylation of biphenyl by isopropanol

a) Isopropanol/biphenyl mixture

We studied the isopropanol alkylation of biphenyl using two different isopropanol to biphenyl ratio. In order to understand this system, it was important to be aware of the thermodynamic properties of the biphenyl/isopropanol binary system. At 250 °C, the vapor pressure of biphenyl and isopropanol are 1 and 80 ATM, respectively. An ideal mixture (following Raoult's Law) of these molecules would give a linear relationship between the mixture composition and its vapor pressure. The corresponding straight line is represented in Figure 12 (dashed line). Biphenyl and isopropanol have very different inter molecular interactions and are not expected to form an ideal mixture. We obtained two different experimental vapor pressures of the mixture in order to draw the vapor pressure to composition relationship in Figure 12 (solid line).

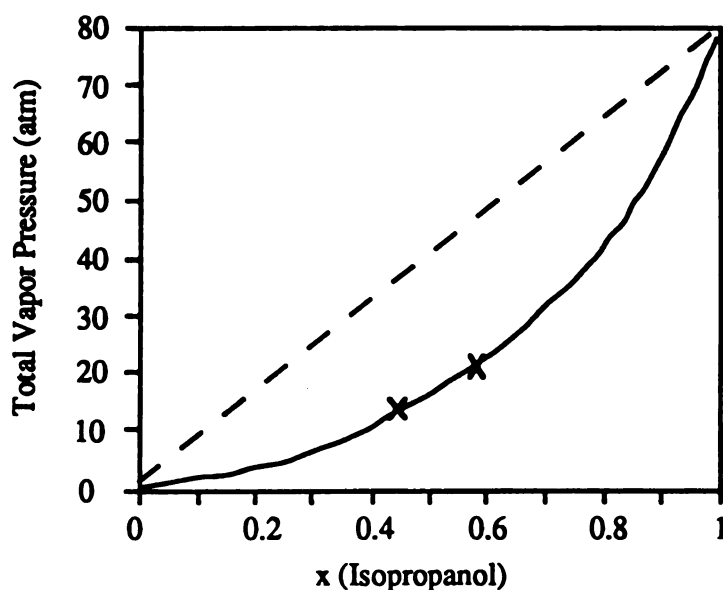


Figure 12. Vapor pressure to composition relationship for the biphenyl/isopropanol binary mixture, solid line. Raoult's Law, dashed line.

b) Catalysis

The isopropanol alkylation of biphenyl was carried out in a 300 ml Parr instruments pressure reactor, equipped with a pressure gauge. 22 ml of isopropanol (0.287 mol) and 30g (0.195 mol) or 15g (0.097 mol) of biphenyl were placed in the reactor with 100 to 200 mg of catalyst. The reactor was then closed and heated to 250 °C. The pressure increased and classically reached 25 to 35 ATM during the course of the 20 hours reaction. After cooling down the reactor to room temperature, the pressure was recorded. A sample of the gases present was collected over water and analyzed by gas chromatography. The pressure was then released and the reactor opened. Two phases were usually present. The aqueous phase was collected with a Pasteur pipette and weighed. The organic phase was then diluted in 250 ml of toluene and analyzed by gas chromatography.

The biphenyl conversion was calculated from the following equation:

$$\text{Conversion}_{\text{Biph}} (\%) = \frac{(\text{Biphenyl})_{\text{converted}}}{(\text{Biphenyl})_{\text{unreacted}} + (\text{Biphenyl})_{\text{converted}}} \cdot 100$$

Where $(\text{Biphenyl})_{\text{unreacted}}$ refers to the area of the biphenyl peak in the GC chromatogram and $(\text{Biphenyl})_{\text{converted}}$ was calculated as follows:

$$(\text{Biphenyl})_{\text{converted}} = \sum \left((\text{area alkylbiphenyl}) \cdot \frac{12}{x} \right)$$

where x is the carbon atom number of the alkylbiphenyl considered. Isopropanol was mainly converted to propene and to alkylbiphenyl. The number of moles of propene remaining at the end of the reaction was calculated from the final pressure of the reactor and the gas phase analysis.

$$n_{\text{propene}} = \% \text{ of propene in gas phase} * \frac{P_{\text{final}} * V_{\text{reactor}}}{RT}$$

The number of moles of isopropyl groups on biphenyl was calculated from

$$n_{\text{isopropyl}} = n_{\text{biphenyl}} * \text{Biphenyl conversion} * (\% \text{ monoalkyl} + 2 * \% \text{ dialkyl} + 3 * \% \text{ trialkyl} + 4 * \% \text{ tetraalkyl})$$

The isopropanol conversion was estimated from

$$\text{Conversion}_{\text{isop}}(\%) = \frac{n_{\text{propene}} + n_{\text{isopropyl}}}{n_{\text{isopropanol initial}}} * 100$$

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CHAPTER THREE
CATALYTIC ACTIVITY OF ALUMINA PILLARED CLAYS FOR
BIPHENYL ISOPROPYLATION

A. Introduction

As we noted in Chapter 1, catalytic shape selectivity for pillared clays has been reported by Kikuchi et al.¹ for 1,2,4-trimethylbenzene disproportionation in the gas phase between 200 and 400°C. Mori et al. also observed differences in shape selectivity for meta-xylene conversion in the gas phase at 350°C.² However, both of these examples did not provide with unquestionable proofs of shape selectivity because chemical effects were alternative explanations for the selectivity observed. Also, the mononuclear aromatics used might have been somewhat too small to interact with the micropores of pillared clays, which are typically in the range 8-10Å. We have been interested by the isopropyl alkylation of biphenyl for this purpose. It has been demonstrated by Lee et al.³ that the zeolite mordenite is a very effective catalyst for the production of p,p'-diisopropylbiphenyl. This zeolite exhibit elliptic channels of 6.7 x 7.8 Å and smaller cylindrical channels of 2.8 Å of diameter. Pillared clays, having micropores of similar dimensions, could, thus, be expected to exhibit shape selective properties for propene alkylation of biphenyl. This reaction was also of interest to us because it occurs under relatively mild, liquid phase conditions. We hoped that the coke formation problem, which typically is very serious in the gas phase, would be minimized in these conditions. Finally, this reaction can be operated conveniently with two different alkylating agents. Propene can be introduced in the reactor and allow for relatively anhydrous conditions. On the other hand, the reaction can be carried out with isopropanol in a closed reactor. In this latter case, water is a reaction product and the water content is, thus, relatively well defined. The option of varying the water content in the system is an attractive feature, because, as was observed in

Chapter 1, water can greatly modify the acidity function of a solid acid catalyst.

Finding new alkylation catalysts is furthermore a major concern nowadays. There is an increasing need to replace traditional Friedel-Crafts alkylation catalysts such as AlCl_3 by less corrosive and less polluting solid acids.⁴ Shape selectivity is thus only one among the many advantages of solid acids over traditional alkylation catalysts. To obtain very active alkylation catalysts is of primary importance.

In order to better understand the physical properties of pillared clays that govern their catalytic properties, we have included in this work pillared clays of various compositions. We have chosen clays with different charge densities (e.g., Arizona montmorillonite and Wyoming montmorillonite with cation exchange capacities of 75 and 115 meq/100g, respectively), as well as clays with different charge localization (e.g., tetrahedrally charged beidellite and octahedrally charged montmorillonite). In addition, related solid acids with dramatically different pore structure were included as reference materials in the study. K10 montmorillonite, an acid-leached montmorillonite, was incorporated in the study as an example of a clay-derived catalyst with virtually no microporous structure.⁵ Two zeolites, namely, H-mordenite and ultra stable Y, were included as examples of solid acids with a crystalline microporous structure. The catalysts were characterized by several techniques including, elemental analysis, X-ray diffraction, nitrogen adsorption and pyridine thermodesorption as monitored by FTIR. This chapter will deal with the catalytic activities of alumina pillared clays for the isopropylation of biphenyl and their relationship with the catalysts porosity and acidity. In

chapter 6, the selectivity between the different possible isomers will be addressed.

B. Pillared clays synthesis and characterization

1. X-ray diffraction and elemental analysis

Basal spacings for the alumina pillared clays are reported in Table 4. The values are similar ($\sim 18\text{\AA}$) for the different clays, demonstrating that the intercalation of the Al_{13} polymer occurred. With Laponite, however, an amorphous X-ray diffraction pattern was observed. Laponite platelets are very small ($< 1\mu\text{m}$) and the aggregation mechanism is mainly edge-face rather than face-face.⁶ The catalyst obtained is called a "delaminated" clay.

The measured CEC values for beidellite, Wyoming montmorillonite, Arizona montmorillonite and fluorohectorite were, respectively, 45, 75, 115 and 140 meq/100g. These values might not be directly correlated with the charge densities on the layers, because of the presence of some impurities (quartz in montmorillonites and, probably, kaolin in beidellite). The errors are, however, too low to affect the order of charge densities. The amount of aluminum incorporated per $\text{O}_2\text{O}(\text{OH})_4$ unit correlated well with the CEC as shown on Figure 13.

Thus, the pillar density increased in the order APB (aluminum pillared beidellite) < APWM (aluminum pillared Wyoming montmorillonite) < APAM (aluminum pillared Arizona montmorillonite) < APFH (aluminum pillared fluorohectorite).

Table 4. Typical unit cell compositions of the starting clays and basal spacings of calcined alumina-clay products

	Sample	Typical Unit Cell Formula of the clay	d001(Å) calcined 350°C
APFH	Alumina Pillared Fluorohectorite	$\text{Li}_{1.6} [\text{Mg}_{4.4}\text{Li}_{1.6}] -$ $(\text{Si}_{8.0}) \text{O}_{20} \text{F}_4$	18.2
APAM	Alumina Pillared Arizona Montmorillonite	$\text{Ca}_{0.5} [\text{Al}_{3.0}\text{Mg}_{1.0}] -$ $(\text{Si}_{8.0}) \text{O}_{20} (\text{OH})_4$	18.8
APWM	Alumina Pillared Wyoming Montmorillonite	$\text{Na}_{0.8}$ $[\text{Al}_{3.3}\text{Mg}_{0.5}\text{Fe}_{0.3}] -$ $(\text{Si}_{8.0}) \text{O}_{20} (\text{OH})_4$	18.7
APB	Alumina Pillared Beidellite	$\text{Na}_{0.7} [\text{Al}_{4.0}] -$ $(\text{Si}_{7.3}\text{Al}_{0.7}) \text{O}_{20} (\text{OH})_4$	18.2
ADL	Alumina Delaminated Laponite	$\text{Li}_{0.4} [\text{Mg}_{5.6}\text{Li}_{0.4}] -$ $(\text{Si}_{8.0}) \text{O}_{20} (\text{OH})_4$	amorphous

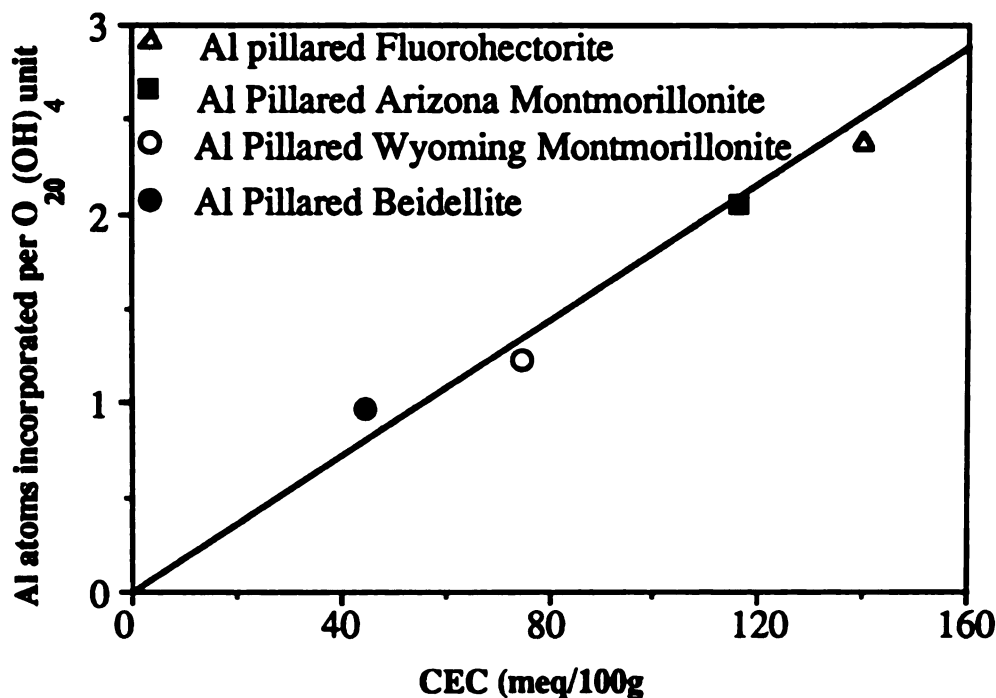


Figure 13. Relationship between the amount of aluminum incorporated into the pillared clay and the CEC of the starting material.

2. Pore structure by N₂ adsorption-desorption

The pore structures of the non-porous acid catalysts, pillared clays, and microporous zeolites were studied by N₂ adsorption-desorption measurements. Many different methods can be used to analyze this data. First of all, the shape of the adsorption-desorption isotherms helps to identify qualitatively the pore structure. The isotherms of the different catalysts are presented in Figure 14. It clearly appears that the pillared clays and zeolites exhibit type I isotherms whereas delaminated clays (K10 and alumina delaminated Laponite) exhibit type IV isotherms. Type I and type IV isotherms, as defined by Gregg and Sing,⁷ are characteristic of microporous and mesoporous solids, respectively. Among the Type I isotherms, it can be noted that the shape of the hysteresis loop differs

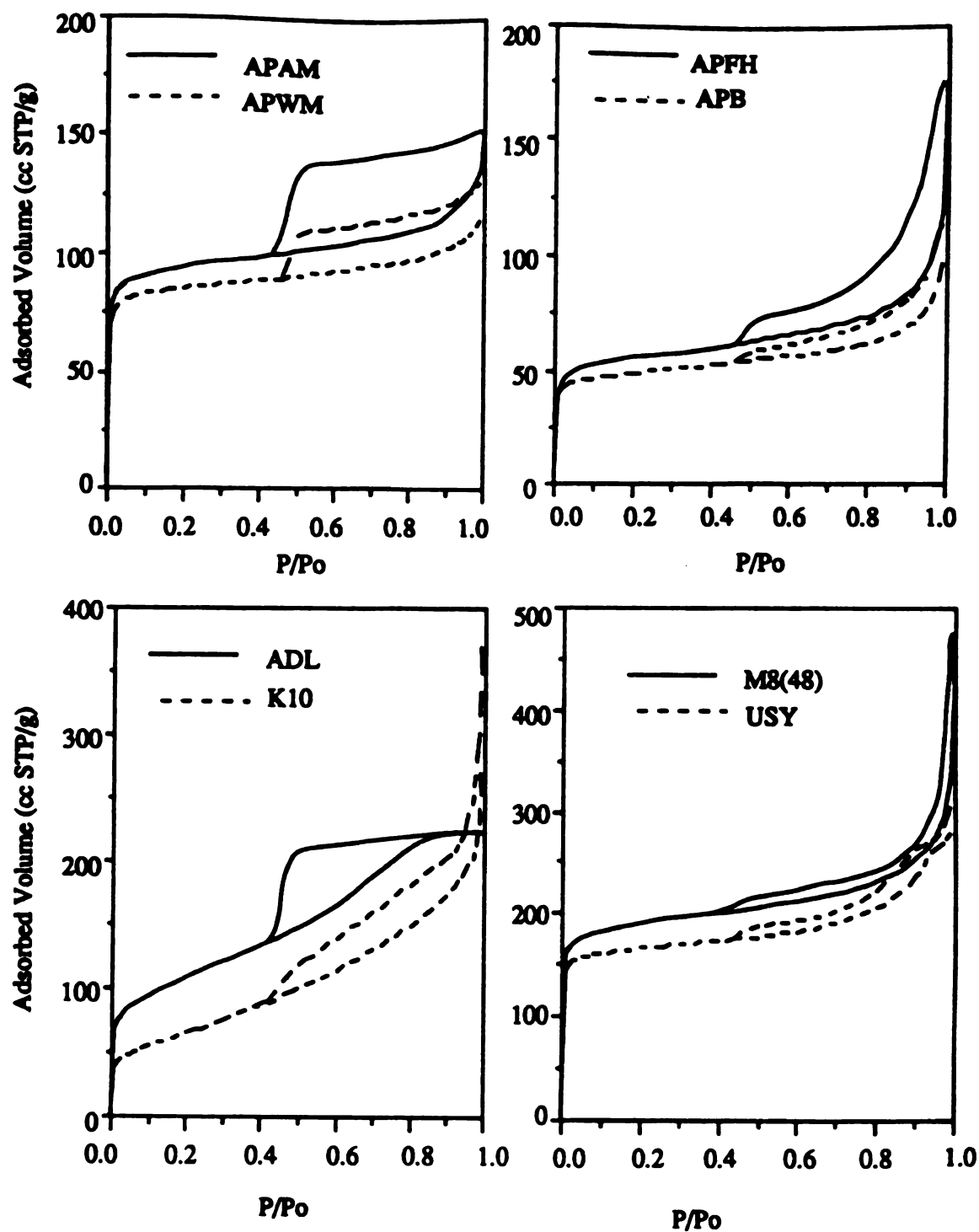


Figure 14. N₂ adsorption-desorption isotherms of the different catalysts.

between the catalysts. We paired the similar isotherms in Figure 14, *i.e.* the two zeolites, alumina pillared fluorohectorite and beidellite, and alumina pillared montmorillonites. We then analyze the significance of these differences.

a) Analysis of the adsorption data

The adsorption data were treated by the BET equation in the range of linearity and by the t-plot method. The t-plots are presented in Figure 15. Several classes of porosity can be distinguished (Table 5).

Table 5. Surface area analysis by the t-plot method obtained from N₂ adsorption isotherms

Catalyst	S _{BET} (m ² /g)	t-plot			
		S(m ² /g)	S _{meso,macro}	S _{micro}	%micro
K10	233	232	232	0	0
ADL	360	387	294	92	24
APFH	214	234	56	175	75
APB	186	213	39	169	79
APAM	365	415	56	332	80
APWM	334	377	34	327	87
USY	652	751	93	610	81
M8(48)	725	844	119	682	81

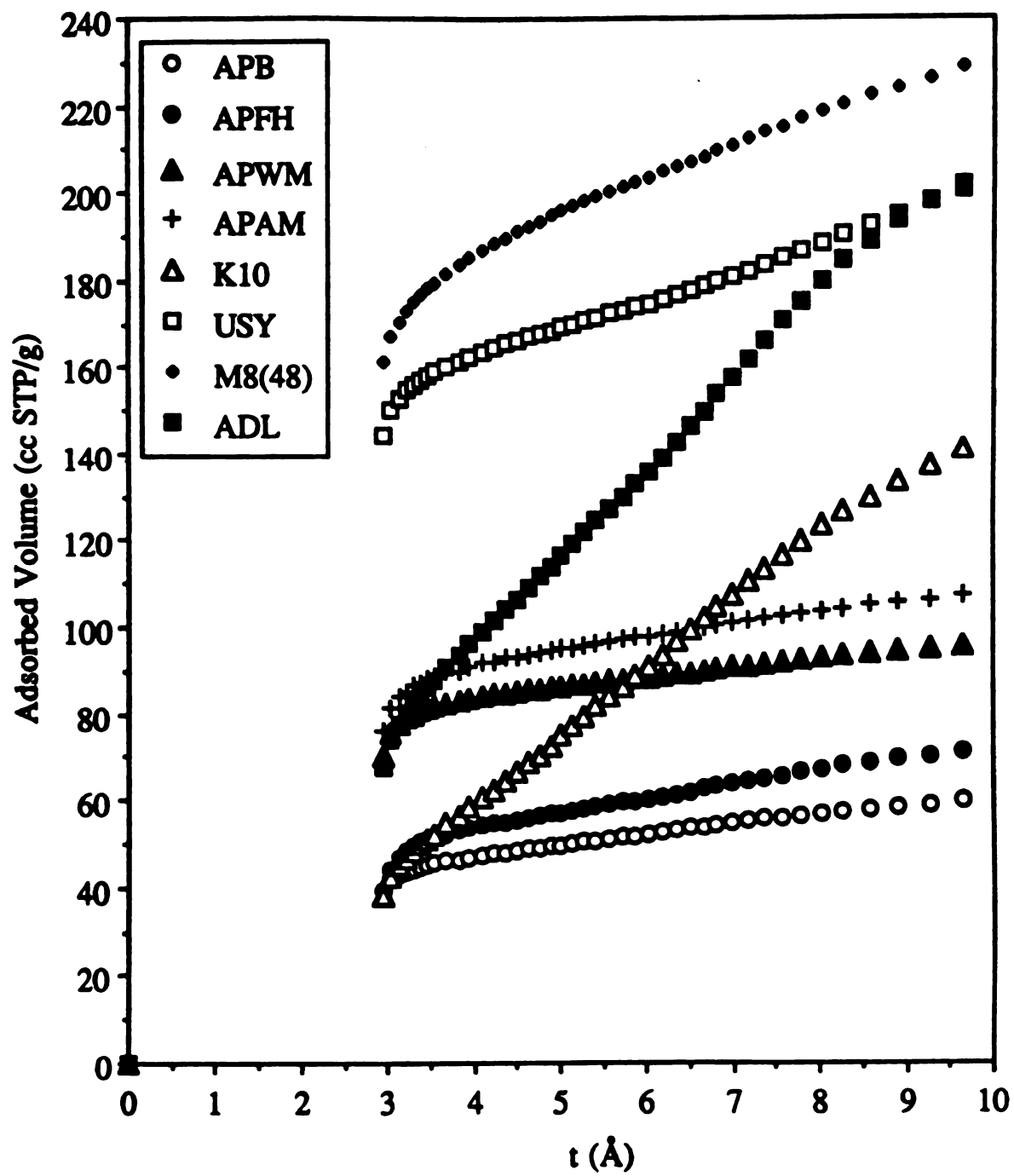


Figure 15. t -plot of the different catalysts.

Alumina delaminated Laponite (ADL) and K10 exhibit few or no micropores. This is a consequence of their delaminated structure. Pillared clays (APAM, APWM, APFH, APB) are microporous materials, but the fraction of the total surface area due to the micropores varies somewhat with the clay layer (from 75% for APFH to 87% for APWM). The fractions of micropores increase in the order $APFH < APB < APAM < APWM$, and the CEC values increase in the order $APB < APWM < APAM < APFH$. Thus, there is no relationship between the micropores to mesopores ratio of the pillared clay and the CEC of the starting clay. The fraction of total surface area due to micropores is certainly more a consequence of the starting clay morphology. The clay particle size determines the aggregation mechanism and thus the micropore to mesopore ratio. The micropore distribution might be correlated with the CEC. It is however difficult to evaluate the interpillar distance, as noted in Chapter 1.

b) Analysis of the desorption data

Mesopore distributions were determined by treating the desorption data using either a slit shape⁸ or cylindrical⁹ pore model. The mesoporous surface area obtained from the t-plot method and from the slit shape and cylindrical pore models are presented in Table 6. For non-microporous ADL, K10, and for the zeolite M8(48), the cylindrical pore model was the more appropriate model, whereas for the other catalysts the slit shape model gave better agreement with t-plots.

Table 6. Comparison of mesoporous surface area obtained from the t-plot method, a slit shape pore model and a cylindrical pore model.

Catalyst	Mesoporous	Surface	Area
	t-plot	Slit shape model	Cylindrical model
K10	232	167	245
ADL	294	211	319
APFH	56	56	68
APB	39	32	53
APAM	56	88	112
APWM	34	47	78
USY	93	85	117
M8(48)	119	87	112

The mesopore distributions obtained from the desorption isotherm are presented in Figure 16. Among the non-microporous clays, K10 exhibited a broad distribution of mesopores, whereas the mesopores of ADL appear more or less uniformly centered around 35Å. However, the mesopore distribution of ADL, as obtained from the desorption isotherm, is probably affected by a bottle neck pore blocking effect. Thus, whereas the adsorbed volume in ADL increases linearly with partial pressure, the desorbed volume drops sharply at $P/P^{\circ}=0.42$ at which point the Kelvin law of capillary condensation no longer applies. A pore blocking effect would also affect the surface area obtained from the desorption analysis. It is thus not clear whether or not the cylindrical pore model is the most accurate to

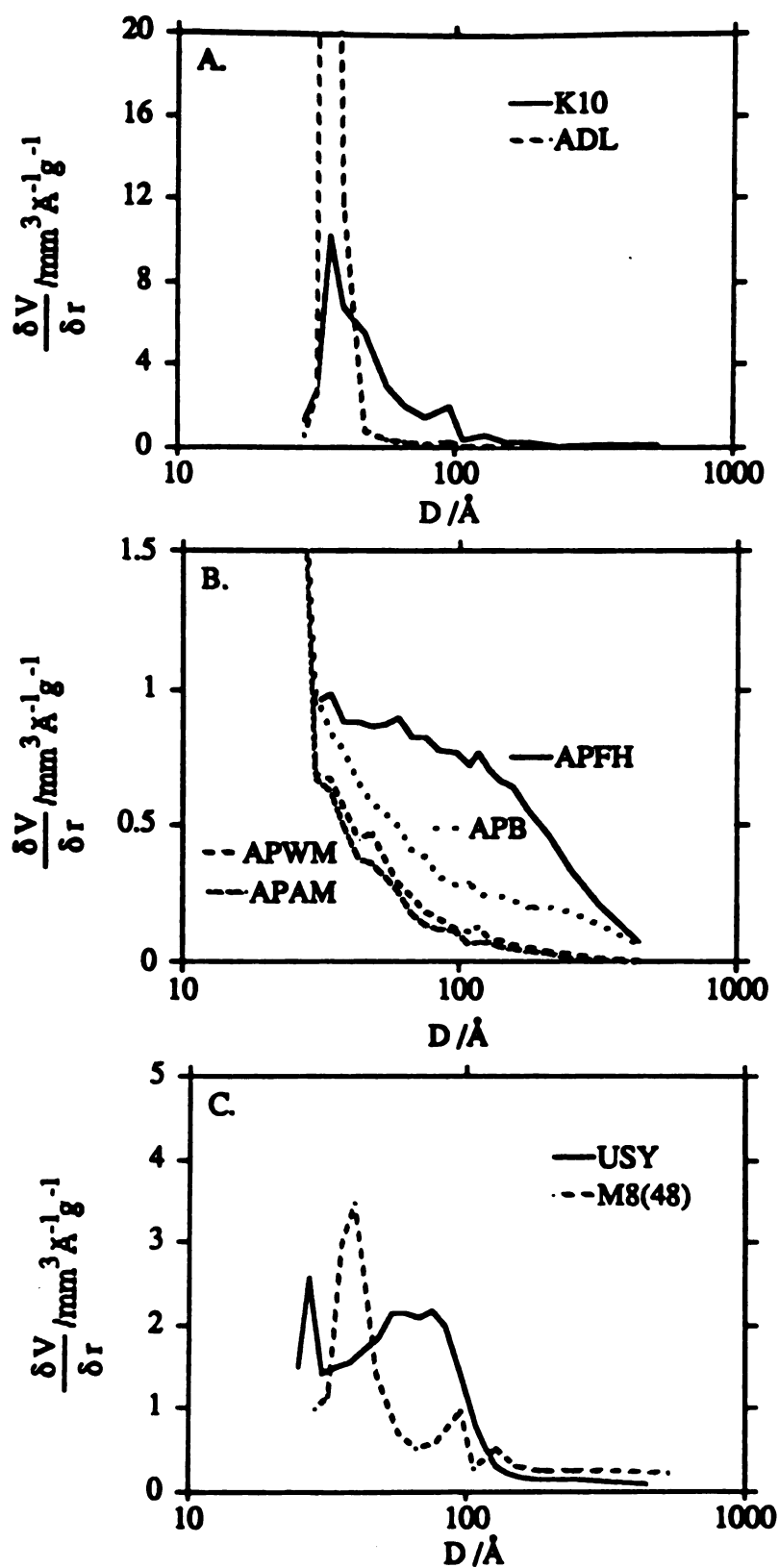


Figure 16. Mesopore distribution of the different catalysts, obtained from the desorption isotherm.

describe delaminated Laponite. Differences in mesopore distribution were also noted for the pillared clays. Alumina pillared montmorillonites exhibited almost no mesopores of diameter larger than 30 Å. In contrast, for pillared fluorohectorite and pillared beidellite, the mesopores of diameter larger than 30 Å contributed to about 65% of the total pore volume, as shown in Table 7. However, like for delaminated Laponite, the absence of large mesopores in alumina pillared montmorillonites might be partly an artifact due to pore blocking effects. The surface area obtained from the desorption isotherm is always too large for these materials. This inconsistency may be an indication that desorption of large pores occurs at a partial pressure below equilibrium because of pore blocking. Mesoporosity also was well developed for USY and M8(48). The percentage of large mesopores was, however, not as large as that of alumina pillared fluorohectorite and beidellite. The large mesoporous volume of pillared fluorohectorite was unexpected. Fluorohectorite is a synthetic clay which exhibit large particles and should thus aggregate mainly face to face. The large mesoporous volume originates probably from defects in the clay lattice.

In conclusion, we distinguish 5 types of materials. K10 is a mesoporous material with cylindrical pores. In ADL mesoporosity originates from delamination and significant pore blocking occurs. Alumina pillared fluorohectorite and beidellite are microporous materials with a significant mesoporous contribution, originating from defects. Alumina pillared montmorillonites are microporous solids with less mesopores and in which pore blocking probably occurs. Dealuminated zeolites are microporous materials with an intermediate mesoporosity.

Table 7. Pore volume analysis.

Catalyst	Pore Volumes (cm³/g)				% pore (>30 Å)
	Total^a	micro^b	meso^c	meso^c (>30 Å)	
K10	0.41	0	0.41	0.27	65
ADL	0.35	0.03	0.30	0.03	9
APFH	0.27	0.06	0.20	0.18	67
APB	0.16	0.06	0.11	0.10	62
APAM	0.25	0.12	0.13	0.03	12
APWM	0.22	0.11	0.12	0.04	18
USY	0.46	0.21	0.24	0.19	41
M8(48)	0.58	0.24	0.33	0.27	46

a: Adsorbed volume at $P/P^0=0.98$. b: Obtained from the t-plot. c: Obtained from the desorption isotherm.

3. Acidity of the catalysts, as studied by base thermodesorption

a) NH₃ Temperature Programmed Desorption (TPD)

The NH₃ TPD experiments for the pillared clays and other catalysts exhibited two maxima centered around 200 °C and 500 °C. The second maximum was also observed in blank experiments (without ammonia) and was, thus, assigned to water loss resulting from dehydroxylation. The first maximum, corresponding to NH₃ desorption, is illustrated in Figure 17 for the different catalysts. Integration of the TPD curves in the range 100-300 °C revealed that the total amount of acid sites per gram decreased in the

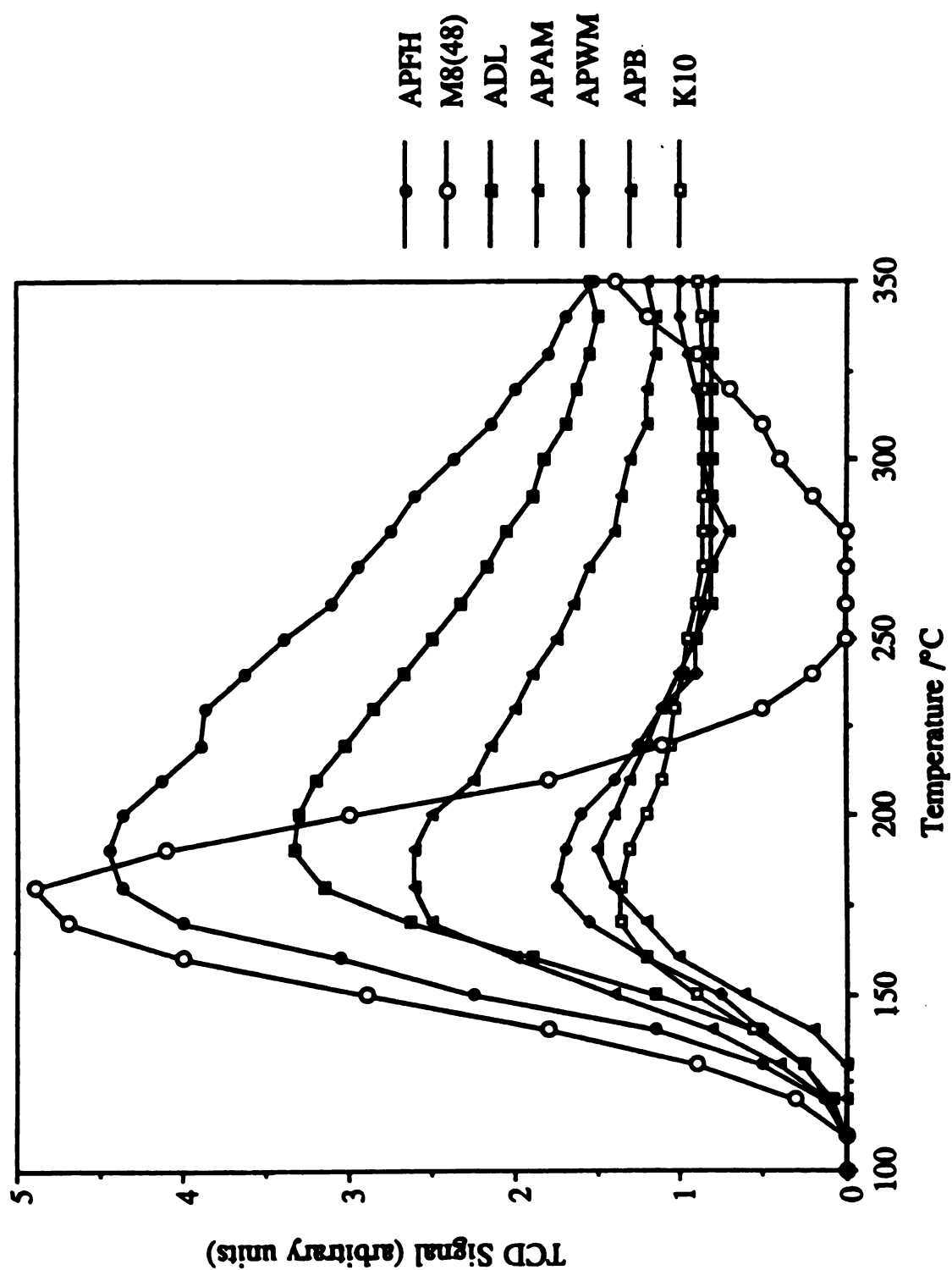


Figure 17. NH_3 temperature programmed desorption profiles of the different catalysts, in the temperature range 100-350 $^{\circ}\text{C}$.

order APFH > M8(48) > ADL > APAM > APWM > APB ~ K10. It was not attempted to obtain absolute values.

b) Pyridine desorption monitored by FTIR

In order to differentiate the type of acidity for each catalyst, FTIR studies of chemisorbed pyridine were carried out. The results are presented in Figure 18. Qualitatively, it is easy to distinguish between Lewis and Brönsted acidity for the catalysts studied. Pyridine adsorbed on Lewis acid sites exhibits absorption bands at 1450 cm^{-1} and 1490 cm^{-1} whereas on Brönsted sites absorption occurs at 1490 cm^{-1} and 1545 cm^{-1} . An attempt to obtain more quantitative results using the extinction coefficients provided by Datka¹⁰ is provided in Table 8. The total amount of acid sites obtained after degassing pyridine overnight at $150\text{ }^{\circ}\text{C}$ decreased in the order M8(48) > APFH > APAM > APWM > ADL > APB > K10. This sequence is comparable to the sequence obtained from NH_3 TPD, although some differences are observed, especially for ADL and M8(48). The Lewis to Brönsted ratio presented in Table 8 show that the zeolite M8(48) is the only true Brönsted acid among the catalysts studied. APFH and K10 exhibit, however, also significant Brönsted acidity. All the other materials had Lewis to Brönsted ratio greater than 3 after degassing overnight at $150\text{ }^{\circ}\text{C}$. This result was surprising for alumina pillared beidellite for which Brönsted acidity has been reported.¹¹ A similar contradiction was observed by Li for pillared derivatives of natural and synthetic beidellite.¹² The Lewis acidity of alumina pillared clays increased with increasing pillar density, except for alumina pillared fluorohectorite. This support the hypothesis discussed in Chapter 1 that Lewis acidity originates from the pillars. The high Brönsted acidity observed with alumina pillared

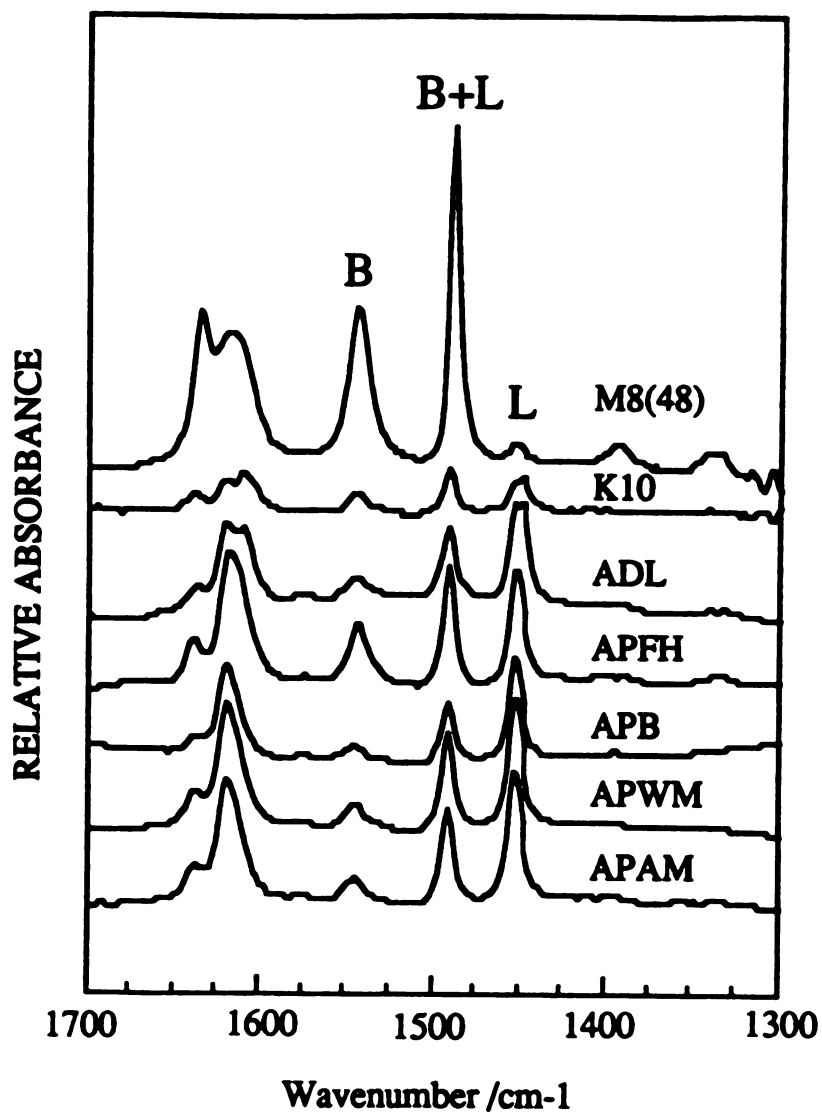


Figure 18. FT-IR spectra of pyridine chemisorbed on the different catalysts, after degassing at 150 °C for 16 hours.

fluorohectorite was atypical as well. A tentative explanation for this high Brönsted acidity is provided in Chapter 5.

Table 8. Pyridine adsorbed on the different samples.

Catalyst	Outgassing temperature	Lewis ^a	Brönsted ^b	Total ^c	Lewis to Brönsted ratio
M8(48)	150 °C	1.7	25.5	27.2	0.1
	250 °C	1.5	22.8	24.3	0.1
	350 °C	2.9	15.2	18.1	0.2
K10	150 °C	3.8	3.5	7.3	1.1
	250 °C	3.7	1.7	5.4	2.2
	350 °C	2.9	0.0	2.9	-
ADL	150 °C	11.7	3.5	15.2	3.3
	250 °C	12.3	1.2	13.5	10.2
	350 °C	9.2	0.2	9.4	46.0
APFH	150 °C	14.0	10.1	24.1	1.4
	250 °C	15.8	6.5	22.3	2.4
	350 °C	14.6	3.7	18.3	4.0
APB	150 °C	12.2	2.0	14.2	6.1
	250 °C	12.8	1.1	13.9	11.6
	350 °C	8.5	0.3	8.8	28.0
APWM	150 °C	15.3	3.9	19.2	3.9
	250 °C	15.9	2.9	18.8	5.5
	350 °C	14.0	0.8	14.8	18.7
APAM	150 °C	18.6	3.3	21.9	5.7
	250 °C	18.1	1.5	19.6	12.0
	350 °C	15.3	0.3	15.6	61.0

a: Lewis-bonded pyridine from 1450 cm⁻¹ absorption band (mmol/100g of clay).

b: Brönsted-bonded pyridine from 1545 cm⁻¹ absorption band (mmol/100g of clay).

c: Total of acid-bonded pyridine (mmol/100g of clay).

C. Catalysts activities for propene alkylation of biphenyl.

1. Results

The catalytic activities of the non-porous catalysts, pillared clays and zeolites were compared for the alkylation of liquid phase biphenyl by propene at 250°C using the same mass of catalyst (0.2g, 100-200 mesh (75-150 μm) fraction). The biphenyl conversion was reproducible to $\pm 5\%$. Pretreatments were carried out in order to obtain the best activity for a given catalyst. A three-optimum hour outgassing period at 350°C under vacuum was necessary to observe activity with the zeolites. Water is less tightly bonded in pillared clays. Thermal pretreatments of the pillared clays had no effect on the conversion obtained with these catalysts, probably because the water present was removed during the purge of the reactor at 100-150°C. Figure 19 represents the evolution of product distribution with time for the reaction catalyzed by APWM.

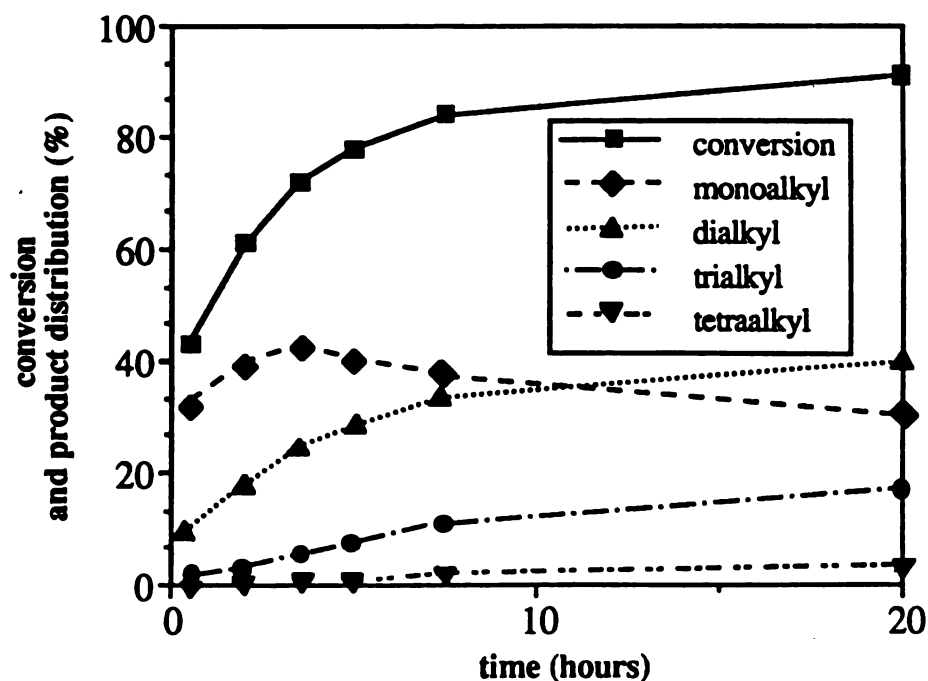


Figure 19. Evolution of the product distribution for propene alkylation of biphenyl over APWM at 250°C and 140 psi propene pressure.

These results show that the mono-, di-, tri- and tetraalkylations were successive. This is further established by experiments at short reaction time. For example, after one hour of reaction with 0.05g of the K10 montmorillonite, the conversion is 11% and 80% of the products are monoalkyl isomers. The results of the activity tests in order of decreasing activity are presented in Table 9.

Table 9. Biphenyl conversion and product isomer distribution obtained for different solid acid catalysts ^a

Catalyst	APB	APFH	K 10	ADL	USY	APWM	M(8)48	APAM
conversion (%)	99	98	96	89	78	64	57(77)	55
% monoalkyl	3	11	16	29	45	63	50(66)	67
% dialkyl	18	33	36	39	40	30	47(33)	27
% trialkyl	48	38	37	25	14	7	3(1)	6
% tetraalkyl	31	17	11	7	2	0	0(0)	0

a: The reaction conditions were as follows: 30g biphenyl, 0.2g catalyst, 140 psi propene, 250°C, 20 hours reaction time. All results were obtained with 100-200 mesh particle size catalysts except for the values presented in parentheses for M8(48). This latter catalyst has an intrinsic particle size <200 mesh and required pelletization and crushing to achieve the desired size. The values in parentheses are for the pristine catalyst with particle size <200 mesh.

APB, APFH and K10 were the most active, with most of the biphenyl converted to di- and trialkylated products. ADL was less active but still it yielded substantial amounts of dialkylated products. The zeolites and pillared montmorillonites exhibited similar activities.

2. Role of diffusion control

To verify that the gas-liquid transport of propene in biphenyl was not a controlling step, we carried out two alkylation experiments at different stirring rates. The results are provided in Table 10 and show that no significant difference of conversion level was obtained by varying the stirring rate.

Table 10. Influence of stirring rate on biphenyl conversion.

Catalyst	K10	K10
Stirring rate (rpm)	135	200
weight(g)	0.09	0.09
conversion	45	52

In order to understand better the importance of diffusion limitations on activities, a series of reactions in which the catalysts particle sizes were varied was carried out. Two clay catalysts with very different pore structures, namely, APWM and ADL were chosen for this study. Some results for the delaminated K10 are also included. The results are presented in Table 11. Particle size had a very dramatic influence on the catalyst activities. For microporous APWM, the conversion varies from 26% to 99% when the particle size decreases from a 75-150 μm fraction to a fraction of particles with a diameter smaller than 45 μm . For mesoporous ADL and K10, the influence of particle size is less dramatic, but it cannot be ignored. The reaction was thus probably under diffusion control for all of the catalysts. This may explain why the less microporous catalysts like ADL and K10 are among the most active. For these materials diffusion limitations are low.

Table 11. Evolution of catalysts activities with particle size ^a

Particle size		150-75 μm	75-50 μm	50-45 μm	< 45 μm
APWM	Conversion	26	36	60	98
(0.1g)	(%)				
	Monoalkyl	86	79	64	8
	Dialkyl	14	18	28	31
	Trialkyl	0	2	8	41
	Tetraalkyl	0	0	0	20
ADL (0.09g)	Conversion	36	65	79	85
	(%)				
	Monoalkyl	77	56	41	35
	Dialkyl	21	33	37	38
	Trialkyl	2	10	16	19
	Tetraalkyl	0	1	6	8
K10 (0.08g)	Conversion	44			78
	(%)				
	Monoalkyl	73			44
	Dialkyl	23			37
	Trialkyl	4			16
	Tetraalkyl	0			3

a: The reaction conditions were as follows: 30g biphenyl, 0.1g (APWM) and 0.09g (ADL) catalyst 140 psi propene, 250°C, 20 hours (APWM) 17 hours (ADL) reaction time.

Pore blocking effects in ADL, noted previously, might be responsible for a slower diffusion in this material than in K10. On the other hand zeolites and pillared montmorillonite are very microporous, which could explain their relatively lower activity. Pillared fluorohectorite and pillared beidellite exhibit a large mesoporous volume which enables the reactant to access the micropores. A similar influence of mesoporosity was noted by Lee et al. who reported an increase in biphenyl conversion from

21% to 98% when the mesoporous volume of mordenite was increased from 31% to 60% of the total pore volume.³

Acidity is also a factor influencing catalytic activity. Among the non-microporous catalysts K10, which is a Brönsted acid is more active than the Lewis acid ADL. Similarly, APFH is a relatively strong Brönsted acid, and is much more active than pillared montmorillonites. However, Brönsted acidity was not clearly evidenced for the very active catalyst alumina pillared beidellite. Also, the only true Brönsted acid, the mordenite M8(48) was not among the most active catalysts. Solid Brönsted acids might thus catalyze the alkylation reaction more efficiently than solid Lewis acids, but this effect is difficult to isolate from pore structure effects. Our preliminary conclusion is that high catalyst activities are a consequence of low diffusional limitations and high Brönsted acidity. Other factors yet to be fully identified may also influence activity, among them, deactivation of the catalyst by coke formation is certainly very important. In order to differentiate between the effects of porosity and acidity, two systems were studied. In alumina pillared Arizona montmorillonite, the incorporation of a non-ionic surfactant during the synthesis enables the preparation of materials with variable mesoporosity and similar acidity. The effect of mesoporosity alone can thus be studied with this system (Chapter 4). On the contrary, the acidity of alumina pillared fluorohectorite is changed by varying the calcination temperature, without affecting the pore structure. The effect of acidity alone can thus be studied with this system (Chapter 5).

3. Coke formation on the catalysts

Surface areas and the weight percentage of carbon remaining on the catalysts after washing the spent catalyst with toluene and treatment at

350°C under vacuum are presented in Table 12. Coke formation was similar for all of the pillared clays except for pillared Wyoming montmorillonite. In pillared Wyoming montmorillonite, coke formation was higher and the micropores nearly plugged. This is probably a consequence of the high iron content of this clay (2.4 wt.%).¹³ Table 12 also shows that coking occurred primarily in the micropores for all catalysts.

Table 12. Percentage of carbon remaining on the catalyst after outgassing at 350°C under 10^{-4} torr and pore analysis of the coked catalysts.

Catalyst:	APB	APFH	K10	ADL	APWM	APAM
wt % Fe present in the catalyst	1.2	0.0		0.0	2.4	1.0
Conversion:	99	98	96	89	65	55
%C remaining on the catalyst	3.8	2.7	3.0	2.8	4.3	2.7
Micropore surface area of fresh catalyst (m^2/g)	169	175	0	92	327	332
Micropore surface area of coked catalyst (m^2/g)	115	135	0	48	74	218
Mesopore surface area of fresh catalyst (m^2/g)	39	56	232	294	34	56
Mesopore surface area of coked catalyst (m^2/g)	36	49	185	309	38	45

D. Isopropanol alkylation of biphenyl catalyzed by alumina pillared clays

1. Introduction

In order to study the influence of water on the catalysis of alkylation reactions by alumina pillared clay, we decided to use isopropanol as an alkylating agent. With this reactant, water is generated in-situ in the reactor. When propene is used as an alkylating agent, the propene purge of the reactor has to be carried out around 100 °C and it is then difficult to introduce water without undergoing evaporation. It is, thus, easier to control the water content inside the reactor when it is formed in-situ.

Several pieces of information in the literature suggested that alumina pillared clays would be efficient alkylation catalysts even in the presence of water. Sugi et al.¹⁴ reported that isopropylation of biphenyl by isopropanol occurred when the catalyst was a high silica mordenite with a Si/Al₂ ratio greater than 20. It is well known that high silica zeolites like silicalite are hydrophobic materials.¹⁵ The hydrophobicity of these zeolites was demonstrated by the shape of their water adsorption isotherms. Simonot-Grange et al. showed that the shape of the water adsorption isotherms of faujasites changes from Type I to type IV upon dealumination.¹⁶ This behavior is explained by the increased hydrophobicity of the zeolite and, to a lesser extent, by the destruction of some micropores. Yamanaka et al. reported that alumina pillared clays are hydrophobic materials.¹⁷ Although the N₂ adsorption isotherms are of type I indicating very microporous materials, the water adsorption isotherms are of type IV and resemble that of AlPO₄-5.¹⁸ The absence of isolated interlayer cations and the migration of protons into the layers are believed to be responsible for this hydrophobic behavior.

The results obtained for the reaction studied at a isopropanol to biphenyl molar ratio of 1.5 are presented in Table 13. The catalysts used are fully characterized in B.

Table 13. Catalytic activities for isopropanol alkylation of biphenyl at 250 °C under autogeneous pressure.^a

Catalyst:	K10	ADL	APWM	APAM	APFH	APB	M8(48)
Final Pressure (atm) at 30 °C	2.75	6.8	1.5	1.5	4.1	2.75	8.2
Aqueous phase collected (g)		2.8		2.41	2.6	2.79	1.88
Biphenyl conversion	62	31	75	67	52	60	8
monoalkyl	66	82	57	59	76	66	90
dialkyl	29	17	31	29	20	28	10
trialkyl	6	2	12	9	4	6	0
tetraalkyl	0	0	0	3	0	0	0
Isopropanol conversion	58	55	79	72	58	62	40
% propene	12	52	5	5	23	11	87
% isopropyl	88	48	95	95	77	89	13

a: The reaction conditions were as follows: 0.287 mol isopropanol, 0.195 mol biphenyl and 200mg of catalyst (100-200mesh fraction), 250 °C, 20 hours.

The evolution of pressure with reaction time at 250 °C was recorded for APWM and is presented in Figure 20. After a sharp increase during the first two hours of experiment, the pressure stabilizes and finally drops slowly. This result suggests that in a first step of the reaction isopropanol is dehydrated to yield propene and water. This dehydration causes the reactor pressure to increase, much above the vapor pressure expected for a biphenyl/isopropanol mixture, which is represented by a dashed line in

Figure 20. In a second step, propene reacts with biphenyl to yield alkylated products. Eventually the consumption of propene results in a decrease of the total pressure. The main experimental differences between propene and isopropanol alkylation are, thus, 1) the presence of water, 2) the higher reaction pressure with the latter alkylating agent.

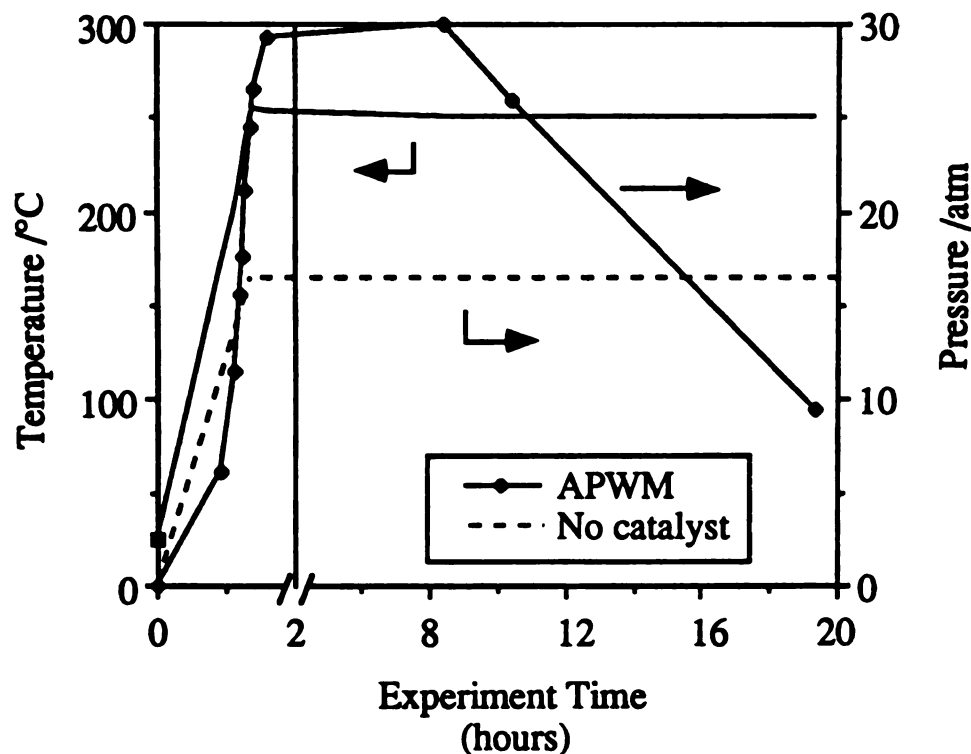


Figure 20. Evolution of the reactor pressure during isopropanol alkylation of biphenyl.

The different pillared clays and K10 montmorillonite exhibit similar catalytic activities for isopropanol alkylation, whereas their activities differed significantly for propene alkylation. Surprisingly delaminated Laponite was relatively unreactive in these conditions. The behavior of the mordenite M8(48) was also special. The conversion of isopropanol to propene over this latter catalyst is within the same magnitude than over

pillared clays. However biphenyl conversion is very low with M8(48). The formation of water has most probably deactivated the zeolite.

It is easy to classify qualitatively the hydrophobicity of the catalysts by the empirical observation of their interaction with the aqueous phase at the end of the reaction. Alumina pillared montmorillonite (APWM and APAM) exhibit no interaction with the aqueous phase. Alumina pillared fluorohectorite, alumina pillared beidellite and K10 montmorillonite are attracted by the aqueous phase but remain mainly in the organic phase. On the contrary, M8(48) was found in the aqueous phase. Hydrophobicity appears to be correlated to catalytic activity in presence of water. Thus, the most hydrophobic catalysts (APAM and APWM) are more active with isopropanol than with propene. The slightly hydrophilic catalysts (K10, APFH, APB) are active with isopropanol, but much less than with propene. Finally, the hydrophilic zeolite (M8(48)) is not active for alkylation in the presence of water. Precise water adsorption isotherms would be very helpful to support this hypothesis. Unfortunately, we were not able to record accurate water adsorption isotherms.

The higher reaction pressure in the case of isopropanol alkylation might also modify the relative activities of the catalysts. Higher pressure could have some effect on the viscosity of the liquid phase and affect diffusion control. Some catalytic results obtained at a higher isopropanol/biphenyl ratio, and thus at a higher reaction pressure, are presented in Table 14.

Table 14. Catalytic activities for isopropanol alkylation of biphenyl at high isopropanol to biphenyl ratio.^a

	K10	APFH	APWM
Final Pressure (atm) at 30 °C	5.45	6.1	4.1
Aqueous phase collected (g)	3.1	2.1	2.25
Biphenyl conversion	64	58	80
monoalkyl	59	68	45
dialkyl	32	27	37
trialkyl	9	5	16
tetraalkyl	0	0	3
Isopropanol conversion	51	80	61
% propene	37	32	21
% isopropyl	63	68	79

a: The reaction conditions were as follows: 0.287 mol isopropanol, 0.0975 mol biphenyl and 100mg of catalyst (100-200mesh fraction), 250 °C, 20 hours.

These results confirm that APWM is a better alkylation catalyst than K10 and APFH in presence of water. The biphenyl conversion did not, however, increase significantly with a higher isopropanol/biphenyl ratio. The higher reaction pressure with this isopropanol/biphenyl ratio might have conflicting effects on the conversion. Higher pressure might facilitate diffusion but on the other hand it might inhibit isopropanol dehydration (Le Chatelier's Law).

E. Conclusion

Catalytic activity of alumina pillared clays for propene alkylation of biphenyl is a function of the materials porosity and acidity. In particular, mesoporosity is very crucial because it enables diffusion and access to the

micropores. Unfortunately, the mesoporosity of pillared clays depends on particle morphology and defects, which are difficult to control. An attempt to control pillared clays mesoporosity with a non-ionic surfactant is presented in Chapter 4.

The hydrophobicity of alumina pillared montmorillonite might be a real advantage for this catalyst in reactions where water is present. Solid acid catalysts are often sensitive to water. Alumina pillared clays represent certainly an alternative to high silica zeolites.

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CHAPTER FOUR
MESOPOROSITY OF SURFACTANT-MODIFIED ALUMINA
PILLARED ARIZONA MONTMORILLONITE

A. Introduction

The importance of porosity in heterogeneous catalysis has long been recognized.¹ Microporous materials, such as zeolites have proved to exhibit outstanding catalytic properties, especially in terms of shape selectivity.^{2,3} The molecular scale channels of these porous materials can indeed govern the evolution of chemical reactions. However, zeolites are limited to applications on relatively small molecules. Moreover, the diffusion limitations in these materials are severe.² There has been an intense activity to design mesoporous materials which could overcome these limitations.^{4,5} We observed in Chapter 3 that mesoporosity was an important factor for the catalytic activity of various materials towards the propene alkylation of biphenyl.⁶ We especially studied alumina pillared clays, a versatile class of microporous acid catalysts. Varying the clay and the preparation of the pillar have enabled authors to prepare pillared clays with tailored gallery height^{7,8} and interpillar distances.⁹ In an effort to improve the porous properties of alumina pillared clays, it was proposed to carry out the synthesis in the presence of a polymer, *i.e.* polyvinyl alcohol¹⁰ or of a non-ionic surfactant.¹¹ The non-ionic surfactants classically used belong to the Tergitol family; they are derivatives of secondary alcohol with a general chemical formula of $C_{12-14}-H_{25-29}-O-(CH_2CH_2O)_5-H$. When the relatively low charge density clay Wyoming montmorillonite is pillared in the presence of surfactant, an uncalcined pillared clay with improved stability and crystallinity is obtained.¹² After calcination, the crystallinity remains improved but with a basal spacing $d_{001} = 15.3\text{\AA}$ which is smaller than the usual $18\text{\AA}$ observed with alumina pillared clays. Photon correlation spectroscopy and infrared studies evidenced an interaction between the

oxygen atoms of the surfactant ethylene oxides and the Al_{13}^{7+} cations.¹³ This interaction probably occurs during the intercalation of the Al_{13}^{7+} cations in the clay and enables an improved regularity of the pillars distribution. In this Chapter, we report that this behavior was not observed with Arizona montmorillonite, which exhibits a higher charge density (CEC = 115 meq/100g). For this latter clay, the presence of non-ionic surfactant yielded pillared clays with increased mesoporosity. As an influence of mesoporosity on the catalytic activity of pillared clays for the propene alkylation of biphenyl was expected, we tested the reactivity of the materials obtained for this reaction.

B. Characterization of the catalysts

1. XRD and elemental analysis

The basal spacing, final surfactant loading and amount of incorporated aluminum are presented in Table 15, for the different surfactant loadings. The final surfactant loadings were obtained from C and H elemental analysis of the uncalcined materials. The final surfactant loading increases, although not linearly, with increasing initial surfactant concentration. The slight increase of basal spacing with increasing surfactant loading evidences the presence of surfactant between the clay layers. As with Wyoming montmorillonite, the layers are further swelled by the surfactant.¹² The presence of surfactant does not seem, however, to affect significantly the amount of incorporated aluminum. This amount is dictated by the cation exchange process which is not influenced by the presence of surfactant. Moreover, unlike with Wyoming montmorillonite, the presence of surfactant does not increase the scattering domain size significantly.

After calcination, the basal spacing decreases slightly with increasing loading of surfactant. This decrease is far less dramatic than with surfactant modified Wyoming montmorillonite.¹²

Table 15. XRD and elemental analysis of surfactant-modified pillared clays.

Initial surfactant loading ^a	Final surfactant loading ^a	Al incorporated/ unit cell	d ₀₀₁ (uncalcined)	d ₀₀₁ (500 °C)
0	0	1.92	19.2	17.9
200		1.99	19.2	17.9
400	248	1.97	19.5	17.2
800	467	2.21	20.2	15.8
1000	575		19.9	17.6

a: mg of surfactant / g of clay.

2. Pore structure by N₂ adsorption-desorption

The pore structure of the surfactant-modified pillared clays was studied by N₂ adsorption-desorption. The adsorption-desorption isotherms are presented on Figure 21. The adsorption isotherms were treated by the BET equation and the t-plot method (Figure 22). The results are provided in Table 16. The presence of surfactant during the synthesis does not affect significantly the BET surface area of the pillared clays. However, increasing loadings of surfactant yield materials with increasing mesoporous surface area. The non-microporous surface area ($S_{\text{meso}} + \text{macro}$) increases, indeed, from 31 to 143 m²/g when the loading changes only from 0 to 400 mg/g. The percentage of microporous surface area drops from 85 to 65 % when the

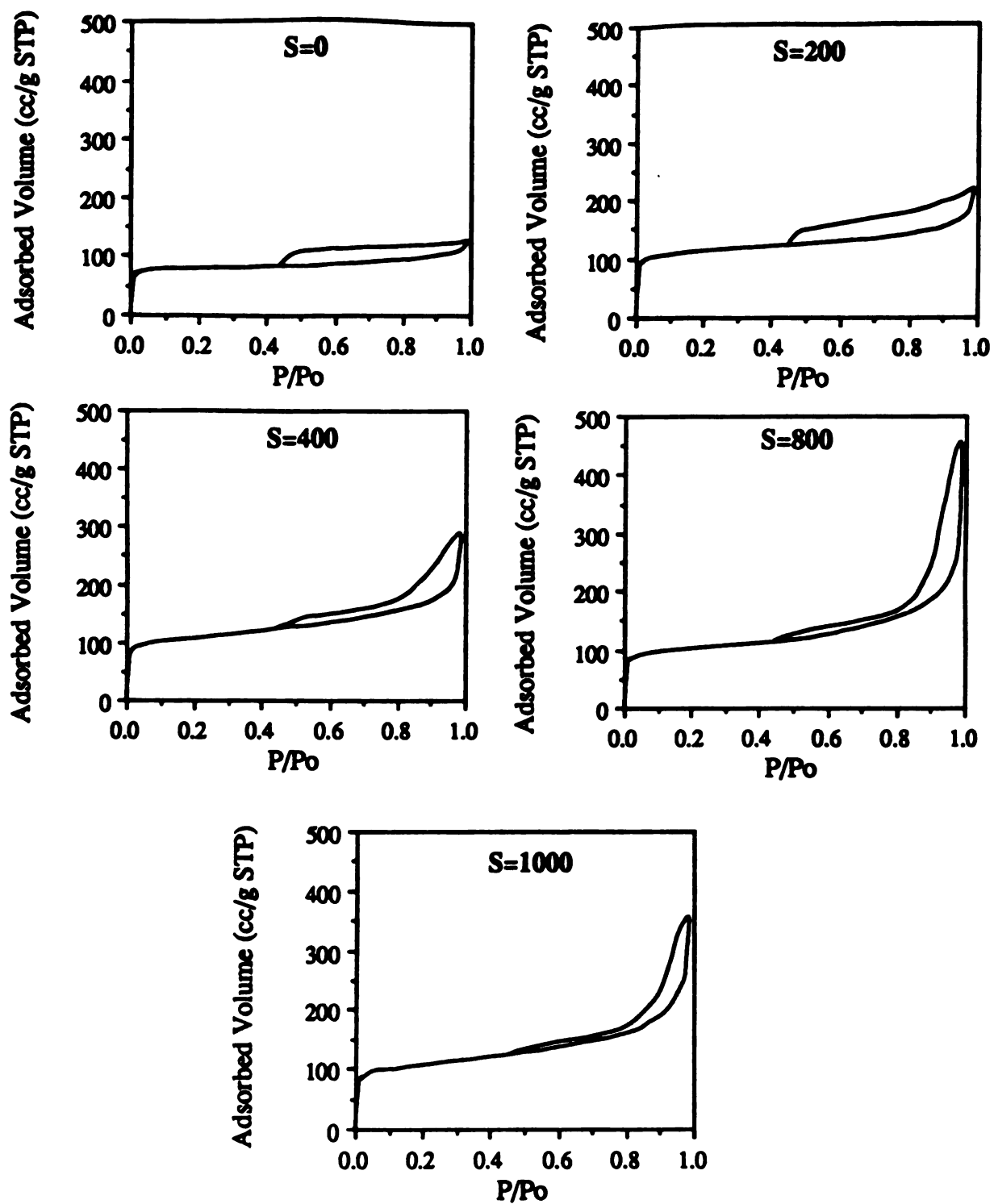


Figure 21. N₂ adsorption-desorption isotherms of surfactant-modified pillared clays.

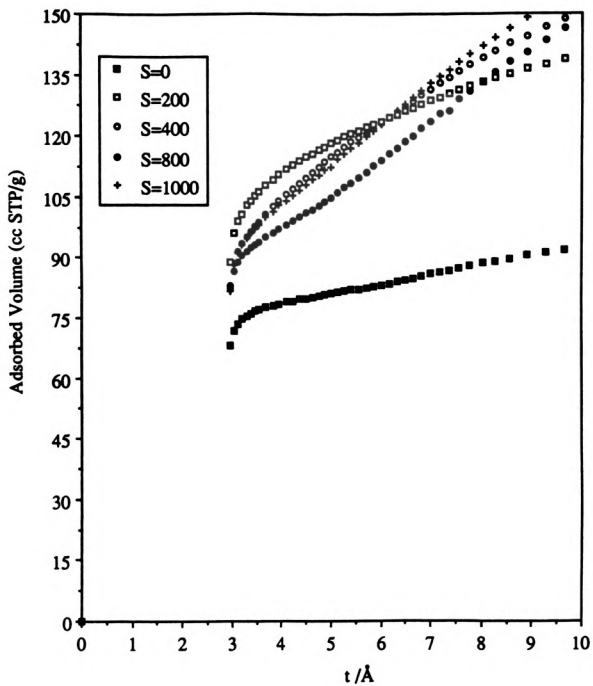


Figure 22. t -plots of surfactant-modified pillared clays.

initial surfactant loading increases from $S = 0$ to $S = 1000$. The surfactant-modified pillared clay with loadings $S = 400$, 800 and 1000 have similar surface area properties.

Table 16. Surface area analysis for surfactant-modified pillared clays calcined at 500°C , analysis obtained less than two weeks after synthesis.

Initial surfactant loading (mg/g)	S_{BET} (m^2/g)	t-plot (m^2/g)			
		S_{total}	$S_{\text{meso, macro}}$	S_{micro}	% micro
0	382	361	31	306	85
200	433	481	89	389	81
400	403	452	143	293	65
800	380	442	124	288	65
1000	396	449	143	288	64

The pore volume properties of the different materials are presented in Table 17. For the surfactant loadings $S = 0$ and $S = 200$, the slit shape model¹⁸ was the more appropriate model, whereas for the other surfactant loadings the cylindrical pore model gave better agreement with t-plots.¹⁹ The total pore volume increases dramatically when the pillared clay synthesis is carried out in the presence of surfactant. However, no significant change of microporous volume (V_{micro}) can be observed for the surfactant-modified pillared clays. The increase in total pore volume is entirely the consequence of a mesoporous volume increase. More precisely, the fraction of the total pore volume coming from large mesopores with $D > 30\text{\AA}$ sharply increases from 21% ($S = 0$) to 82% ($S = 1000$).

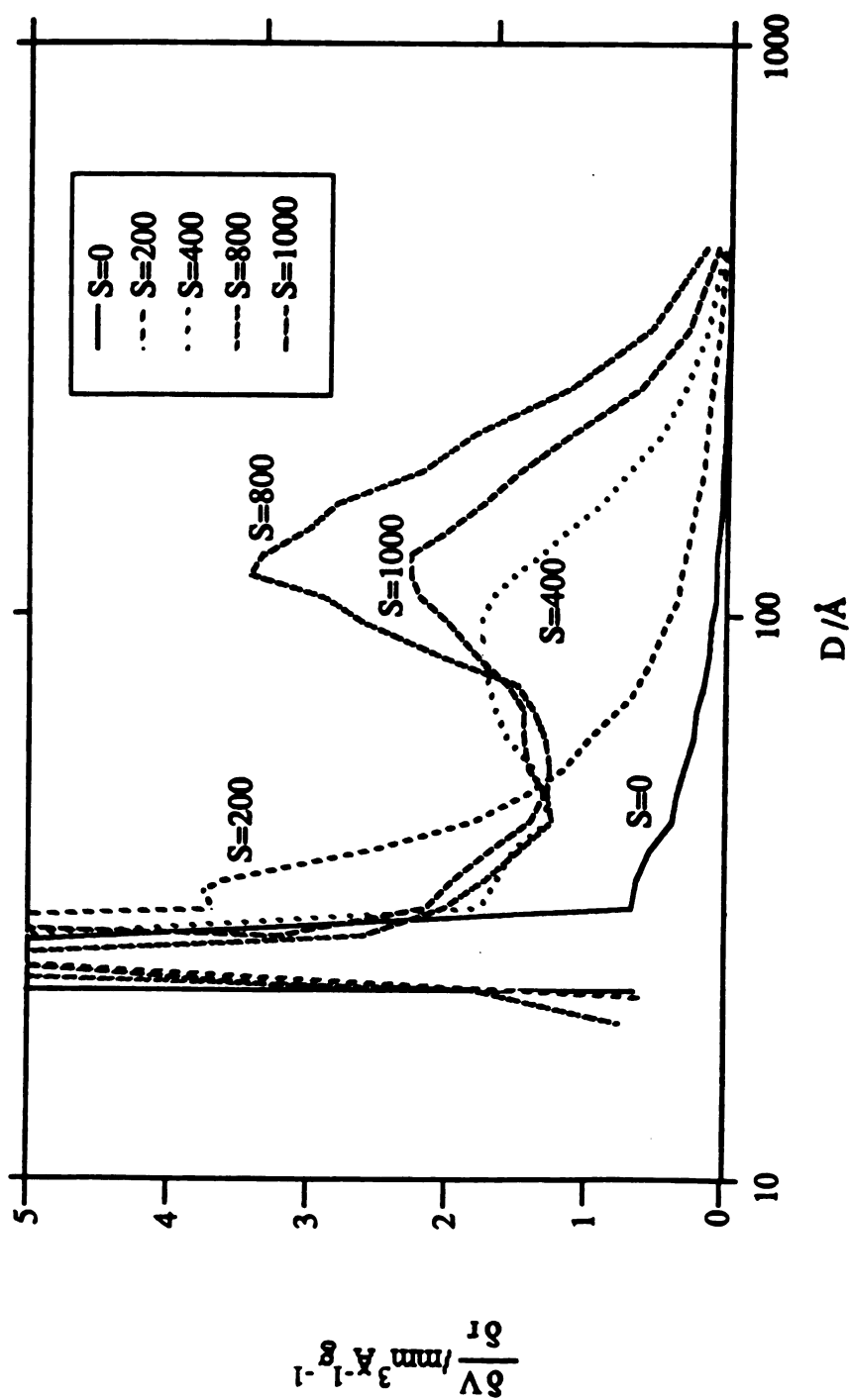


Figure 23. Mesopore size distribution of surfactant-modified pillared clays, obtained from N_2 desorption isotherms.

Table 17. Pore volume analysis of surfactant-modified pillared clays

Surfactant loading ^a	Pore Volumes				% pore (>30Å)
	(cm ³ /g)				
	Total ^b	micro ^c	meso ^d	meso ^d (>30Å)	
0	0.19	0.11	0.08	0.04	21
200	0.34	0.14	0.20	0.19	56
400	0.44	0.10	0.34	0.33	75
800	0.70	0.10	0.63	0.63	88
1000	0.55	0.10	0.45	0.45	82

a: mg of surfactant/ g of clay. b: Adsorbed volume at $P/P^0 = 0.98$. c: Obtained from the t-plot. d: Obtained from the desorption isotherm.

The mesopore distribution was obtained from the desorption branch of the isotherms using the appropriate pore model (Figure 23). All the samples exhibit a peak at 20 Å that has not been fully represented on Figure 23 because it is indicative of connectivity problems and has no physical significance. Figure 23 shows that the mesopore sizes and volumes increase with increasing surfactant loadings. Thus, the average size of the mesopores is about 25, 80 and 100 Å for loading of 200, 400 and 800 as well as 1000 mg/g, respectively.

The surface area of the surfactant-modified pillared clays decreases after aging 6 months to 1 year, as shown in Table 18. A similar behavior has been reported by Chevalier et al. for alumina pillared saponite.²⁰

Table 18 Surface area analysis for surfactant-modified pillared clays calcined at 500°C and subsequently aged (between 6 months and 1 year).

Initial surfactant loading (mg/g)	SBET (m ² /g)	t-plot			
		Stotal (t-plot) (m ² /g)	Vmicro (ml/g)	Smicro (m ² /g)	Smeso+ macro (m ² /g)
0	308	361	0.11	306	34
200	260	324	0.08	215	57
400	391	450	0.11	319	100
800	344	396	0.09	262	103
1000	378	433	0.11	301	103

For the highest loading of surfactant, most of the surface area loss is due to a decrease in the non-microporous surface area. This seems to indicate that some of the large mesopores created by the addition of surfactant are metastable and collapse by reorganization upon aging. After aging, however, a significant difference in porous properties remains observable for the surfactant-modified pillared clays.

We can conclude that the synthesis of alumina pillared Arizona montmorillonite in the presence of the surfactant Tergitol 15S-5 yields pillared products of high mesoporous surface area and high pore volume. This behavior is in contrast with the behavior observed for alumina pillared Wyoming montmorillonite.¹² The cationic exchange capacity difference between these two clays is certainly a key factor to explain this different behavior. With the highly charged Arizona montmorillonite, more Al₁₃

pillars are intercalated, allowing less surfactant molecules between the layers. The excess surfactant molecules probably form micelles which perturb the face to face stacking of the clay layers upon drying. Elimination of these micelles by calcination creates mesopores in the pillared clay. Unfortunately, we were unable to relate the mesopore sizes with the micelles sizes observed from photon correlation spectroscopy. The micelles formed in the presence of Al_{13} and clay are probably of a different nature than the micelles formed with the surfactant and Al_{13} alone.

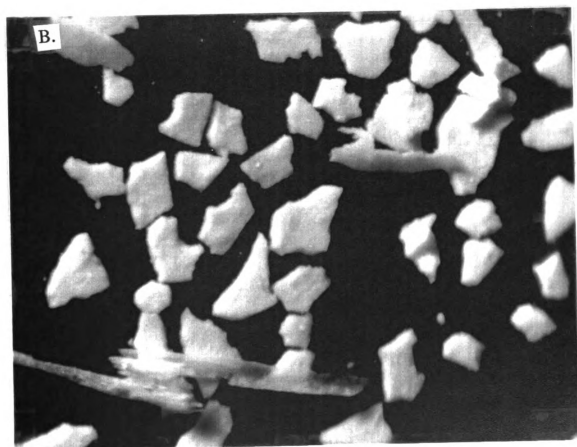
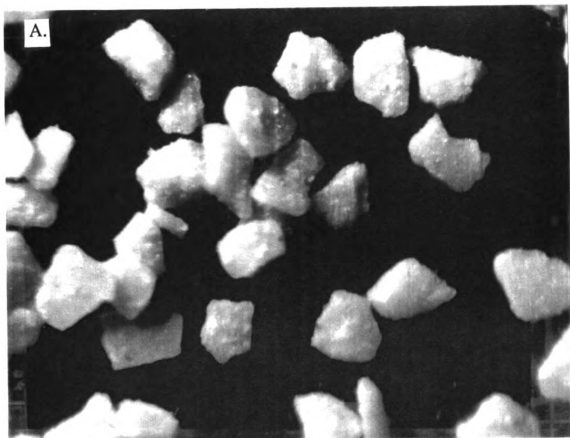
3. Particles shapes

Some of the surfactant modified pillared clays exhibited different particle shapes from those of regular pillared clays. In order to investigate these differences we observed the particles with an optical microscope. The pictures of 100-200 mesh fractions of the $S = 0$ and $S = 400$ materials are presented in Figure 24. The aspect ratio of the surfactant modified pillared clay ($S = 400$ mg/g) and of the regular pillared clay were about 2 and 1.4, respectively. This difference in the particle shape is however difficult to control and might be due to differences in aggregation mechanism during the drying step.

4. Acidity as observed by pyridine thermodesorption

The acidity of surfactant-modified pillared clays was studied by pyridine thermodesorption monitored by FT-IR. IR spectra of adsorbed pyridine after degassing at 250 °C are presented in Figure 25. There is very little difference in acidity between the various surfactant-modified pillared clays. The calculated²¹ amounts of Lewis and Brönsted sites presented in Table 19 confirm this conclusion. We expect the number of acid sites to be

Figure 24. 100-200 mesh (75-150 μm) fraction of catalyst particles as observed with an optical microscope (1 cm = 100 μm). A: S = 0, B: S=400.



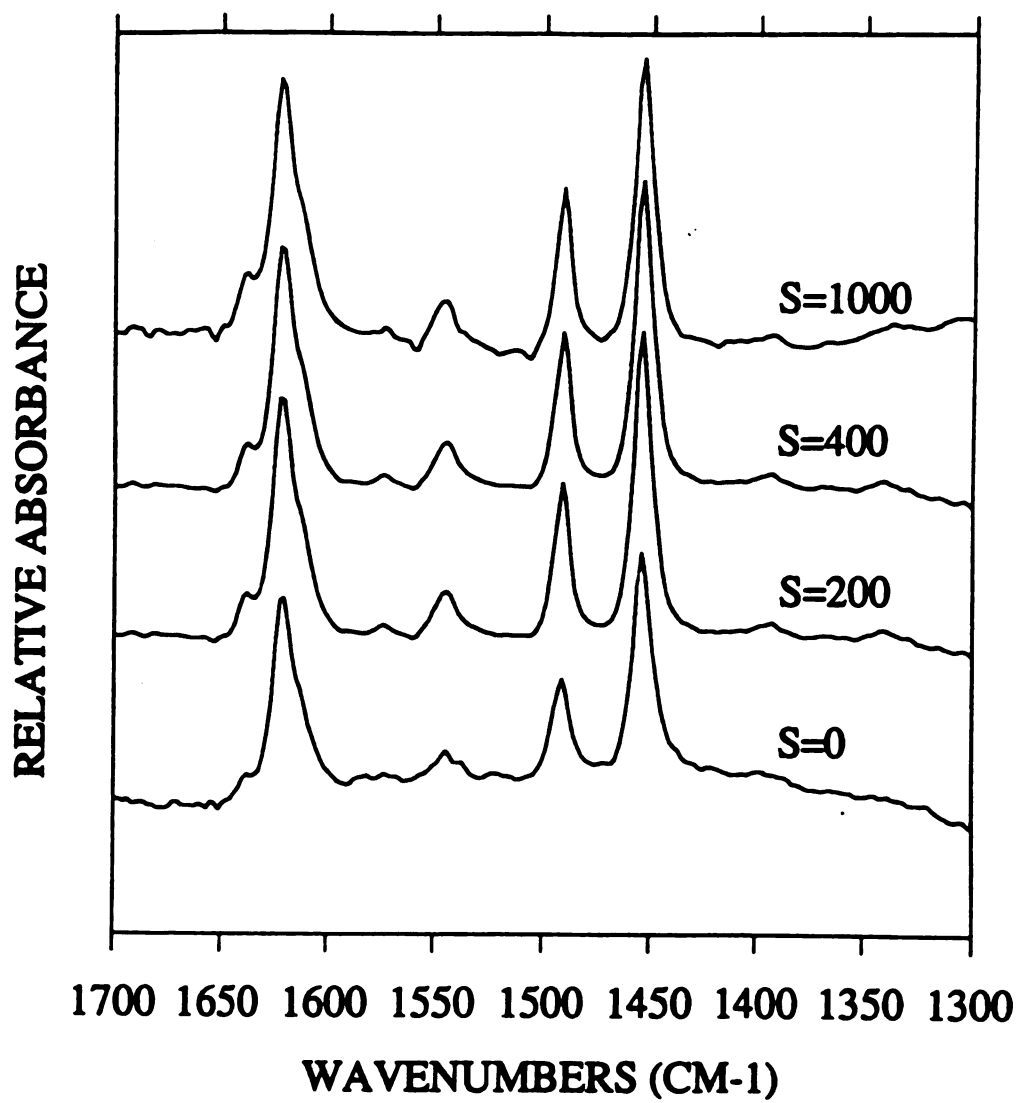


Figure 25. FTIR spectra of pyridine adsorbed on surfactant-modified pillared clays, after outgassing at 250 °C.

related to the amount of incorporated aluminum between the clay layers, since it is generally recognized that the acidity of alumina pillared montmorillonite originates from the pillars. It was shown in Table 1 that the amount of incorporated aluminum does not vary significantly with the surfactant loading. It is thus not surprising that the acidity remains constant regardless of the surfactant loading.

Table 19. Pyridine adsorbed on surfactant modified pillared clay after degassing at 250 °C.

Initial surfactant loading	Lewis-bonded pyridine (mmol/100g)	Brönsted- bonded pyr. (mmol/100g)	Total pyridine (mmol/100g)	Lewis/ Brönsted ratio
0	8.65	1.35	10.00	6.5
200	11.85	2.60	14.45	4.6
400	11.1	2.75	13.85	4.1
1000	11.2	2.60	13.80	4.3

C. Propene alkylation of biphenyl catalyzed by surfactant-modified pillared clays.

The activities of surfactant-modified pillared clays were compared by using either 0.04 g or 0.08 g of a 100-200 mesh (75-150 μm) fraction of catalyst. The results are presented in Table 20

Table 20. Catalytic activity of the surfactant modified pillared clays for the propene alkylation of biphenyl.^a

Initial Surfactant loading	S = 0	S = 200	S = 400	S = 800	S = 1000
Catalyst weight (g)	0.08	0.08	0.04	0.08	0.04
Conversion (%)	4	46	28	100	91
% Monoalkyl	95	73	83	4	27
% Dialkyl	5	24	16	27	41
% Trialkyl	0	3	1	46	28
% Tetraalkyl	0	0	0	23	4

a: The experimental conditions were as follows: 30 g (0.194 mol) biphenyl, 9 atm propene, 250°C, 20 hours.

Increasing loading of surfactant results in a dramatic catalytic activity increase. With 0.08 g of catalyst, the conversion improves from 4% with a conventional pillared clay (S = 0) to 100% for a surfactant-modified pillared clay (S = 800). With a 0.08g catalyst loading, the differences between the surfactant-modified pillared clays (S = 400, 800, 1000) were difficult to observe because of the very high biphenyl conversion level. We thus compared the surfactant-modified pillared clays (S = 400 and S = 1000) for a catalyst loading of 0.04g. Increasing surfactant loadings were also responsible for increasing catalytic activities in this case. No other catalyst that we have tested for this reaction⁶ was as active as the S = 1000 modified pillared clay, which afforded 91% of biphenyl conversion with only 0.13

wt% of catalyst. The number of acid sites on this catalyst is not exceptional, and the Brönsted acidity is not specially strong. Moreover, for all the surfactant-modified pillared clays, the acidity is very similar. We proposed previously that in our experimental conditions, propene alkylation of biphenyl is mainly diffusion controlled. Two main differences between surfactant-modified and non-modified pillared clays are thus relevant to explain the differences in catalytic activity: mesoporosity and aspect ratio. Firstly, the increase in mesoporous volume is certainly a decisive factor to increase the diffusion rate within the catalyst particles. Secondly, the increase of the aspect ratio might also contribute to facilitate access to the micropores since the width of the particle is smaller for the surfactant-modified pillared clays.

It is of interest to compare the catalytic activities of the surfactant-modified pillared clays and of the acid washed montmorillonite K10, which is a mesoporous solid. K10 affords 96% conversion with 0.7 wt% catalyst, whereas S = 800 surfactant modified pillared clay affords 100% conversion with only 0.25 wt%. It, thus, appears that this later catalyst is more active than K10, which is only mesoporous. A combination of large mesopores with micropores seems to be a relevant factor to obtain very active liquid phase catalysts. We compared the catalytic activity of the 100-200 mesh fraction with that of the <325 mesh fraction (Table 21). The increased conversion for the smaller particles, however, clearly shows that for the S = 400 loading, the reaction is still under diffusion control.

Table 21. Effect of particle size on catalytic activity of non-modified and surfactant-modified alumina pillared clay.

Initial surfactant loading (mg/g)	S = 0	S = 400
0.04 g of catalyst (100-200 mesh)		
Conversion	0	28
Monoalkyl		83
Dialkyl		16
Trialkyl		1
Tetraalkyl		0
0.04 g of catalyst (<325 mesh)		
Conversion	5	69
Monoalkyl	89	52
Dialkyl	11	34
Trialkyl	0	14
Tetraalkyl	0	0

D. Conclusion

By adding a non-ionic surfactant to the pillaring agent, it is possible to obtain a modified pillared clay that is highly mesoporous. The formation of micelles which prevent an extensive face-to-face layer stacking may explain this behavior. Surfactant-modified pillared clays exhibit very similar acidity properties, as observed from pyridine thermodesorption. These materials enabled us to study the effect of pore structure at constant acidity for alumina pillared clays catalysts. Very different catalytic activities for the propene alkylation of liquid phase biphenyl in comparison to non modified pillared clays were obtained. Indeed, these highly mesoporous materials

were over one order of magnitude more active than classical pillared clays. Under diffusion control, an increase in the mesoporous volume has, thus, a dramatic effect on the catalytic activity.

We demonstrated in this Chapter that the main factor influencing the catalytic activity of solid acids for the propene alkylation of biphenyl is their pore structure. In Chapter 5, however, we present evidence that strong acid sites are also a requirement to obtain efficient catalysts.

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CHAPTER FIVE
FLUORINE-MEDIATED ACIDITY OF ALUMINA PILLARED
FLUOROHECTORITE

A. Introduction

Owing to growing environmental concerns over the disposal of depleted acid catalysts, there is interest in replacing traditional catalysts, such as aluminum chloride and hydrofluoric acid, with recyclable solid acids. In order to obtain materials competitive with strongest homogeneous acid catalysts for organic isomerization, alkylation and acetylation reactions, several strategies are being explored to improve the acidity of existing acidic compounds. Reactions of inorganic oxides with metal halides, for instance, have afforded strong acid materials.¹ Fluorine, due to its strong electron withdrawing properties can improve the thermal stability and increase both the Lewis and the Brønsted acidity of an oxide when incorporated into the framework structure. It has been known for some time that the incorporation of fluorine in zeolites and related oxides enhances their acidity.^{2,3} Fluorinated aluminas and silica-aluminas, in particular, can be stronger acids than concentrated sulfuric acid.³

Much less work has been reported on the influence of fluorine substitution on the acidity of layered silicate clays. Fijal et al. have reported an improvement in catalytic properties of NH_4F -treated montmorillonite.⁴ However, it is difficult to introduce fluorine into a 2:1 smectite lattice without causing extensive destruction of the octahedral layer.⁵ It is much easier to introduce structural fluorine during the clay synthesis. Indeed, the synthesis of fluorohectorite has been known for some time.⁶ Suzuki et al. observed that fluorohectorite was much more active for the conversion of 2-propanol and ethanol than its non-fluorinated analogues.⁷ In the case of metal oxide pillared clays, Sakurai et al. reported an acidity enhancement for alumina pillared fluor-tetrasilicic mica containing La^{3+} exchange ions.⁸

We reported in Chapter 3 that alumina pillared fluorohectorite was very active for the propene alkylation of liquid phase biphenyl. This catalyst exhibited significant Brönsted acidity, which is unusual for alumina pillared smectite clays. Only alumina pillared beidellite was previously known to be a strong Brönsted acid.⁹ Most alumina pillared clays exhibit strong Lewis acidity. We also have observed that the acid catalytic activity of alumina pillared fluorohectorite clay is greatly reduced upon outgassing at temperatures above 350 °C. That is, the presence of fluorine in the layer structure enhances the acidity of the alumina pillared clay at outgassing temperatures below 350 °C, but at higher temperatures, the acidity is greatly diminished. In the present work we elucidate the structural factors which mediate the acidic properties of alumina pillared fluorohectorite.

B. Results

1. Synthesis

The reaction of Li⁺-fluorohectorite (CEC = 150 meq/100 g) with excess $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ formed by base hydrolysis of $AlCl_3$ (OH⁻/Al=2.4, 15 mmol Al/meq clay) affords an alumina pillared fluorohectorite (henceforth abbreviated APF) with a basal spacing of 19.2 Å (gallery height = 9.6 Å) under air-dried conditions.

As shown by the data in Table 22, the N₂ BET surface area of the pillared derivative depends greatly on the calcination temperature. An air-dried APF sample, when outgassed at 150 °C, exhibits an optimum surface area of 348 m²/g. Calcination at 250 °C and 350 °C results in a loss of up to one-third the initial surface area, but calcination at 500 °C restores the surface area to nearly its original value (325 m²/g). The surface areas

derived from t-plots of the nitrogen adsorption data parallel the BET values. Also, the t-plots reveal that the pillared product remains highly microporous at calcination temperatures up to 500 °C. The microporous surface areas in Table 22 indicate that at least two-thirds of the total N₂ surface area falls in the microporous region (< 20 Å diameter), regardless of the calcination temperature. The mesoporous surface areas, as determined from the t-plots, fall in the range 45-69 m²/g. The mesopore surface areas are not correlated with the calcination temperature. This is the behavior expected based on mesoporosity originating from particle texture and interparticle contacts. However, the dependence of microporosity on temperature suggests that important structural changes occur in the pillar and/or the layers with increasing calcination temperature. Also, earlier ²⁹Si MAS-NMR work has shown that some rearrangement of the layers most likely occurs upon calcination of APF.¹⁰

Table 22. Basal spacing and surface area analysis of alumina pillared fluorohectorite calcined at various temperatures.^a

Sample	Calcination Temperature	Basal spacing d ₀₀₁ (Å)	S _{BET} (m ² /g)	S _{t-plot} (m ² /g)		
				S _{total}	S _{micro}	S _{meso-macro}
APF	uncalcined	19.2	348	380	319	45
APF-250	250 °C	18.7	301	334	248	66
APF-350	350 °C	18.2	214	234	175	56
APF-500	500 °C	17.9	325	340	273	69

a: The outgassing of the samples was carried out under vacuum (10⁻⁴ torr) at 150 °C for a period of 12 hours.

Since the basal spacing of APFs decreases from 19.2 Å at 25 °C to 18.2 Å at 350 °C (cf., Table 22), a contraction in gallery height could contribute to the decrease in surface area over this temperature range. However, the effects of gallery height contraction on surface area most likely are small, because calcination at 500 °C causes the surface area to increase, despite an additional 0.3 Å decrease in gallery height. Thus, the temperature dependence of the surface area and microporosity of APF is attributable to changes in the constitution or distribution of the pillars, not on the reduction of gallery height.

2. Catalytic Activity and Acidity

We previously have shown in Chapter 3 that alumina pillared smectite clays are effective catalysts for the propene alkylation of liquid phase biphenyl at 250 °C. In general, alkylation activity is retained even when the clay is calcined at 500 °C. Under the reaction conditions described in Table 23, alumina pillared montmorillonite calcined at either 350 °C or 500 °C converts about 60% of liquid phase biphenyl to mainly mono- and dialkylated products. However, APF is an exception. As shown by the activity data in Table 23, catalysts, APF-250 and -350, which were prepared by calcination at 250° and 350 °C, respectively, exhibit conversions that are dramatically higher than the material calcined at 500 °C (ie APF-500). For APF-350, which is somewhat more active than APF-250, almost all the biphenyl was alkylated, mainly to di- and trialkyl isomers. Thus, APF-350 is substantially more active as an alkylation catalyst than a typical non-fluorinated pillared smectite clay. In fact, APF-350 is even more active than the strong Brönsted acid catalyst dealuminated mordenite, which affords only ~ 60% biphenyl conversion under analogous reaction conditions.

Although APF-350 is an exceptionally active alkylation catalyst, calcination of the clay at 500 °C dramatically reduces the alkylation activity. As shown by the data in Table 23 for APF-500, only 23% biphenyl conversion is achieved with this material, as compared with 98% conversion with APF-350.

Table 23. Biphenyl conversion and product distributions achieved with alumina pillared fluorohectorite and alumina pillared montmorillonite.^a

Catalyst	APF-250	APF-350	APF-500	Alumina Pillared Montmorillonite ^b
Biphenyl Conversion (%)	84	98	23	64
Product Distribution (%):				
monoalkyl isomers	44	11	85	63
dialkyl isomers	41	33	14	30
trialkyl isomers	13	38	1	7
tetraalkyl isomers	2	17	0	0

a: The reaction conditions were as follows: 30g biphenyl, 0.2g of a 100-200 mesh fraction of catalyst, 140 psi propylene, 250 °C, 20 hours reaction time.

b: The alumina pillared montmorillonite (Wyoming) was calcined at 350 °C before use. Similar conversions were obtained for the same catalyst after calcination at 500 °C.

In order to better elucidate the differences in alkylation activity for APF-350 and -500, we have examined the sorption of ammonia and pyridine on these materials. Figure 26 illustrates the results of the ammonia TPD experiments. Included in the Figure are curves for blank samples of the two

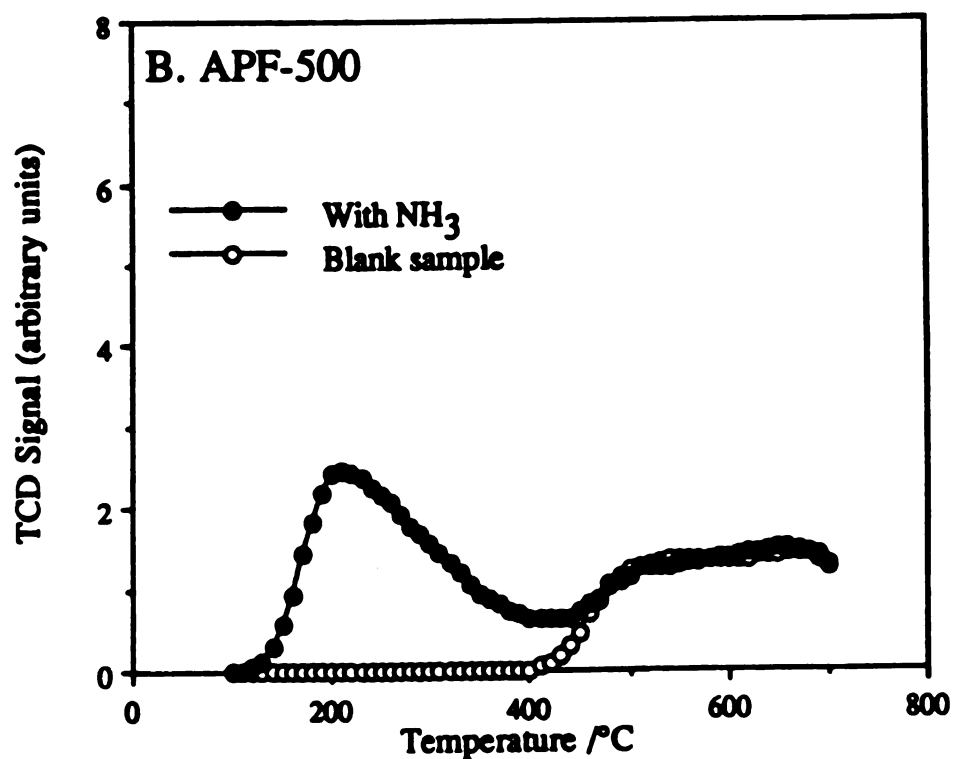
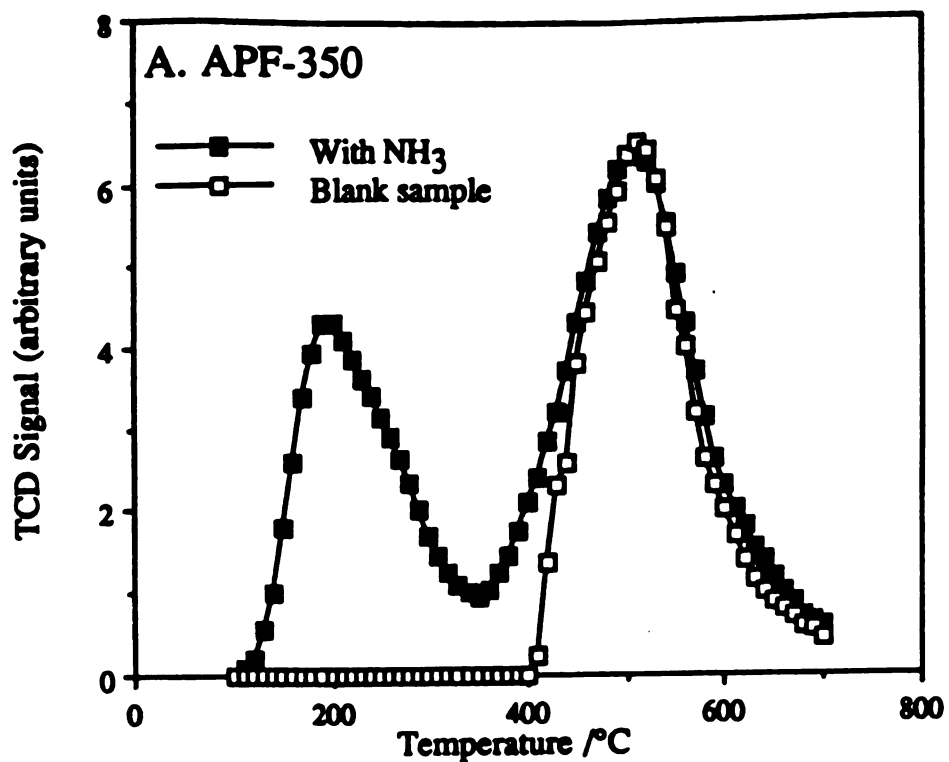


Figure 26 Ammonia TPD experiments of Alumina Pillared Fluorohectorite calcined at 350 $^{\circ}\text{C}$ (APF-350 and APF-500), solid symbols, and blank experiments (without ammonia adsorption) on the samples, open symbols.

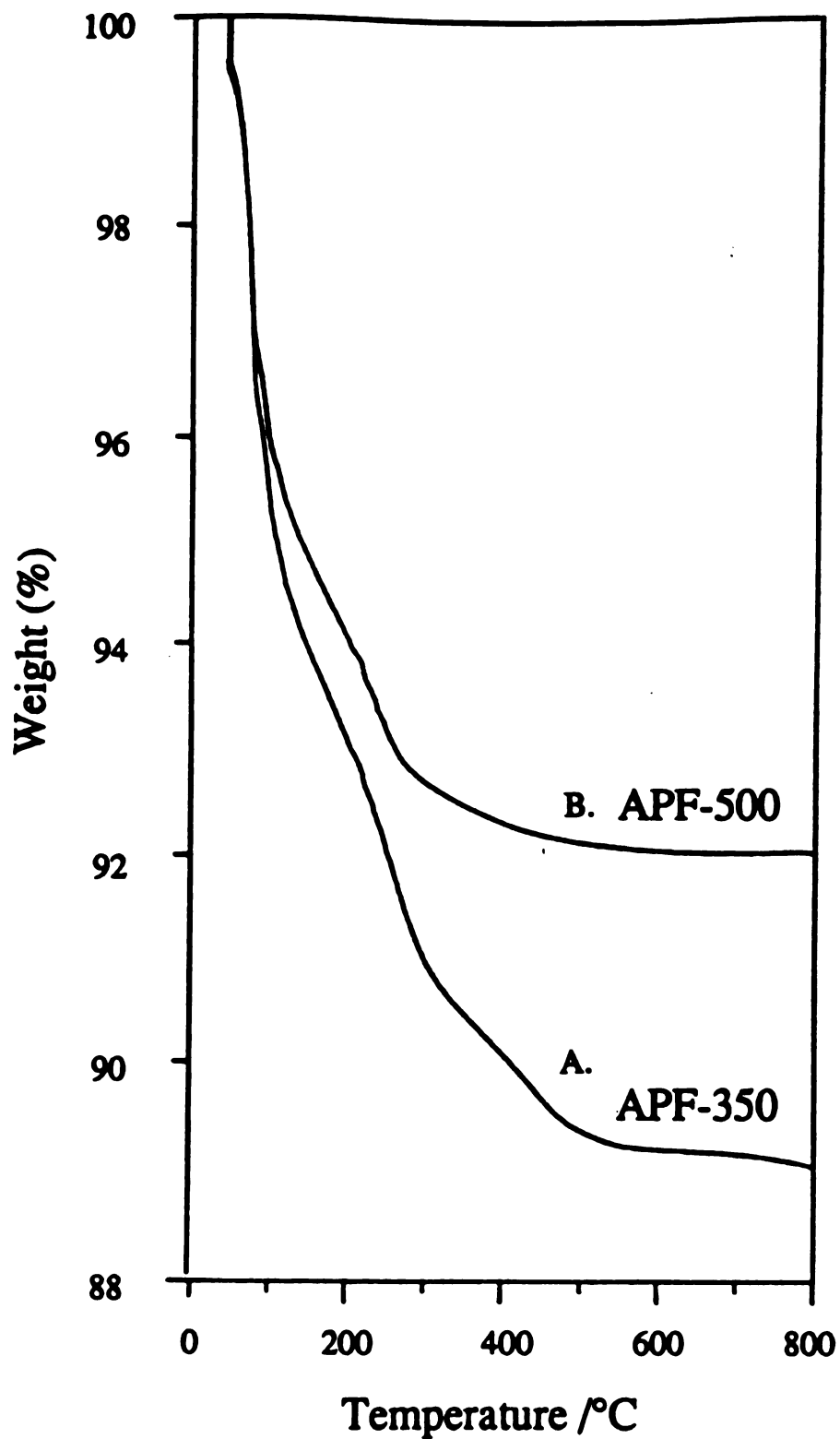


Figure 27. Thermogravimetric analysis of : (A) alumina pillared fluorohectorite calcined at 350 °C (APF-350), (B) alumina pillared fluorohectorite calcined at 500 °C (APF-500).

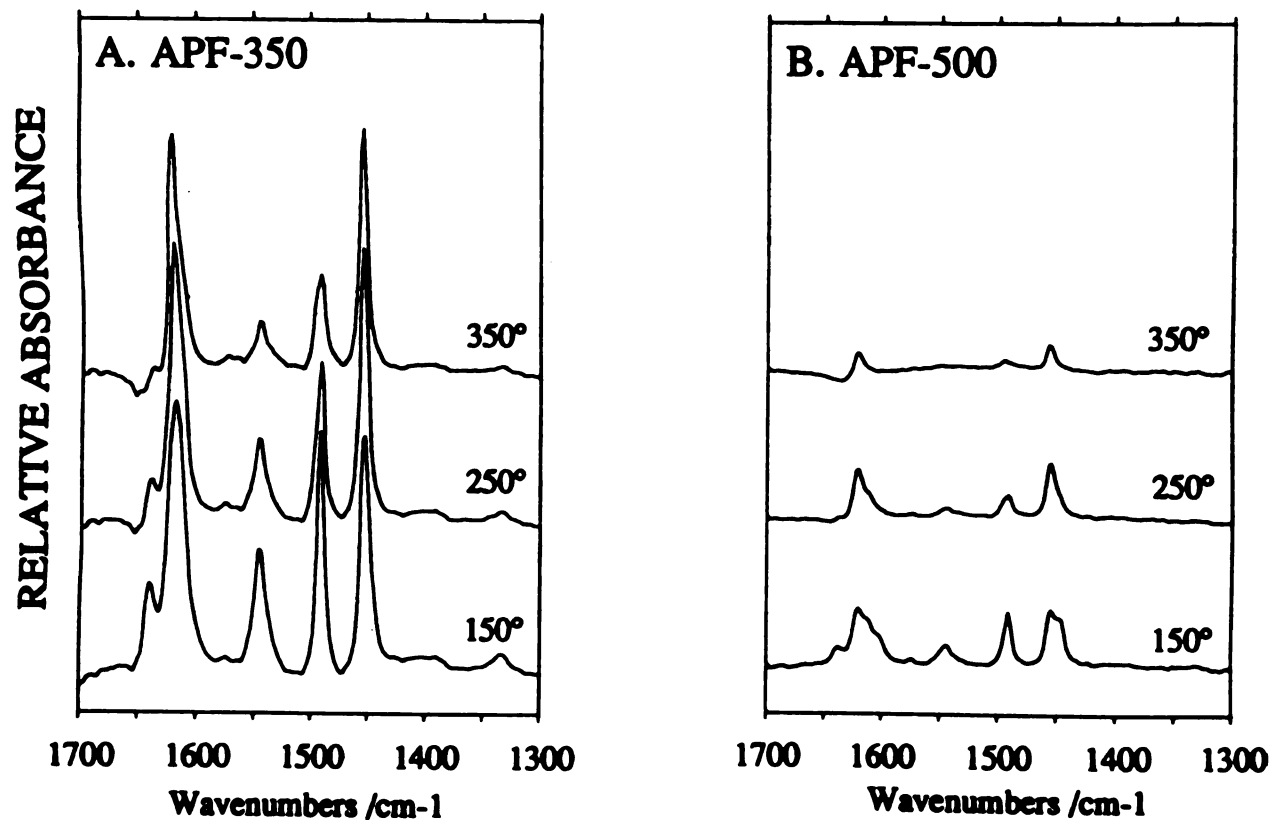


Figure 28. Infrared spectra of pyridine adsorbed on alumina pillared fluorohectorite calcined at 350 °C (APF-350) and 500 °C (APF-500). Pyridine-adsorbed samples were evacuated at 150 °C, 250 °C and 350 °C.

clays in the absence of adsorbed ammonia. The maxima centered near 500° for the blank samples are attributable to volatile products resulting from structural rearrangement. TGA curves shown in Figure 27 for the pristine clays verify the loss of mass above 350°. Returning to the TPD curves in Figure 26, we see that APF-350 and -500 both exhibit NH₃ desorption peaks centered near 200 °C. The asymmetry in the peaks suggests a distribution of acid strengths. Integration of the TPD curves over the temperature range 100-350° reveals that the amount of NH₃ chemically bound to APF-350 is approximately twice that for APF-500. Thus, the ammonia TPD results verify the presence of a substantially larger number of acid sites for APF-350.

The thermal desorption of chemisorbed pyridine, as monitored by FTIR, is shown in Figure 28. These results also reveal significant differences in the acidity of APF-350 and APF-500. For APF-350, both Brönsted and Lewis acid sites are present even after desorption at 350 °C, as evidenced by the pyridine ring stretching frequencies at 1545 and 1450 cm⁻¹, respectively. In contrast, the fewer acid sites present on APF-500 are mostly of the Lewis type. Using the molar extinction coefficients provided by Datka¹¹ for chemisorbed pyridine, we estimate the total number of acid sites present on APF-350 at 150° to be 24 mmol/100g with the Lewis to Brönsted ratio being 1.4. For APF-500 the total amount of bound pyridine at 350° is 1.5 mmol/100 g with no Brönsted sites present. Thus, the acid sites on APF-350 are both more numerous and stronger than those present in APF-500.

3. MAS-NMR Spectroscopy

The thermochemical alterations indicated by the differences in NH₃ and pyridine sorption for APF-350 and -500, as well as by the TGA curves

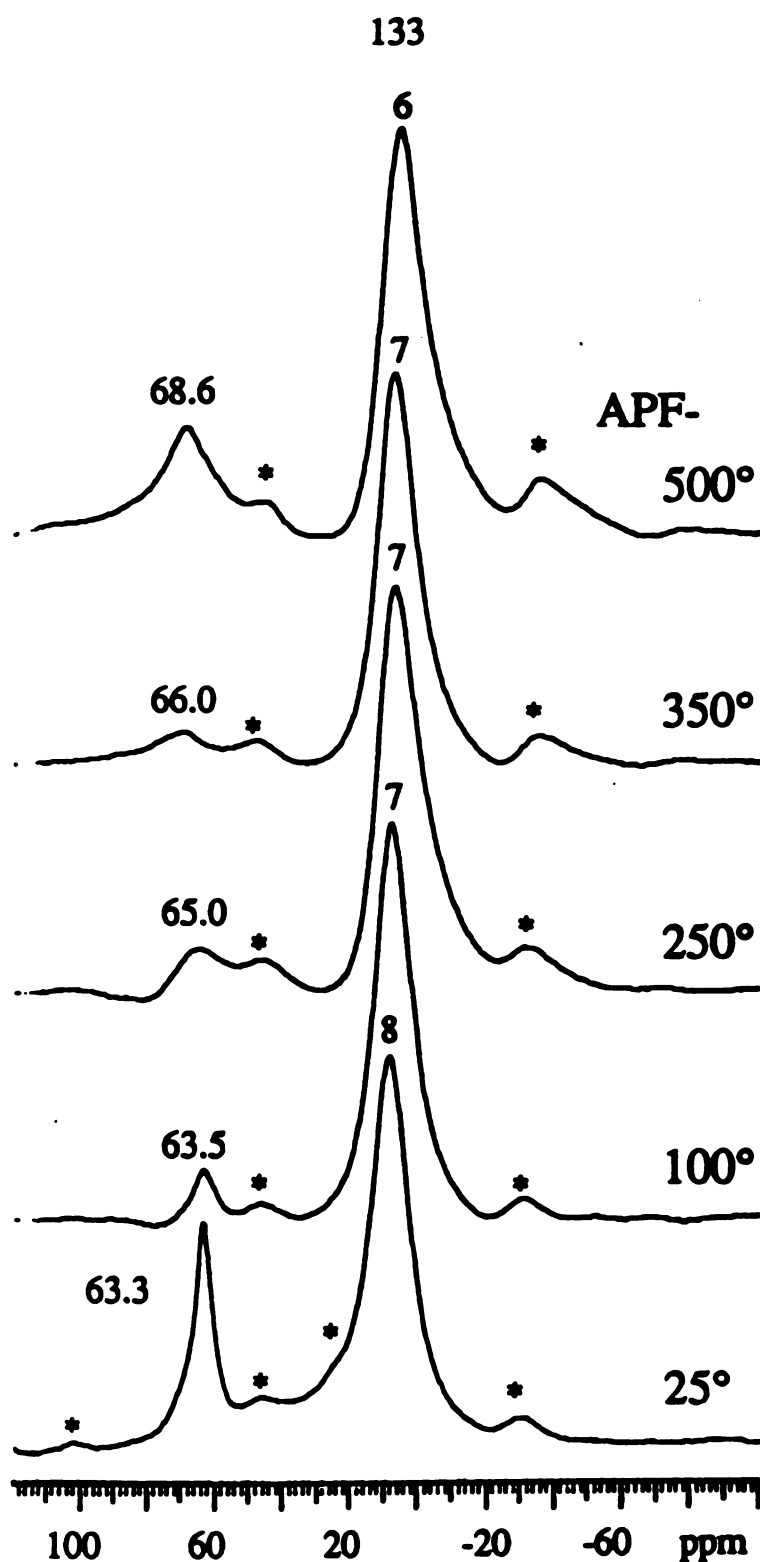


Figure 29. ^{27}Al MAS-NMR spectra of alumina pillared fluorohectorite that have been dried in air at the following temperatures: 25 °C, 100 °C, 250 °C, 350 °C, 500 °C. Chemical shifts are relative to $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$.

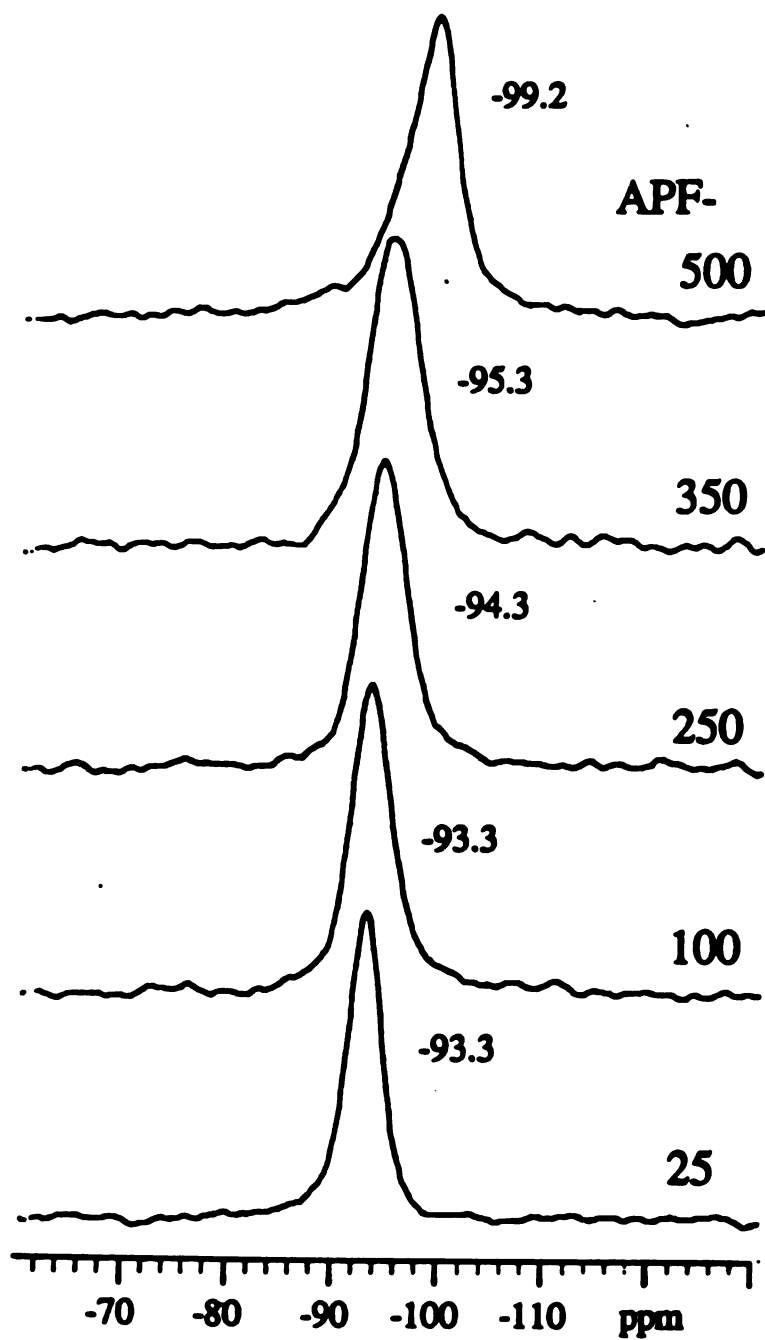


Figure 30. ^{29}Si MAS-NMR spectra of alumina pillared fluorohectorite that have been dried in air at the following temperatures: 25 °C, 100 °C, 250 °C, 350 °C, 500 °C. Chemical shifts are relative to TMS.

(cf., Figure 29), were further studied by ^{27}Al , ^{29}Si and ^{19}F MAS-NMR. As shown by the ^{27}Al spectra in Figure 29, a resonance characteristic of tetrahedral aluminum is observed for air-dried APF before calcination. This resonance, together with the peak for octahedral aluminum near 8 ppm, is characteristic of the intercalated Al_{13} oligomer.¹² Upon calcination of the sample up to 350 °C, the tetrahedral signal gradually decreases in intensity and broadens. After calcination at 500 °C the tetrahedral signal increases in intensity and shifts downfield to 69 ppm, while the octahedral signal shifts slightly upfield to 8 ppm. A shift in the ^{29}Si resonance of APF also is observed upon calcination. As shown in Figure 30, the silicon chemical shift moves from -92 ppm for air-dried APF to -99 ppm for APF-500. The appearance of a high field ^{29}Si resonance has been observed previously for calcined alumina pillared derivatives of fluorohectorite¹⁰ and hectorite.¹³ These changes in the ^{27}Al and ^{29}Si chemical shifts indicate that important structural changes occur upon calcination of APF, especially when the calcination temperature is near 500 °C.

The ^{19}F MAS NMR spectrum of a natural fluorine-containing hectorite has been recently reported by Huve et al.¹⁴ to exhibit two resonances. We also observe two non-equivalent environments for fluorohectorite. To assist in the ^{19}F chemical shift assignments, we have included in this study the spectrum for Laponite B, a low charge density fluorohectorite. Figure 31 compares the ^{19}F spectrum for the high charge density Li^+ -fluorohectorite used in the pillaring experiments (CEC=150 meq/100g) with the spectrum for low charge density Laponite (CEC = 73 meq/100g). The two clays exhibit two ^{19}F signals near -10 and -16 ppm. The low field/high field peak intensity ratio, as determined by deconvolution of overlapping Lorentzian and Gaussian line shapes, were dependent on the

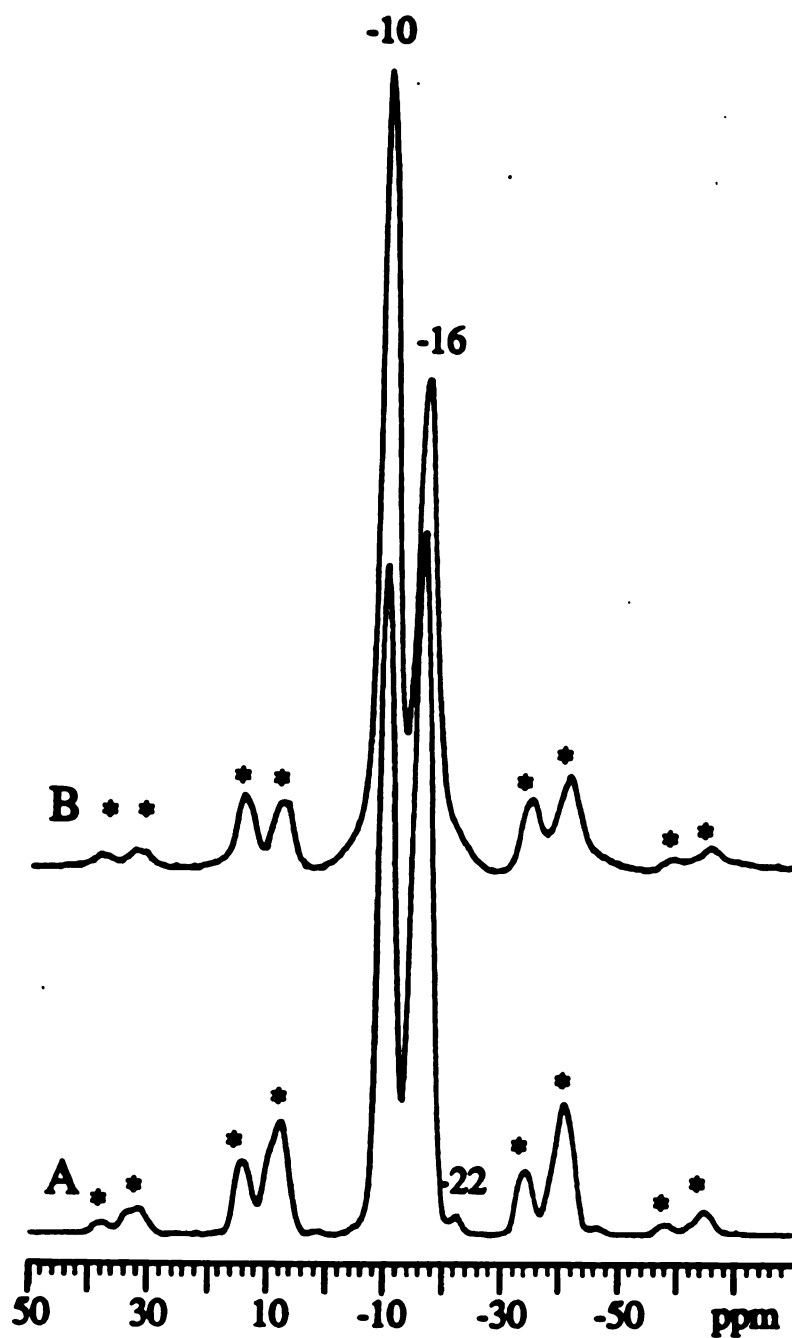


Figure 31. ^{19}F MAS-NMR spectra of (A) Li^+ -fluorohectorite, (B) Li^+ -Laponite B. Chemical shifts are relative to C_6F_6 .

layer charge densities of the two clays. These ratios are presented in Table 24 together with the CEC and elemental analyses for these clays.

Table 24: Octahedral metal ions composition based on a O_{20}F_4 unit cell of two fluorohectorite obtained from ^{19}F NMR, CEC measurement and elemental analysis.

	Fluorohectorite	Laponite B
Ratio of -10/-16 ppm ^{19}F intensities	0.78	1.85
Composition calculated from ^{19}F NMR	$\text{Mg}_{4.88}\text{Li}_{1.12}$	$\text{Mg}_{5.3}\text{Li}_{0.70}$
Cation Exchange Capacity, meq/100g	150	73
Composition calculated from CEC	$\text{Mg}_{4.82}\text{Li}_{1.18}$	$\text{Mg}_{5.42}\text{Li}_{0.58}$
Mg/Li molar ratio	1.47	6.57
Composition calculated from elemental analysis	$\text{Mg}_{4.46}\text{Li}_{1.54}$	$\text{Mg}_{5.58}\text{Li}_{0.42}$

The changes which occur in the ^{19}F MAS-NMR spectra for APF as a function of calcination temperature are presented in Figure 32. The pillared clay dried at 25 °C exhibits the same two ^{19}F resonances as the Li^+ -exchanged form. However, upon calcination of the pillared clay over the

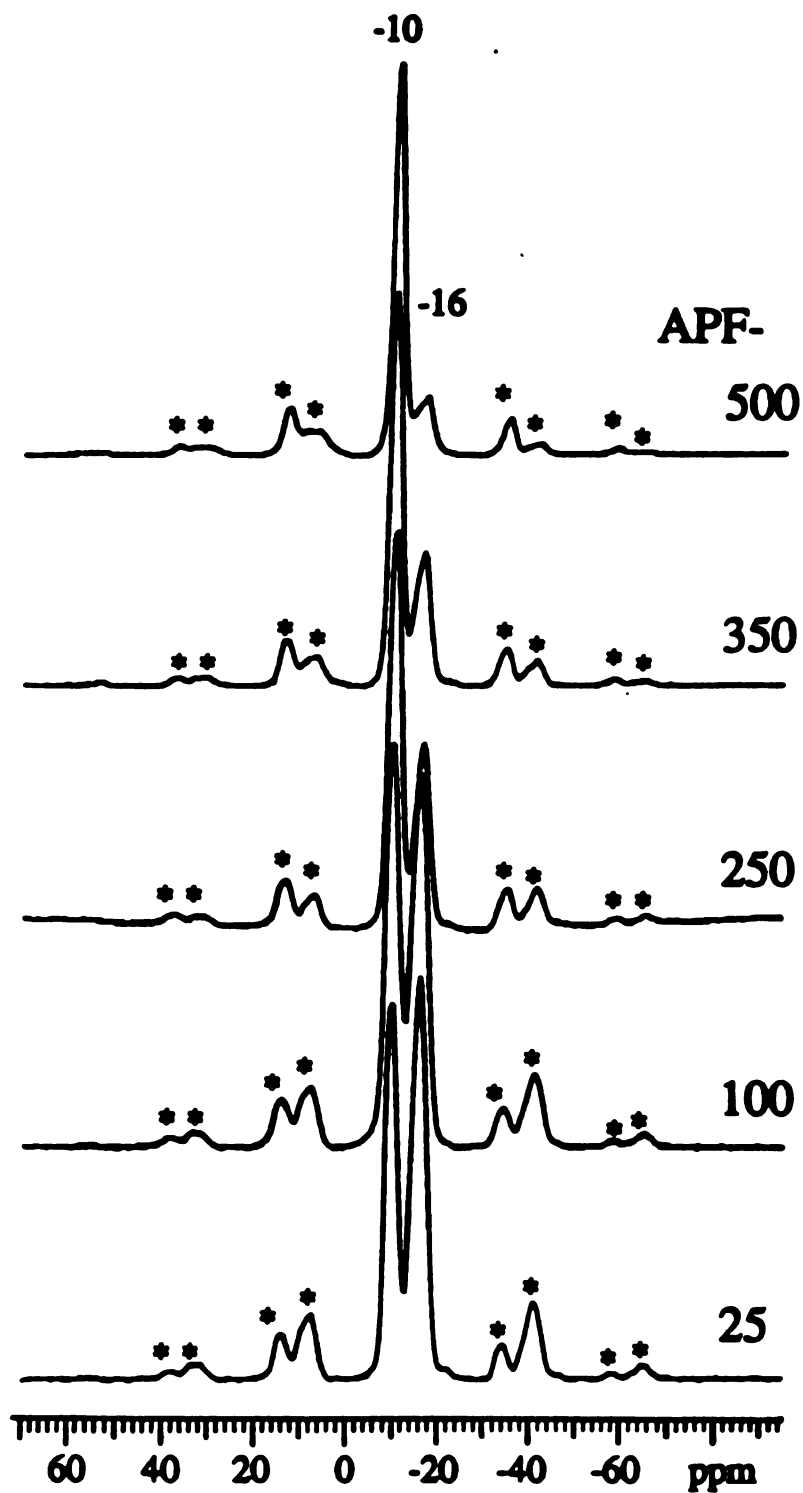


Figure 32. ^{19}F MAS-NMR spectra of alumina pillared fluorohectorite that have been dried in air at the following temperatures: 25 $^{\circ}\text{C}$, 100 $^{\circ}\text{C}$, 250 $^{\circ}\text{C}$, 350 $^{\circ}\text{C}$, 500 $^{\circ}\text{C}$. Chemical shifts are relative to C_6F_6 .

temperature range 100-500 °C, the intensity of the high field resonance decreases eventually to ~ 15% of its initial value. This loss of structural fluorine over the temperature range 350-500 °C is correlated with the decrease in acid catalytic activity.

4. FTIR Spectroscopy

An effort was made to examine the loss of structural fluorine from APF by FTIR spectroscopy. The temperature dependent vibrational spectra for Li⁺-fluorohectorite in Figure 33 are compared with those for APF in Figure 34. Li⁺-fluorohectorite outgassed at 30 °C exhibits stretching frequencies characteristic of coordinated water ($\nu_s = 3600$, $\nu_a = 3640$ cm⁻¹) and water of hydration (3490 cm⁻¹).¹⁵ Several bands characteristic of the layered framework structure appear in (region 1300-400 cm⁻¹), including symmetric and asymmetric SiOSi vibrations at 1095 and 993 cm⁻¹, a shoulder at ~ 530 cm⁻¹ corresponding to MgO stretching, and a SiO bending band at 470 cm⁻¹.¹⁶ The relatively weak band at 712 cm⁻¹ is assigned to a metal-fluorine stretching vibration.¹⁷ As the outgassing temperature is increased to 250 °C and beyond, the galleries become dehydrated and the vibrations due to OH stretching bonds are verbally eliminated. Little or no change occurs, however, in the vibrations of the layered framework upon outgassing Li⁺-fluorohectorite at temperatures as high as 500 °C.

Owing to the presence of the intercalated Al₁₃ oligomer, the FTIR spectral features of APF differ significantly from those of the Li⁺-exchanged precursor. As shown by a comparison of Figures 33A and 34A, the OH stretching region of APF-30 is broader than that observed for the corresponding Li⁺ derivative. Also, a new band is present at 756 cm⁻¹, which we tentatively assign to a Al-O stretching vibration of the Al₁₃

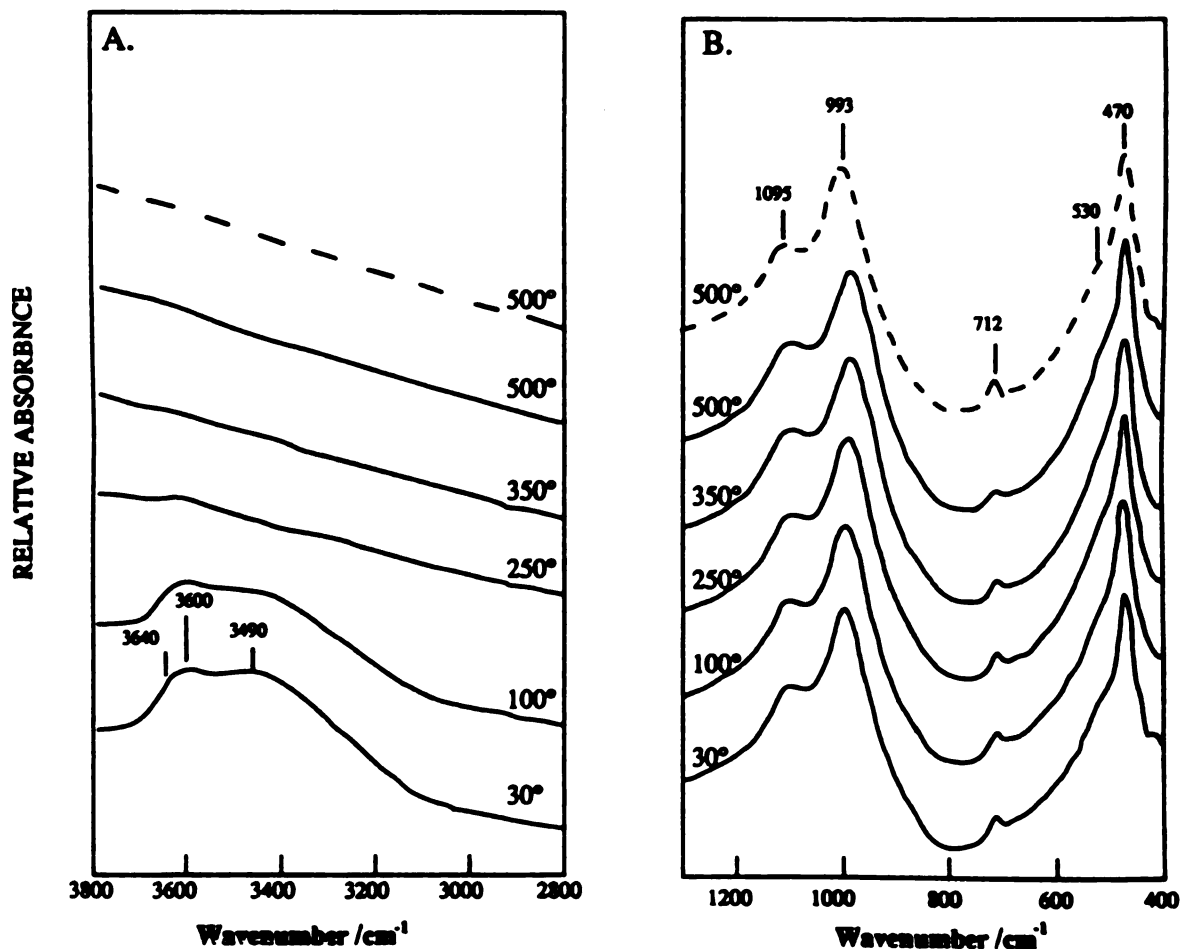


Figure 33. Infrared spectra for Li^+ fluorohectorite obtained at different temperatures: (A) for the spectral range 3800-2800 cm^{-1} ; (B) for the spectral range 1300-400 cm^{-1} . All spectra recorded under vacuum at the temperature indicated, except for the dashed spectrum for which the sample was heated at 500 °C and subsequently cooled to room temperature to record the spectrum.

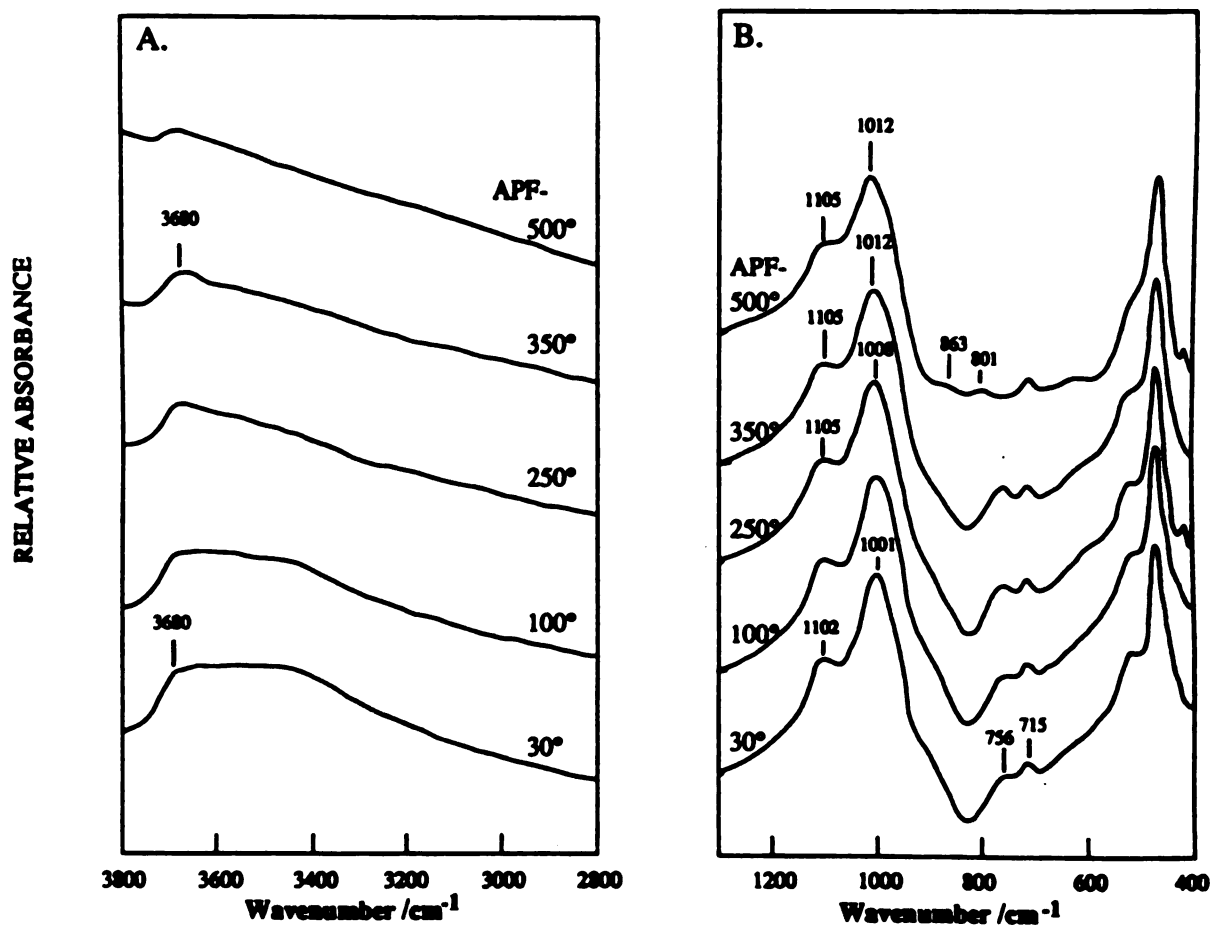


Figure 34. Infrared spectra for alumina pillared fluorohectorite obtained at different temperatures: (A) for the spectral range 3800-2800 cm^{-1} ; (B) for the spectral range 1300-400 cm^{-1} . All spectra recorded under vacuum at 30 °C.

oligomer. Upon thermal dehydration of APF, the absorbance in the hydroxyl group region decreases, but a OH vibration at 3680 cm^{-1} persists even after outgassing at 500° (see spectrum APF-500 in Figure 34A). Also, significant changes occur in the framework vibrations of APF, especially above 350°C . The SiOSi band at 1001 cm^{-1} in APF-30 shifts progressively to 1012 cm^{-1} in APF-500. Also, a comparison of the spectra for APF-350 and APF-500 in Figure 34B indicates the replacement of the 756 cm^{-1} band of the oligomer by two new bands at 863 and 801 cm^{-1} . These latter changes suggest a possible modification of the pillar, even though the basal spacings for APF-350 and APF-500 are similar ($d_{001} \sim 18\text{ \AA}$). However, the FTIR data do not provide a direct indication for the loss of fluorine from the layer framework, as the metal-fluorine vibration at 715 cm^{-1} is retained throughout the entire temperature range investigated.

5. Mass Spectrometry

Our mass spectral studies suggest that at least some of the fluorine lost from the framework structure of APF can be detected in the gas phase. Figure 35A presents the mass spectra for the volatiles eliminated from Li^+ -fluorohectorite when heated at 250°C . The spectra for this unpillared precursor show the elimination of water and trace amounts of surface contaminants such as CO_2 . Analogous mass spectra for APF are given in Figure 35B. In contrast to Li^+ -fluorohectorite, the alumina pillared product eliminates volatiles with mass numbers of 19 and 20, corresponding to F and HF, respectively. The evolution of the intensity of the mass 18, 19 and 20 peaks with temperature is presented in Figure 36. The intensities of mass 19 and 20 increase most rapidly between $200^\circ - 350^\circ\text{C}$.

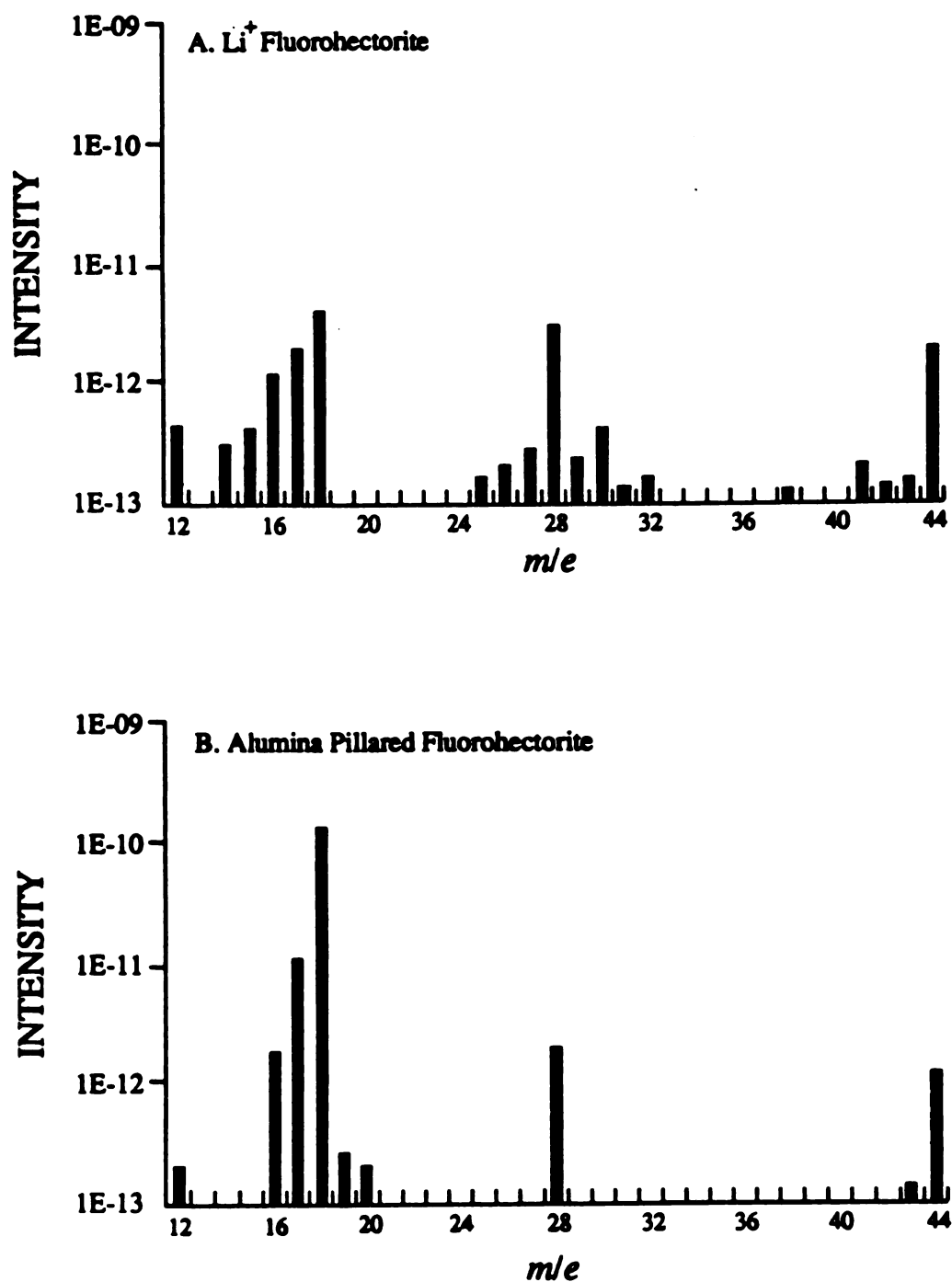


Figure 35. Mass spectra of volatile products formed upon heating fluorohectorite clays at 250 °C: (A) Li⁺-fluorohectorite, (B) alumina pillared fluorohectorite.

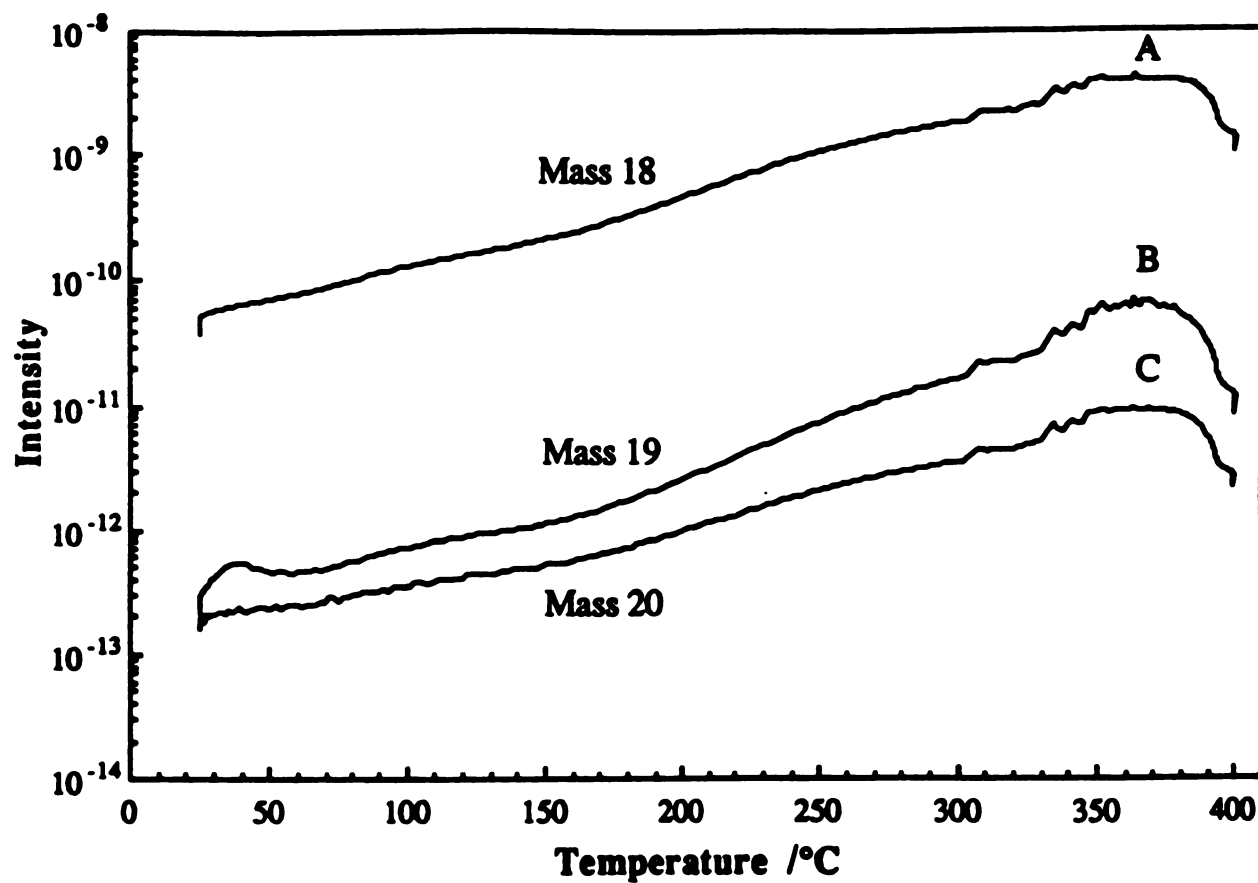


Figure 36. Temperature dependence of the mass spectral intensities for the volatile products formed on heating alumina pillared fluorohectorite: (A) mass 18, (B) mass 19, (C) mass 20.

C. Discussion

Alumina pillared fluorohectorite calcined at 350 °C (*ie*, APF-350) is an exceptionally active pillared clay catalyst. The acidity of this material is reflected in the propylene alkylation of liquid phase biphenyl (*cf.*, Table 23) the adsorption of ammonia (*cf.*, Figure 26), and in the chemisorption of pyridine through Lewis and Bronsted acid mechanisms (*cf.*, Figure 28). On the other hand, alumina pillared fluorohectorite calcined at 500 °C (*ie*, APF-500) is less active than a conventional alumina pillared smectite clay such as montmorillonite. The differences in acidity appear to be related to the thermal behavior of fluorine in the 2:1 layered silicate framework. Thus, we consider first the significance of our ^{19}F MAS-NMR results.

Pristine Li^+ -fluorohectorite exhibits two ^{19}F resonances at -10 and -16 ppm. The same two lines are found for Li^+ -Laponite B, a related perfluorinated 2:1 structure with a lower charge density. Since the relative intensities of the ^{19}F resonances depend on layer charge density (*cf.*, Figure 31), the two fluorine environments are determined by the composition of the 2:1 silicate layers. In both clays all of the tetrahedral sites are occupied by silicon and all of the octahedral sites are occupied by Mg^{2+} and Li^+ . However, the ratio of Mg^{2+} to Li^+ differs for the two clays.

In order to assign the fluorine resonance to specific layer environments, we consider the filling of octahedral interstices in a 2:1 layered structure. Figure 37 depicts the octahedral sheet of such a structure.¹⁸ Fluorine atoms are represented by full and open circles, depending on whether they are located in the upper or lower plane of the sheet. In a non-fluorinated clay these same positions would be occupied by hydroxyl groups. In a O_{20}F_4 framework unit cell, there are four fluorines

and six octahedral interstices. The fluorine atoms bridge three octahedral positions, which we refer to as "octahedral triads." Each octahedral triad consists of one M1-type octahedron in which the fluorine atoms are arranged at trans positions and two M2-type octahedra with the fluorines at cis positions. For a trioctahedral smectite in which all octahedral positions are filled by Mg^{2+} and Li^+ ions, the Li^+ ions will prefer to occupy M1 type octahedra in order to better distribute the net negative charge on the trans fluorines. The M2 sites filled by Mg^{2+} are formally electrically neutral. Thus, two types of octahedral triads are anticipated. One triad, designated T1, bears a net negative charge with Li^+ in a M1 site and two Mg^{2+} ions in M2 sites. The other triad, designated T2, is electrically neutral with the M1 and M2 octahedral filled by Mg^{2+} . Triads containing more than one Li^+ should be strongly disfavored on electrostatic grounds. The exceedingly weak resonance at -22 ppm in the spectrum of fluorohectorite (cf., Figure 31A) might represent a Li_2Mg triad, though we cannot preclude the possibility of alternative assignments based on trace amounts of impurity phases.

For the two ^{19}F resonances in Li^+ -fluorohectorite and Li^+ -Laponite B, we assign the upfield line at -16 ppm to the fluorine atoms in electrically charged T1 triads. The downfield line at -10 ppm is attributed to the fluorines of neutral T2 triads. Analogous chemical shift assignments have been proposed recently by Huve et al.¹⁴ in their ^{19}F NMR studies of a fluorinated hectorite. Our assignments are consistent with the more negatively charged fluorine occurring at higher field. For instance, the chemical shift for NaF and MgF_2 occur at -58 ppm and -31.8 ppm, respectively.¹⁹ Also, the shifts are in agreement with the layer charge densities of fluorohectorite and Laponite B. The layer unit cell formulas can

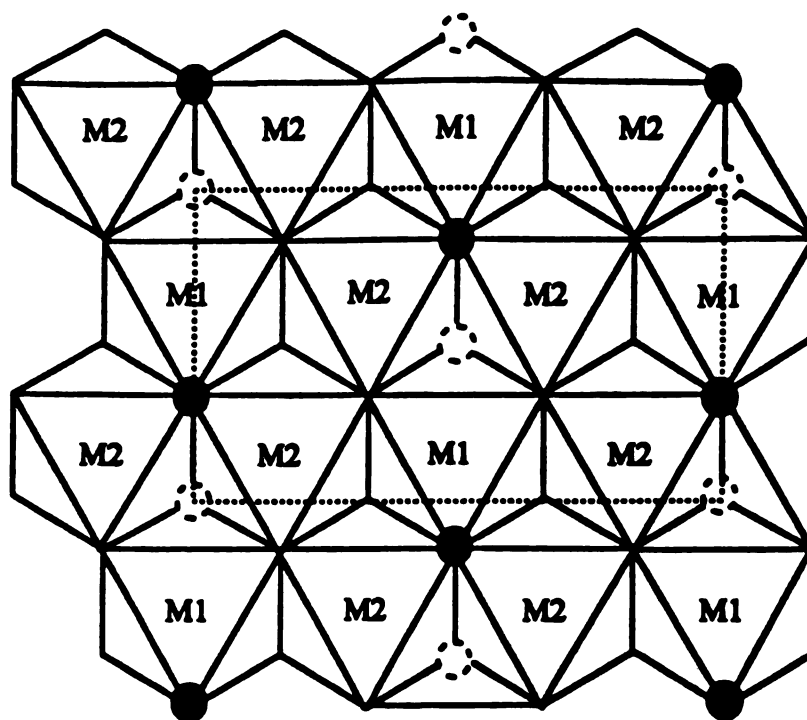


Figure 37. Representation of the octahedral sheet in fluorohectorite (see text). Fluorine atoms are represented by full or dashed circles depending whether they lay above or below the layer plane. The dashed line represents the octahedral sheet of a $O_{20}F_4$ unit cell.

be expressed in general as $[\text{Mg}_{6-x}\text{Li}_x]\text{Si}_8\text{O}_{20}\text{F}_4$, or, alternatively, as $[\text{Mg}_3]_{2-x}[\text{Mg}_2\text{Li}]_x\text{O}_{20}\text{F}_4$. The latter formulation indicates the T1 to T2 triad ratio to be $x/2-x$. Table 24 compares the octahedral metal ion compositions obtained by ^{19}F NMR with the compositions estimated from the cation exchange capacities. The agreement in compositions confirms the chemical shift assignments. Included in the Table are compositions obtained from chemical analyses. It would appear that the analytical results are less reliable estimates of composition owing perhaps to the difficulty in achieving accurate silicon analyses in the presence of fluorine.

We consider next the catalytic significance of the dramatic temperature dependence of the ^{19}F spectrum for the alumina pillared derivative (cf., Figure 32). As the pillared clay is heated in air to 350 °C, a hydrolysis reaction occurs which preferentially replaces fluorine at charged T1 sites with hydroxyl groups. At 350 °C, approximately 70% of the T1 fluorines have been hydrolyzed. Evidence for hydrolysis is provided by the concomitant appearance of an OH stretching band at 3680 cm^{-1} characteristic of layer hydroxyl groups (cf., Figure 33).^{15,16,20} The preferential hydrolysis of fluorine in charged T1 sites presumably is the result of an energetically more favorable charge distribution within the layer framework.

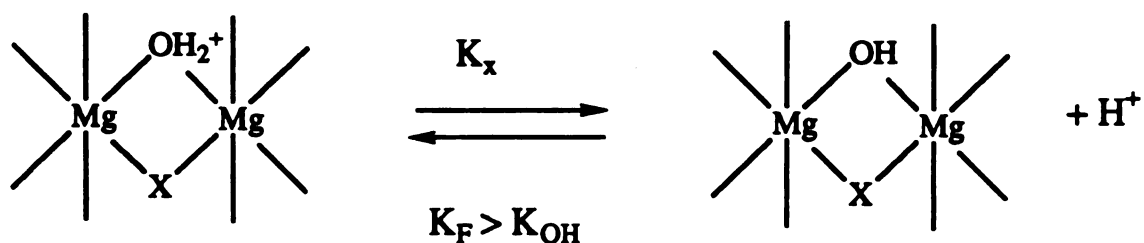
Our mass spectroscopic results (cf., Figures 35 and 36) indicate that HF can be detected as a volatile reaction product. It is unlikely that the replacement of fluorine by hydroxyls is accompanied by formation of SiF_4 or MgF_2 , because these latter species should form with equal facility from fluorine in both T1 and T2 sites. Also, we find no experimental evidence for SiF_4 or MgF_2 by-products. Thus, the main mechanism for replacement of T1 fluorine by hydroxyls up to a reaction temperature of 350 °C is the simple

hydrolysis reaction. Further confirmation for hydrolysis is provided by the parallel relationship between the amount of water liberated in the hydrolysis process and the intensities of the mass 19 and 20 peaks characteristic of F^+ and HF^+ (cf., Figure 36). Presumably, the water is supplied in large part by the dehydroxylation of the alumina pillars on the gallery surfaces.

A plausible pathway for the hydrolysis of T1 fluorines is the interlayer transport of water to the basal hexagonal cavities of the tetrahedral sheet, below which the fluorine atoms are located. The proposed mechanism is schematically illustrated in Figure 38. It is important to emphasize that access to the hexagonal cavities is facilitated by the pillared galleries ($d001 \sim 18 \text{ \AA}$). No hydrolysis occurs for the collapsed Li^+ -exchanged form of fluorohectorite ($d001 \sim 10 \text{ \AA}$ at 350°), as judged from the absence of layer OH vibrations in the FTIR spectrum (cf., Figure 35).

The hydrolysis of the charged T1 fluorine sites in APF-350 most likely contributes significantly to the exceptional acidity of this pillared clay. It has been previously proposed that the calcination of non-fluorinated alumina pillared clays, such as beidellite or montmorillonite, transforms the Al_{13} aggregates into a $\gamma-Al_2O_3$ type structure and causes protons to migrate to basic hydroxyl sites in the layers.¹³ These protons are labile and can migrate back to the gallery region for catalytic reaction. The layer hydroxyl groups of APF-350 can also act as binding sites for protons. Hydrolysis of the trans fluorine positions in T1 octahedral triads places the resulting hydroxyl groups at positions cis to the fluorines of adjacent neutral T2 triads (cf., Figure 37). The electron withdrawing effect of the cis fluorine will enhance the acidity of the protonated hydroxyl group, relative to a non-fluorinated smectite clay (cf., Figure 38). That is, the dissociative

equilibrium constant defined by the equation below is larger when the *cis* position X is fluorine rather than hydroxide:



Although APF-350 is an exceptionally acidic pillared clay catalyst, a dramatic decrease in activity occurs when the clay is calcined at 500 °C. The loss in acidity may be judged from the decrease in biphenyl alkylation activity (*cf.*, Table 23), a 50% loss in ammonia binding capacity (*cf.*, Figure 26), and an order-of-magnitude decrease in pyridine chemisorption by Lewis and Brønsted acid mechanisms (*cf.*, Figure 28).

Several factors can contribute to the temperature sensitivity of an alumina pillared clay catalyst. For instance, a decrease in the activity of an alumina pillared montmorillonite catalyst has been observed for the gas phase conversion of 1, 2, 4 - trimethylbenzene when the catalyst is calcined at 500 °C. In this case the loss in activity most likely was due to loss of Brønsted acidity.²¹ However, for the liquid phase alkylation of biphenyl, the reactivity of an alumina pillared clay is generally not sensitive to calcination temperature over the range 350-500 °C. Thus, the difference in alkylation activity for APF-350 and APF-500 is atypical. Our previous studies of liquid-phase biphenyl alkylation suggest that reactivity depends in part on the meso- to micropore ratio. The pore structure is important for this reaction because the reaction is under diffusion control. However, the dramatic difference in acid catalytic activity between APF-350 and APF-500 cannot

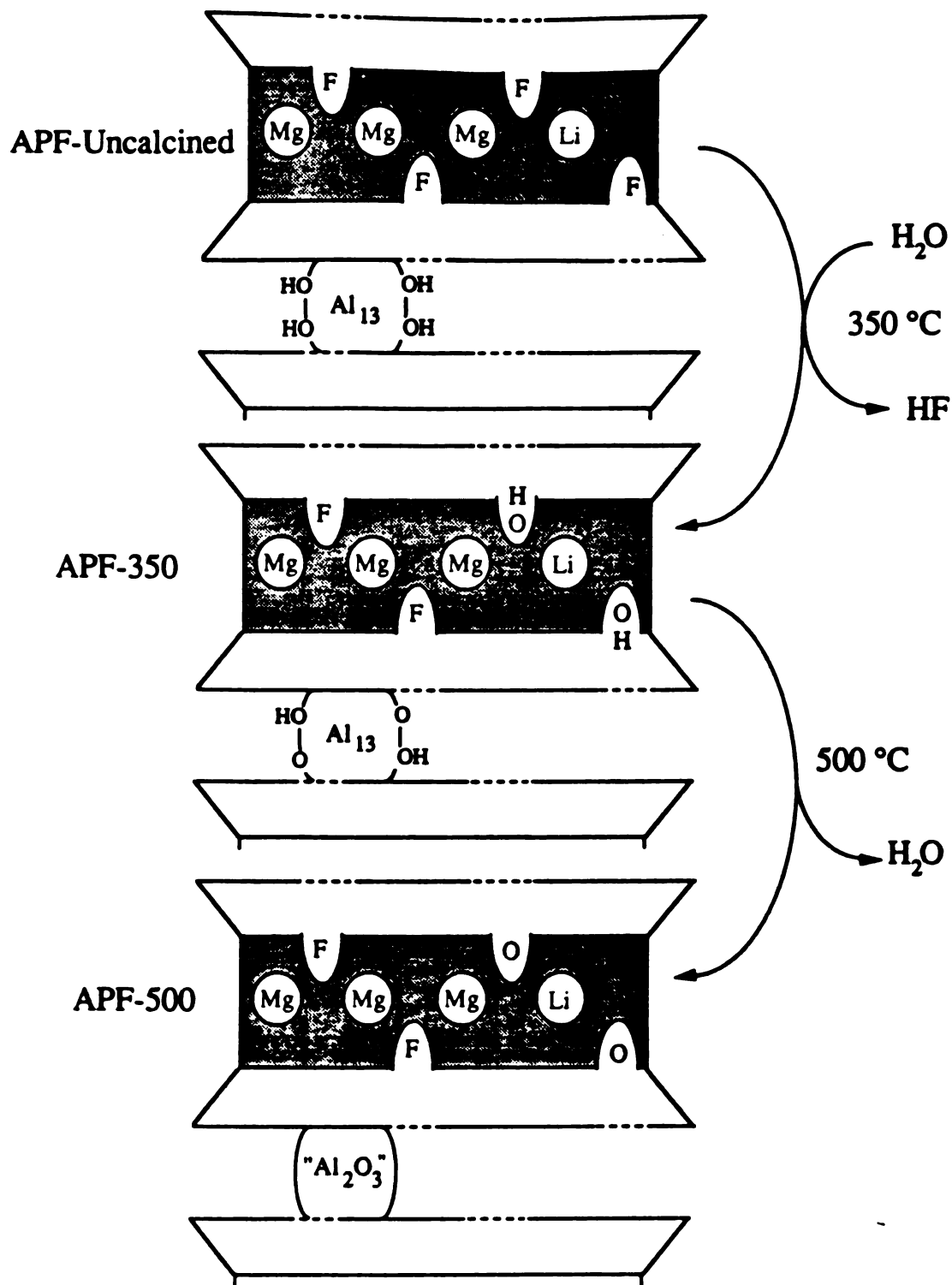


Figure 38. Proposed model for the exchange of F by OH upon calcination of alumina pillared fluorohectorite. The hexagonal holes in the tetrahedral sheet are represented by dashed lines.

be traced to a substantial difference in pore structure. Both materials possess pillared microporous structures, as judged from the basal spacings and nitrogen surface area data (cf., Table 22).

The most likely cause of the reduced acidity for APF-500 is the dehydroxylation of the layers and associated structural rearrangements of the 2:1 layered structure. As shown by the FTIR spectra in Figure 33, the intensity of the framework OH band at 3680 cm^{-1} decreases substantially upon calcining the clay at $500\text{ }^{\circ}\text{C}$. If the structural hydroxyl groups are indeed the main source of catalytic activity in APF-350, then dehydroxylation explains why the activity is so repressed after calcination at $500\text{ }^{\circ}\text{C}$. The rather substantial changes in the NMR chemical shifts for the tetrahedral ^{27}Al (cf., Figure 29) and the ^{29}Si (cf., Figure 30) resonances point to significant structural rearrangement of the pillars and the layers. It has been previously suggested that the upfield chemical shift for the ^{29}Si resonance upon calcination is the result of crosslinking between the pillar and the layers.¹⁰ Structural changes upon calcination at $500\text{ }^{\circ}\text{C}$ also are indicated by the loss of an IR band at $\sim 756\text{ cm}^{-1}$ for the pillar and the appearance of two new bands at 801 and 863 cm^{-1} (cf., Figure 29). Although there is the possibility of the pillars reacting with liberated HF between 350° and $500\text{ }^{\circ}\text{C}$, we find no evidence from ^{19}F MAS NMR spectra for AlF_3 formation.

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CHAPTER SIX
SELECTIVITY OF BIPHENYL MONOISOPROPYLATION

A. Introduction

The monoalkylation of biphenyl can yield three regioisomers, in which the carbon chain is positioned ortho, meta or para. We have been studying isopropylation in particular, typical isomer distributions for the mono alkylation are presented in Table 25.

Table 25: Isomer distributions obtained for catalytic biphenyl isopropylation.

Catalyst	Temperature	Reaction condition	Alkylating agent	Biphenyl conversion (%)	o	m	p	Ref.
SiO ₂ /Al ₂ O ₃	140°C	5 bar	propene	71	35			1
SiO ₂ /Al ₂ O ₃	>180°C	Gas phase	propene	85	3	38	59	2
H ₂ SO ₄	120-130°C	1 bar	propene	100	44	24	32	3
BF ₃ -H ₃ PO ₄	120-130°C	1 bar	propene	100	43	24	33	"
BF ₃	165-170°C	1 bar	i-propanol	69	43	23	34	"
BF ₃ -H ₃ PO ₄	165-170°C	1 bar	i-propanol	17	42	25	32	"
AlCl ₃	80°C	1 bar	propene	79	32	32	36	4
SiO ₂ /Al ₂ O ₃	155°C	10 bar	propene	98	46	18	36	"
SiO ₂ /Al ₂ O ₃	180°C	a	propene	67	36	15	49	5
HL zeolite	180°C	"	propene	70	40	17	43	"
HY zeolite	130°C	"	propene	35	50	30	20	"
HY zeolite	250°C	"	propene	90	9	47	44	"
H-mordenite	250°C	"	propene	48	5	24	71	"

a: 50mmol biphenyl, 100 mmol propene, 20cc trans-decalin

In spite of the expected strong steric hindrance between the incoming isopropyl chain and the phenyl ring, relatively high yields of the ortho isomer, typically between 35 and 50%, are obtained. With mordenite, a

different behavior is observed and the shape selective formation of the para isomer obtained.^{5,6} Shape selective effects were also observed when the zeolite ZSM12 was used as a catalyst.⁷ Prior to presenting our selectivity results for this reaction, we want to consider the different effects which govern its orientation.

The selectivity of electrophilic aromatic substitution is one of the most studied problem of organic chemistry. It has generated a huge amount of literature which would be very difficult to cover thoroughly. All organic textbooks present the basics of this reaction.^{8,9} It can be summarized by an energy profile like the one shown in Figure 39.

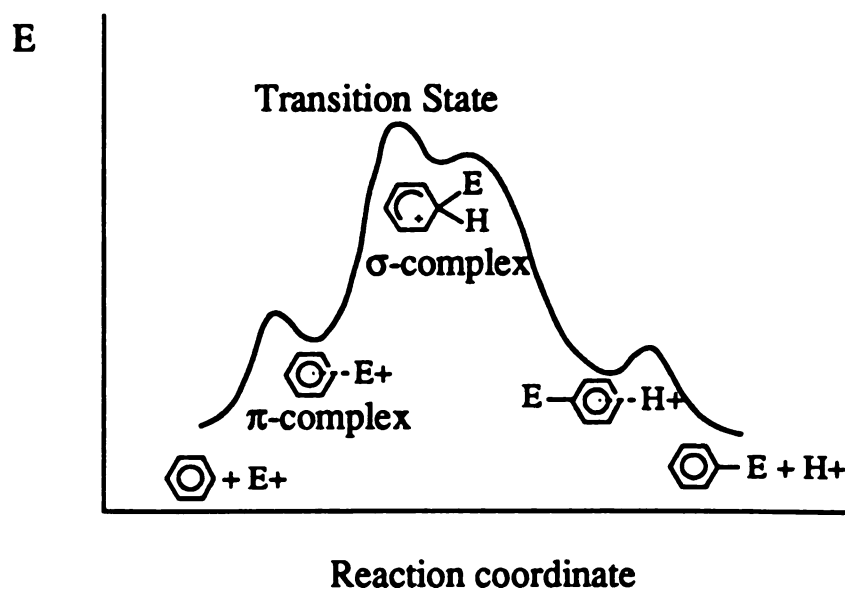


Figure 39. Energy profile for an electrophilic aromatic substitution

The pathway shown on Figure 39 is one in which the transition state of the rate determining step resembles the σ -complex. The σ -complex, also called Wheland intermediate, has generally been considered to be close to the transition state according to the Hammond postulate. The stability of the

σ -complex can explain the orientation effects of substituents on the benzene ring by simple resonance considerations (Figure 40).

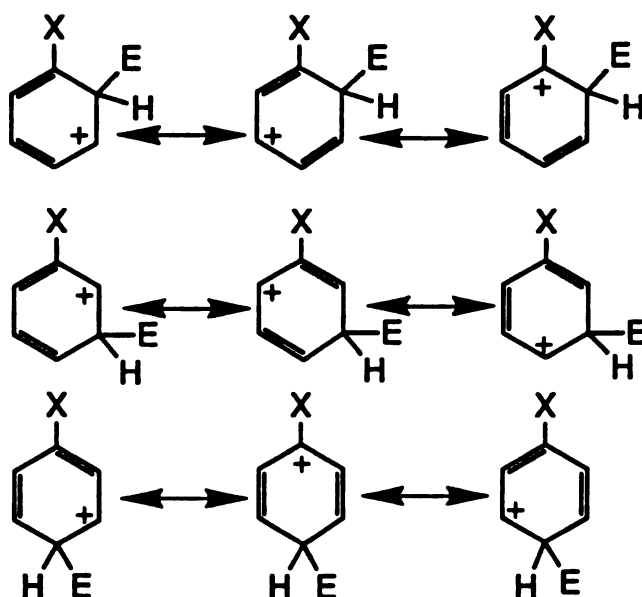
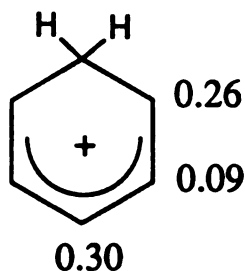


Figure 40. Resonance structures of ortho, meta and para σ -complexes.

If X is an electron donating group by inductive (+I) or resonance (+M) effect, it stabilizes better the ortho and para complexes since only these isomers develop a positive charge on the ring carbon linked to the X substituent. On the other hand, the destabilizing effect of (-I) or (-M) substituents is less severe for the meta isomer. Thus (+I, +M) and (-I, +M) substituents orient in the ortho and para positions, whereas (-I, -M) orient in the meta position. The ortho/para ratio is more difficult to predict. Thus, several conflicting effects are present when dealing with the ortho/para ratio. First, it can be argued that statistically, there are two ortho positions for one para position. As we shall see, it might be appropriate to consider that the statistical factor is in fact a part of the molecule or transition state entropy. Also, steric hindrance is present only

for the ortho isomer, and can be demonstrated by varying the size of X. Finally, electronic effects can differ between the ortho and para positions, for example because inductive effects are usually quite local. These conflicting effects have led people to different conclusions. For example, there has been some controversy in the literature over the ortho/para ratio observed in the nitration of toluene. For reactions involving strongly electrophilic reagents, low substrate selectivity in terms of $k_{\text{toluene}}/k_{\text{benzene}}$ was observed but high positional selectivity (in terms of ortho/para ratio) was obtained. Olah suggested that this was a consequence of an early transition state with a high π character.¹⁰ In the case of less electrophilic reagents, the transition state was considered to be closer to the σ -complex. The nitration experiments of Olah were criticized, because they were stopped flow measurements and extensive reaction might have occurred during the mixing of the reactants.¹¹ However, gas phase nitration studies recently reported by Attina et al.¹² suggested again that the formation of a similar early complex would be rate determining for the reaction. Olah proposed an explanation based on the partial charges of the σ -complex. The partial charges on the σ -complex are the following:



When the electrophilic reagent is not very strong, the transition state will be close to the σ -complex. An electron withdrawing group in the para position will have a stronger stabilizing effect than one in the ortho

position since the charge in the para position is higher. Thus the ortho/para ratio will be smaller when the transition state is late.

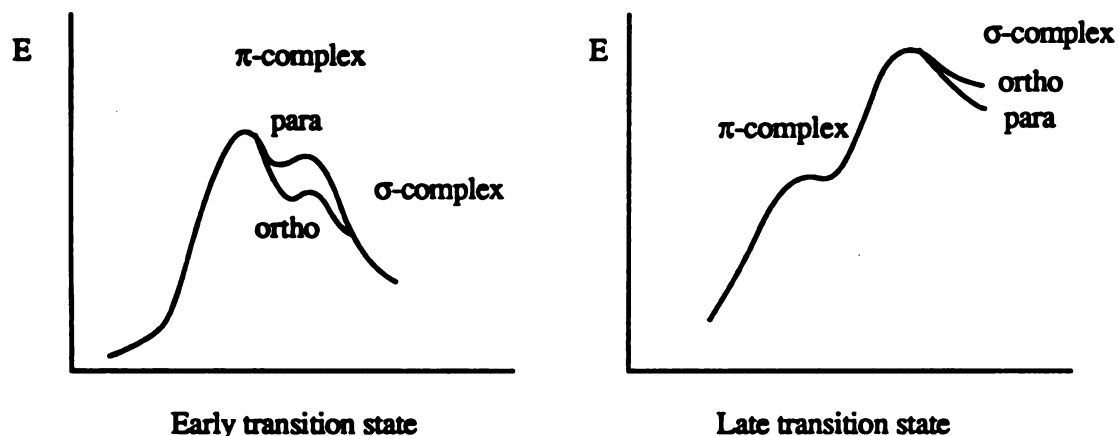


Figure 41. Early and late transition states for electrophilic aromatic substitution.

This explanation does not help to understand why steric hindrance is not severe and why the ortho π -complex would be more stable than the para π -complex. Thus, it is of great interest to try to study the relative stabilities of different π -complexes. Experimentally, this would be a very difficult task. Now that computational methods are relatively affordable, it has become possible to study transition states quite easily. As we noted before, relatively high yields of the ortho isomer are observed in spite of the expected steric hindrance between biphenyl and an isopropyl chain. We decided to investigate the stability of the different isomers, of their σ -complex, and tried to obtain the transition state for this reaction. The MNDO-PM3 ^{13,14} semi-empirical calculations were obtained on a Silicon Graphics Indigo computer equipped with the Spartan software.¹⁵

B. A computational study of biphenyl isopropylation: kinetic vs thermodynamic control

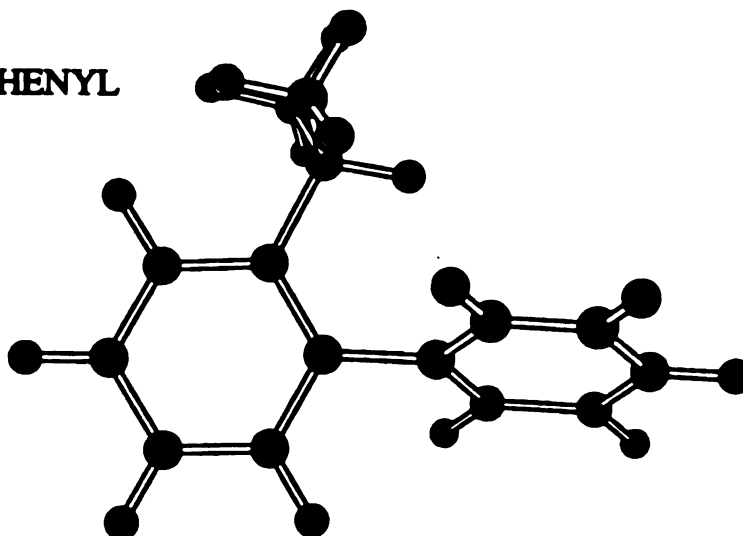
1. Thermodynamic equilibrium between ortho, meta and para isopropyl biphenyl

The optimized geometries obtained with a MNDO-PM3 calculation for the ortho, meta and para isomers are presented in Figures 42 and 43. The calculated energy values are probably in relatively good agreement with the experimental ones; for reference the calculated ΔH°_f for biphenyl was 48.1 kcal/mol whereas the experimental value was 42.7 kcal/mol¹⁶. The effect of the chain position on the molecules' geometries is clearly observed. The steric hindrance of the isopropyl chain causes the two phenyl rings to twist from about 47° (twist angle for biphenyl) to 70°, and also increases the ΔH°_f for this molecule by nearly 2 kcal/mol compared to the meta and para isomers. In terms of kinetic diameter, it appears clearly from Figure 43 that the para isomer is smaller than the meta and ortho isomers. The higher twist angle of the ortho isomer compared to that of the meta might result in a slightly increased size for this isomer. However, the size difference between ortho and meta isomers is probably quite small.

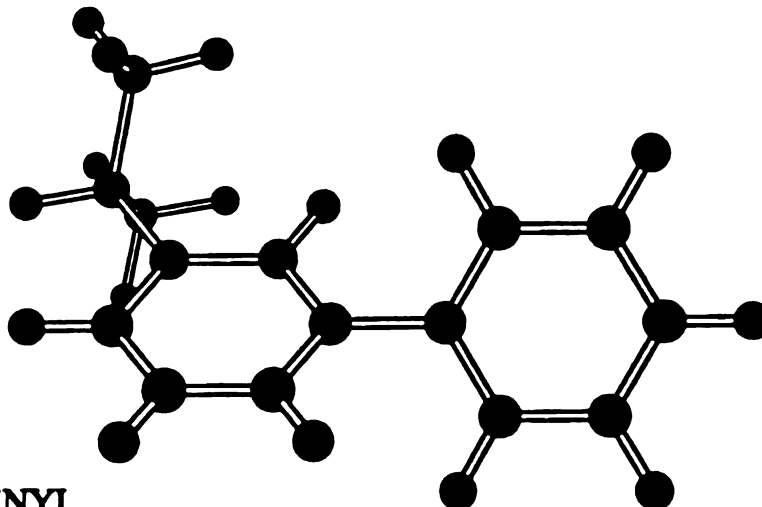
In order to calculate an isomer distribution from the thermodynamic data, one needs to know the differences in ΔG°_f between the different compounds. The MNDO-PM3 calculation provides us with ΔH°_f which ignores any entropy contribution. Entropy contributions can be relevant in the case of aromatic isomers since the symmetry of the molecule can differ with the chain position. For example, para dichlorobenzene belongs to the D_{2h} symmetry point group whereas the ortho isomer belongs to the C_{2v} point group. The para and ortho isomers have thus a symmetry number σ of 4 and 2, respectively.¹⁷ The entropy difference is $-R \ln 4 + R \ln 2$

ORTHO-ISOPROPYLBIPHENYL

31.2 kcal/mol

**META-ISOPROPYLBIPHENYL**

29.4 kcal/mol

**PARA-ISOPROPYLBIPHENYL**

29.3 kcal/mol

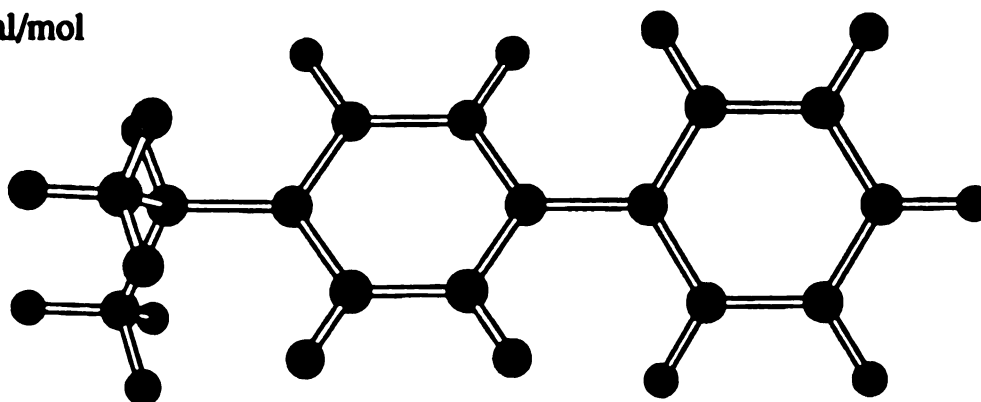
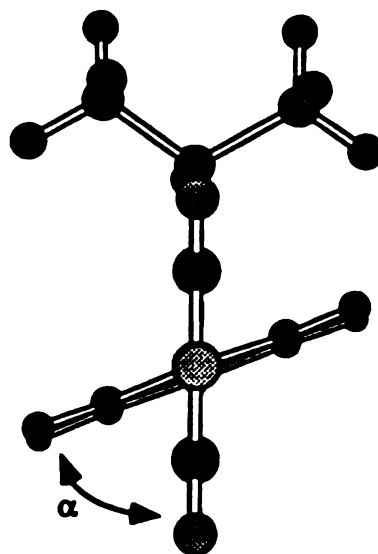


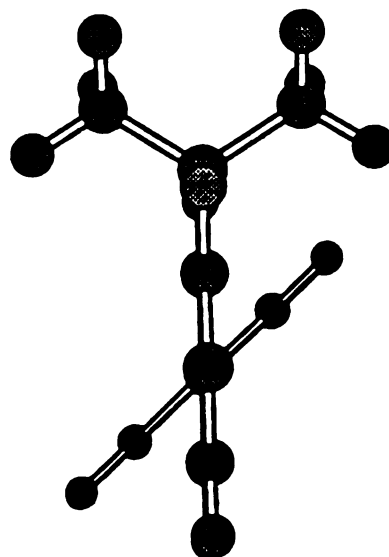
Figure 42. Energy and geometry of the monoisopropylbiphenyl isomers, front view.

ORTHO-ISOPROPYLBIPHENYL

31.2 kcal/mol

 $\alpha = 70^\circ$ **META-ISOPROPYLBIPHENYL**

29.4 kcal/mol

 $\alpha = 48^\circ$ **PARA-ISOPROPYLBIPHENYL**

29.3 kcal/mol

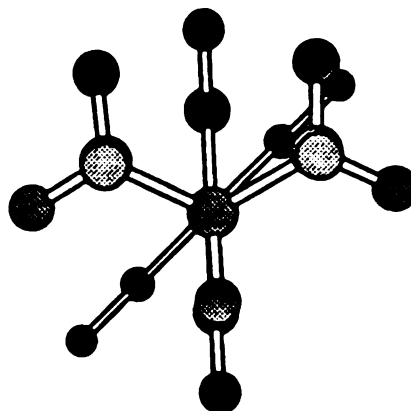
 $\alpha = 47^\circ$ 

Figure 43. Energy and geometry of the monoisopropylbiphenyl isomers, side view.

in this case, or $-1.38 \text{ cal.mol}^{-1} \text{ K}^{-1}$. This term contributes a $0.4 \text{ kcal.mol}^{-1}$ energy difference to ΔG°_f at 298K between the ortho and para isomers, the para isomer being higher in energy. This term is taking into account energetically the "statistical factor". In the case of monoisopropyl biphenyl, however, the symmetry number is less easy to obtain. Due to the asymmetry of the isopropyl chain, no additional elements of symmetry are present for the para isomer. Thus, we can consider that the entropies of the ortho, meta and para isomers are close to each other and we will not consider them any further.

If we just consider differences in ΔH°_f , the thermodynamic equilibrium can be easily obtained from the equilibrium constant formula:

$$K = e^{\frac{-\Delta(\Delta G^\circ_f)}{RT}} = e^{\frac{-\Delta(\Delta H^\circ_f)}{RT}}$$

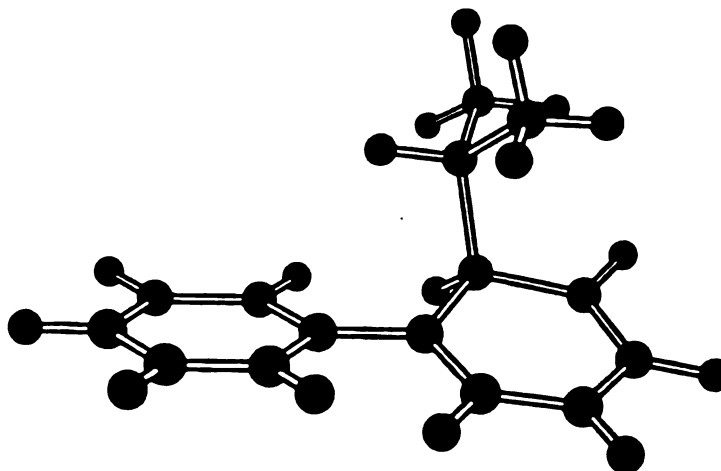
At 523K, the 2 kcal energy difference between the ortho and meta, para isomers results in a 8% ortho, 45% meta and 47% para equilibrium. This result seems quite close to the equilibrium observed at 250 °C with the HY zeolite (Table 25). It is, on the other hand, far from the most commonly observed distribution which affords much more ortho isomer. Thus, in most cases thermodynamic equilibrium between the isomers is not reached and the reaction is under kinetic control. In order to account for the high ortho yield under kinetic control, we first investigated the equilibrium between the σ -complexes.

2. Equilibrium between ortho, meta and para isopropyl biphenyl σ -complexes.

The optimized geometries and calculated energies of the different isomeric σ -complexes are presented in Figure 44. As expected from the classical orientation rules, the phenyl substituent (+I, +M) favors the ortho and para positions. However, due to steric constraints, the ortho position is

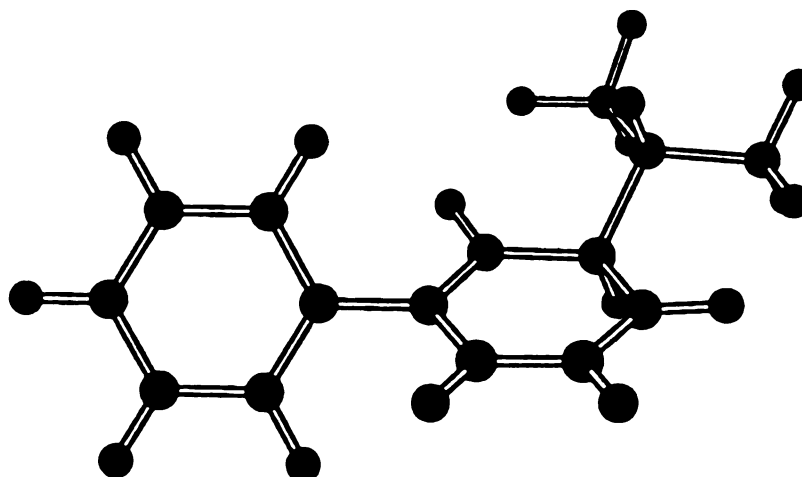
ORTHO

$\Delta H^\circ_f = 214.6 \text{ kcal/mol}$



META

$\Delta H^\circ_f = 219.4 \text{ kcal/mol}$



PARA

$\Delta H^\circ_f = 209.6 \text{ kcal/mol}$

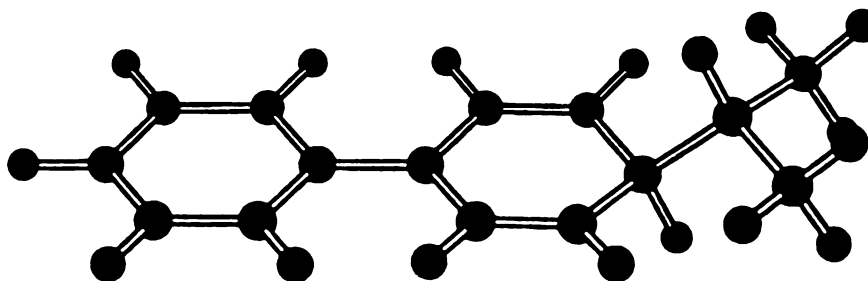


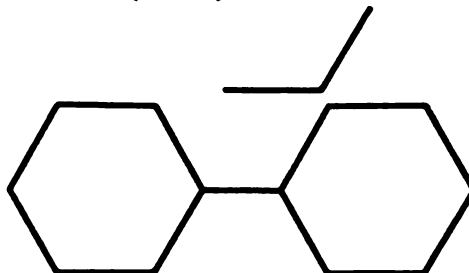
Figure 44. Energy and geometry of the σ -complexes.

much higher in energy than the para position and relatively closer to the meta position. These energy differences would result in 99% para, 1% ortho and 0% meta equilibrium between the 3 σ -complexes. Such a product distribution is never observed. It is, thus, very unlikely that the σ -complexes govern the orientation of the alkylation reaction. Our next effort was to investigate the geometry of the transition state by increasing the distance between the incoming 2-propenium ion and the biphenyl molecule.

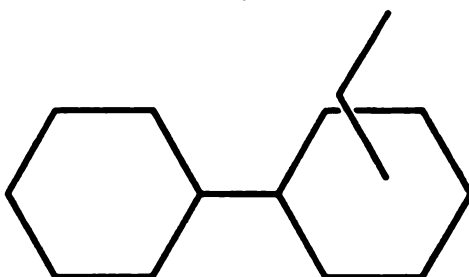
3. Investigation of the transition state for the propene alkylation of biphenyl

We considered three different positions of the incoming 2-propyl cation relative to the biphenyl molecule. In the first one, which we will call the "frontal attack", the central carbon atom of the 2-propyl cation interacts first with one of the rings. In the second one, "sideways attack", one of the methyl groups of the attacking cation lies above one of the rings. In the third one, "backwards attack", the 2-propyl cation is almost eclipsed with the aromatic ring. These different orientations of attack are summarized in Figure 45. Plots of the calculated ΔH°_f as a function of the C-C distance of approach for the various paths are presented in Figure 46. The backwards attack for the meta and para isomers was not represented because it was very unfavored. The first conclusion that we can draw from Figure 46 is that the ortho transition state is significantly lower in energy than the meta and para transition states, whatever the orientation of the isopropyl chain. Also, we observe that for the meta and para positions the sideways attack should be preferred to the frontal attack, and on the contrary the backwards and frontal attack are most favored for the ortho isomer. The transition states lowest in energy obtained are represented in

FRONTAL ATTACK (ortho)



SIDEWAYS ATTACK (ortho)



BACKWARDS ATTACK (ortho)

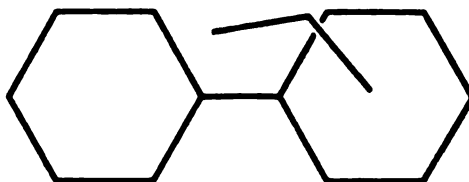


Figure 45. Different geometries considered for the attack of the 2-propenium cation.

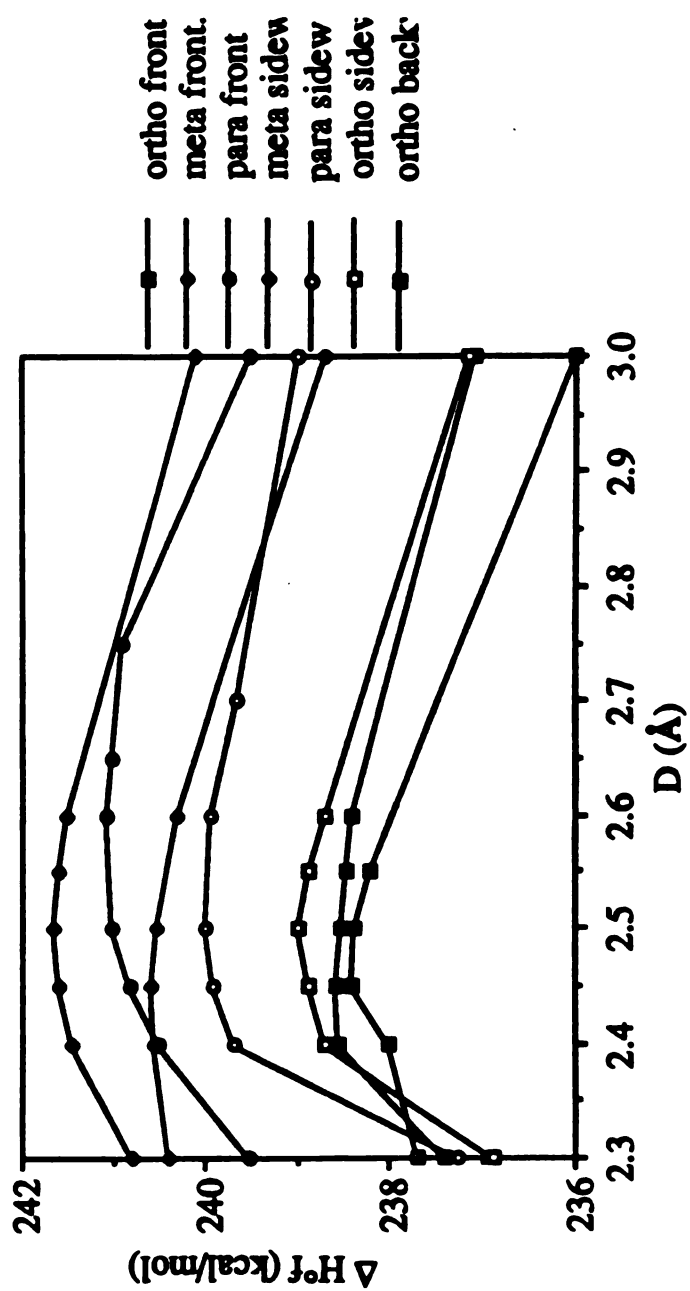
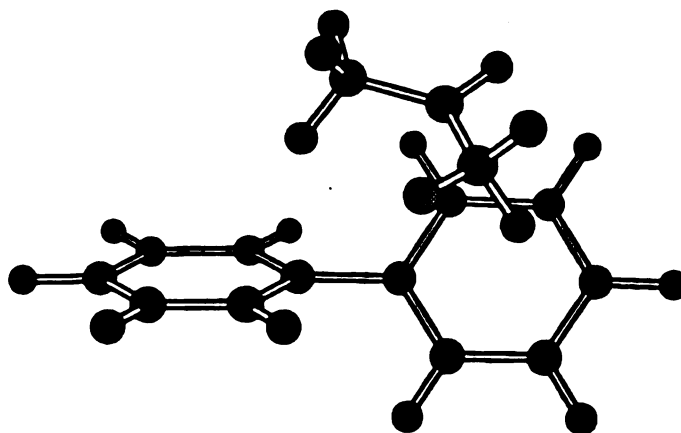


Figure 46. Evolution of energy with distance of approach.

ORTHO BACKWARD

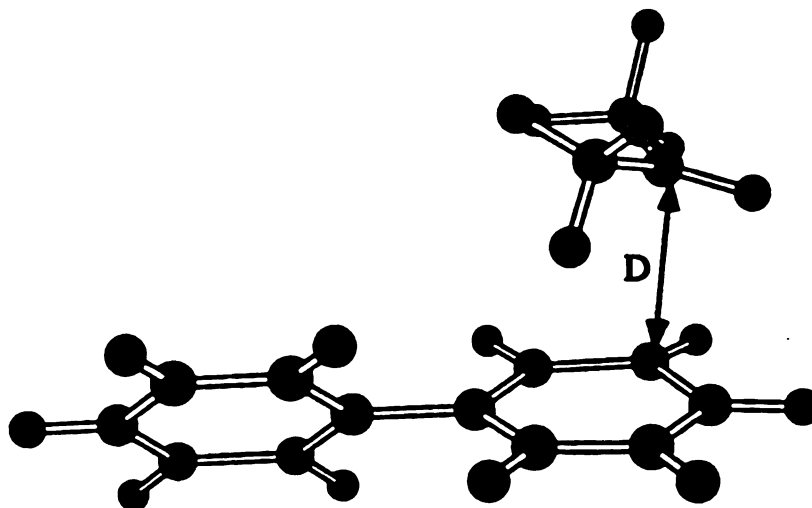
$$D=2.46 \text{ \AA}$$

$$\Delta H^\circ_f=238.4 \text{ kcal/mol}$$

**META SIDEWAYS**

$$D=2.44 \text{ \AA}$$

$$\Delta H^\circ_f=240.6 \text{ kcal/mol}$$

**PARA SIDEWAYS**

$$D=2.52 \text{ \AA}$$

$$\Delta H^\circ_f=240.0 \text{ kcal/mol}$$

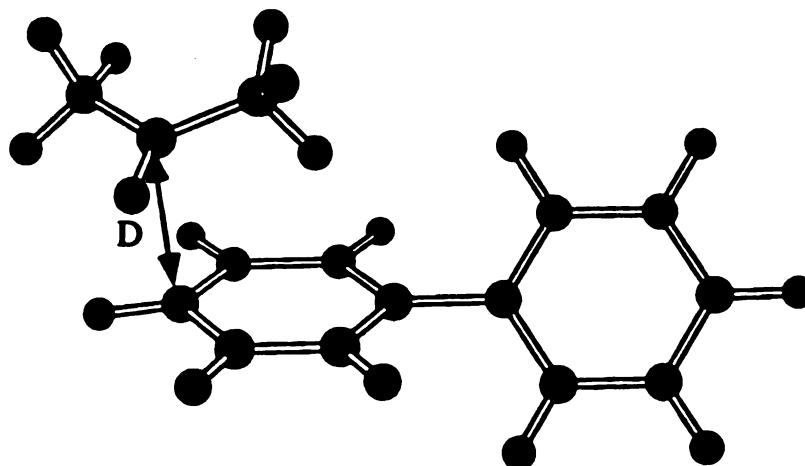


Figure 47. Energy and geometry of the transition states.

Figure 47, they consist of a sideways attack for the meta and para isomers and of a backwards attack for the ortho isomer. This behavior can be explained by electronic considerations. If we consider the HOMO of biphenyl (Figure 48) we can notice that the π orbital in the para position is surrounded by two bonding π orbitals, the π orbital in the meta position is surrounded by one bonding and one antibonding π orbitals, and the π orbital in the ortho position is in the same environment as the meta, however, antibonding π orbitals from the other ring are quite close. The LUMO of the 2-propyl cation is mainly located on the central carbon atom, however two adjacent C-H bonds from the methyl groups support a significant antibonding contribution, so that we can draw this orbital like a π -allyl. It results that the ortho position from the HOMO of biphenyl and the LUMO of the 2-propyl cation have very compatible symmetries, whereas the para position exhibits an opposite symmetry to the LUMO of the incoming cation (Figure 48). The sideways attack is favored for the meta and para position because it minimizes the unfavorable interactions, on the other hand the backwards attack is preferred for the ortho position because it maximizes favorable interactions. In summary, we propose that the ortho position is favored by a stereoelectronic effect. If we calculate the isomer distribution from the energies of the transition states, we obtain 75% of ortho isomer, 16% of para and 9% of meta. This distribution is higher in ortho alkylation than any of the experimental distributions reported in Table 25, however it explains qualitatively well the behavior observed.

In conclusion, at thermodynamic equilibrium between the different isopropylbiphenyl isomers, there should be 8% ortho, 45% meta and 47% para. The ortho isomer is thermodynamically disfavored because of steric

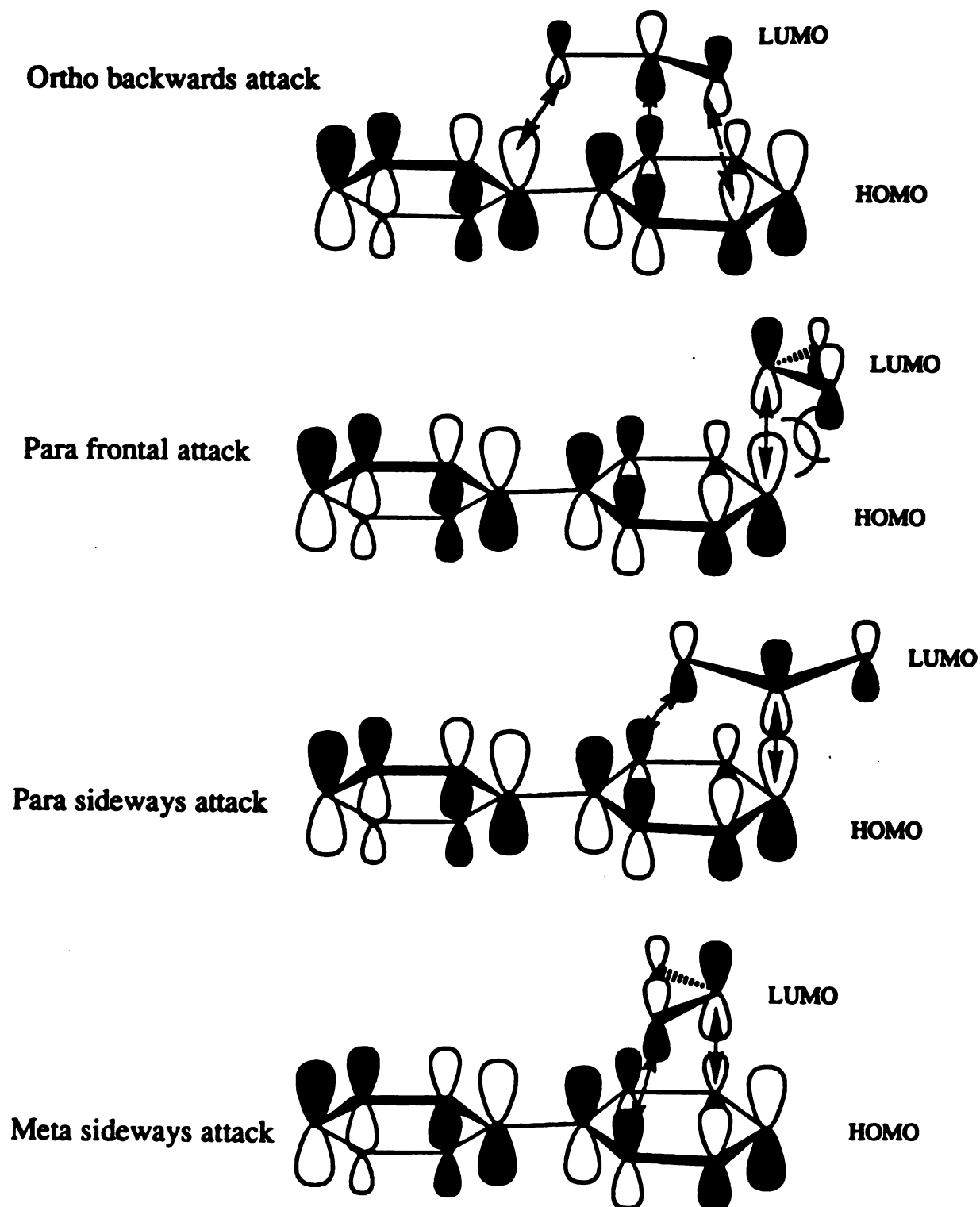


Figure 48. Electronic interactions between the HOMO of biphenyl and the LUMO of the 2-propenium ion.

interactions. On the other hand, the equilibrium between transition states and thus the kinetic orientation is around 75% ortho, 16% para and 9% meta. The ortho isomer is kinetically favored because of electronic interactions between the biphenyl HOMO and the 2-propyl cation LUMO.

C. Selectivity of alumina pillared clays towards the different biphenyl monoalkyl isomers

1. Propene alkylation

The product selectivity towards the three possible mono-alkylated isomers was studied in the range 50-65% of conversion. It is important to compare selectivities only at similar conversion because the product distribution depends on the conversion.

Table 26. Distribution of monoalkylated products for propene alkylation.^a

Catalyst:	weight	conversion:	monoalkyl:	ortho	meta	para
	(g):	(%)	(%)			
K10	0.09	61	60	32	27	41
ADL	0.1	63	58	32	30	37
APFH	0.06	50	73	23	34	43
APB	0.08	54	69	16	39	44
APAM	0.2	55	67	15	44	41
APWM	0.2	64	63	15	42	43
USY	0.18	63	59	22	33	44
M8(48)	0.2	57	66	7	27	66

a: The reaction conditions were as follows: 30g biphenyl, 140 psi propene, 250°C, 20 hours reaction time.

The desired conversions were obtained by using different amounts of a 100-200 mesh (150-75 µm) fraction of catalyst. At this particle size, the

reaction was probably under diffusion control. The results, presented in Table 26, show that for the heterogeneous catalysts studied the yields of meta and para isomers are higher than that obtained with most of the catalysts presented in Table 25, which is an indication of selectivity even though the conditions were not the same. Moreover, catalysts with few micropores such as ADL and K10 afforded a lower yield in meta and para isomers than microporous catalysts. Several explanations can be considered to account for this behavior. As shown in Figure 42 and 43, the twist angle between the two benzene rings calculated in the MNDO-PM3 approximation increases from 45° in meta- and para-isopropylbiphenyl to 70° in ortho-isopropylbiphenyl. The twist angle between the two benzene rings is also known to increase from 20° in biphenyl to 60.7° in ortho-isopropylbiphenyl in the solid state.¹⁸ Packing forces might be responsible for the differences observed between the gas phase calculation and the solid state measurement. Overall, the ortho isomer is somewhat bigger and its formation could be restricted in the micropores. However, as we shall demonstrate in D, no significant difference in selectivity is observed by varying the interlayer spacing of the pillared clay from 6 to $15\text{\AA}$. It can also be considered that the ortho isomer diffusion could differ from that of the other isomers, resulting in larger contact time with the catalyst. We cannot, however, support this hypothesis with any diffusivity data. With the insights given by the computational study, we have proposed that the ortho isomers is favored in kinetically controlled conditions. With very microporous catalysts, diffusion control is stronger and thus the reactant and products spend a longer period of time inside the catalyst particles. During that time, they tend to reach thermodynamic equilibrium, resulting in lower ortho yields. When diffusion is faster, the isomers tend to retain

the kinetic orientation, the yield of ortho isomerization is then larger. In the special case of mordenite, the exceptional selectivity towards para alkylation has been interpreted as a consequence of shape selectivity of the two channels structure of this material.⁶ The aromatic nuclei are believed to occupy the larger channel, while propene fills the smaller channel.

Table 27. Influence of the catalyst particle size on selectivity.

Catalyst	Particle Size(μm)	weight (g)	Conversion (%) ^a	Monoalkyl (%)	ortho	meta	para
APAM	< 45	0.05	44	74	20	37	43
"	150-300	0.2	45	75	10	49	41
APWM	< 75	0.05	43	76	21	34	45
"	45-50	0.1	60	64	22	34	44
"	75-150	0.2	64	63	15	42	43
"	150-300	0.6	80	50	8	52	40
ADL	< 45	0.1	85	35	36	30	34
"	75-150	0.2	89	29	28	36	36
K10	< 75	0.08	78	44	40	23	37
"	<75	0.06	41	76	34	23	43
"	75-150	0.1	76	48	33	27	40
"	75-150	0.08	44	73	27	30	42
S=0 ^b	75-150	0.2	56	65	14	44	42
S=400 ^c	< 45	0.04	69	52	32	32	36

a: 30g biphenyl, 20 hours of reaction, 250 °C, 140 psi of propene.

b: Alumina Pillared Arizona Montmorillonite calcined at 500 °C (see Chapter 4).

c: Surfactant-modified Alumina Pillared Arizona Montmorillonite (see Chapter 4).

The influence of diffusion control on product selectivity is supported by the fact that the yield of ortho isomer decreases as the particle size

increases. Several examples of particle size influence on the monoalkyl isomer distribution are gathered in Table 27. The most dramatic difference is observed between a 75-150 μm fraction of unmodified alumina pillared Arizona montmorillonite ($S = 0$) and a fraction of $S = 400$ surfactant modified pillared clay with particle size less than 45 μm . In the latter material, high mesoporosity allows limited diffusion control and, additionally, the small particle size enables a high yield of ortho alkylation.

In an effort to compare the catalysts selectivities at a lower biphenyl conversion level, a series of reactions were carried out with a lower loading of a 100-200 mesh catalyst fraction. The results are presented in Table 28.

Table 28. Catalyst selectivities at low conversion.

Catalyst:	weight (g):	conversion: (%)	monoalkyl: (%)	ortho	meta	para
K10	0.06	25	83	26	30	44
ADL	0.05	18	87	19	40	41
APFH	0.035	15	90	17	39	44
APB	0.035	16	89	18	37	45
APWM	0.08	15	91	11	46	43
LZY84	0.2	23	90	14	46	39

a: The reaction conditions were as follows: 30g biphenyl, 140 psi propene, 250°C, 20 hours reaction time.

Unexpectedly, the ortho alkylation was not favored at these low conversion levels. A significant difference is, however, still observed between the very microporous APWM and the less microporous pillared clays like APFH and APB or the mesoporous catalysts (K10 and ADL). It

appears that during the long reaction time, thermodynamic equilibrium is reached more easily at these low conversion levels. A few results indicate that when low conversion was a consequence of short reaction times, higher yields of ortho isomer were obtained. For example, after one hour of reaction with 0.05g of K10, the conversion is 11% and 33, 26 and 41% of ortho, meta and para isopropylbiphenyl are obtained, respectively.

2. Isomerization/transalkylation of 4,4'-diisopropylbiphenyl

An effort to study the isomerization and transalkylation of isopropylbiphenyl was made. 4,4'-diisopropylbiphenyl kindly supplied by the Dow Chemicals Co was reacted with biphenyl under 5.4 atm of nitrogen at 250 °C. The catalyst used in this test was K10, because it is a rather unselective material. The results, provided in Table 29, show that 86% of 4,4'-diisopropylbiphenyl reacted in these conditions, more by transalkylation (73%) than by isomerization (27%). It is worth noticing that very few ortho isomer was obtained by transalkylation and isomerization. This result confirms that the ortho position is not favored by thermodynamic equilibration which involves isomerization reactions.

Table 29. Isomerization/transalkylation of 4,4'-diisopropyl biphenyl.^a

		Initial Composition	Final Composition
Biphenyl		90%	83%
Monoalkyl	ortho	0%	0.4%
	meta	0%	5.1%
	para	0%	8.3%
Dialkyl	o-m,o-p	0%	0.3%
	m-m	0%	0.3%
	m-p	0%	1.3%
	p-p	10%	1.4%

a: The reaction conditions were as follows: 0.175 mol biphenyl, $1.95 \cdot 10^{-2}$ mol 4,4'-diisopropylbiphenyl, 200 mg K10 (100-200 mesh fraction), 250 °C, 20 hours, 5.4 atm N₂.

3. Isopropanol alkylation

When isopropanol was used as an alkylating agent (see Chapter 3 section D), high yields of ortho isomer were obtained, as shown in Table 30. Also included in Table 30 are the results of two alkylation reactions carried out with propene in the presence of water. ADL and APWM afford relatively low ortho isomer yield when the alkylation reaction is carried out with propene in the presence of water, whereas they are very selective towards ortho alkylation with isopropanol. The isomer distribution is, thus, not influenced by the presence of water but more probably by the high reaction pressure. The different catalyst do not exhibit significant selectivity differences when isopropanol is used as an alkylating agent. The

ortho isomer proportion varies from 34 % with APWM to 49 % with ADL. However, the ortho isomer proportion seems to be mainly correlated with the conversion level in this case. The high reaction pressure probably limits significantly the diffusion control and the products tend to retain a kinetically controlled orientation. Also, the presence of isopropanol in the liquid phase certainly modify the reaction mixture viscosity and its diffusion properties.

Table 30. Selectivity of the different catalyst for isopropanol alkylation.

Catalyst	weight (g)	Pressure (atm) ^a	conversion (%) ^b	monoalkyl (%)	ortho	meta	para
K10	0.2	27	62	66	45	20	35
ADL	0.2	29	31	82	49	19	32
APFH ^c	0.2	32	52	76	48	20	32
APB	0.2	35	60	66	46	20	34
APWM	0.2	30	75	57	34	35	31
APAM	0.2	31	67	59	39	29	32
M8(48)	0.2	35	8	90	7	15	77
APWM	0.2	9 ^c	71	57	20	42	38
ADL	0.2	9 ^c	20	91	17	38	44

a: The pressure indicated is the maximum reaction pressure during the course of the reaction. b: Except for the last two entries, the reaction conditions were as follows: 22 ml isopropanol, 30g biphenyl, 200 mg catalyst, 250 °C, 20 hours, autogeneous pressure. c: The reaction was carried out with propene as an alkylating agent and 3 ml of water were added, other conditions were: 30g of biphenyl, 250 °C, 9 atm propene. c: APFH is called APF-350 in Chapter 5.

D. Selectivity of a supergallery pillared clay

1 Characterization of a Ce/Al pillared fluorohectorite

Supergallery pillared clays are defined as materials in which the interlayer spacing is larger than the layer thickness.¹⁹ A supergallery pillared clay was prepared according to the procedure described by McCauley.²⁰ The large Ce/Al pillars are prepared hydrothermally by refluxing Chlorohydrol in presence of cerium. The X-ray diffraction patterns of the uncalcined and calcined pillared products are presented in Figure 49. The materials calcined at 350 °C and 500 °C exhibit a d_{001} peak around 25 Å, which means that the gallery height in these materials are around 16 Å. The presence of supergalleries was confirmed by N₂ adsorption-desorption. The isotherms are presented in Figure 50. A special behavior is observed in the P/P° range between 0.1 and 0.4. This is better observed in the t-plot presented in Figure 51. At t-values between 3 and 4, an upward swing of the isotherm is observed. This behavior has been described as capillary condensation without hysteresis and is characteristic of the presence of supermicropores or small mesopores,²¹ probably in the range 15-25 Å.

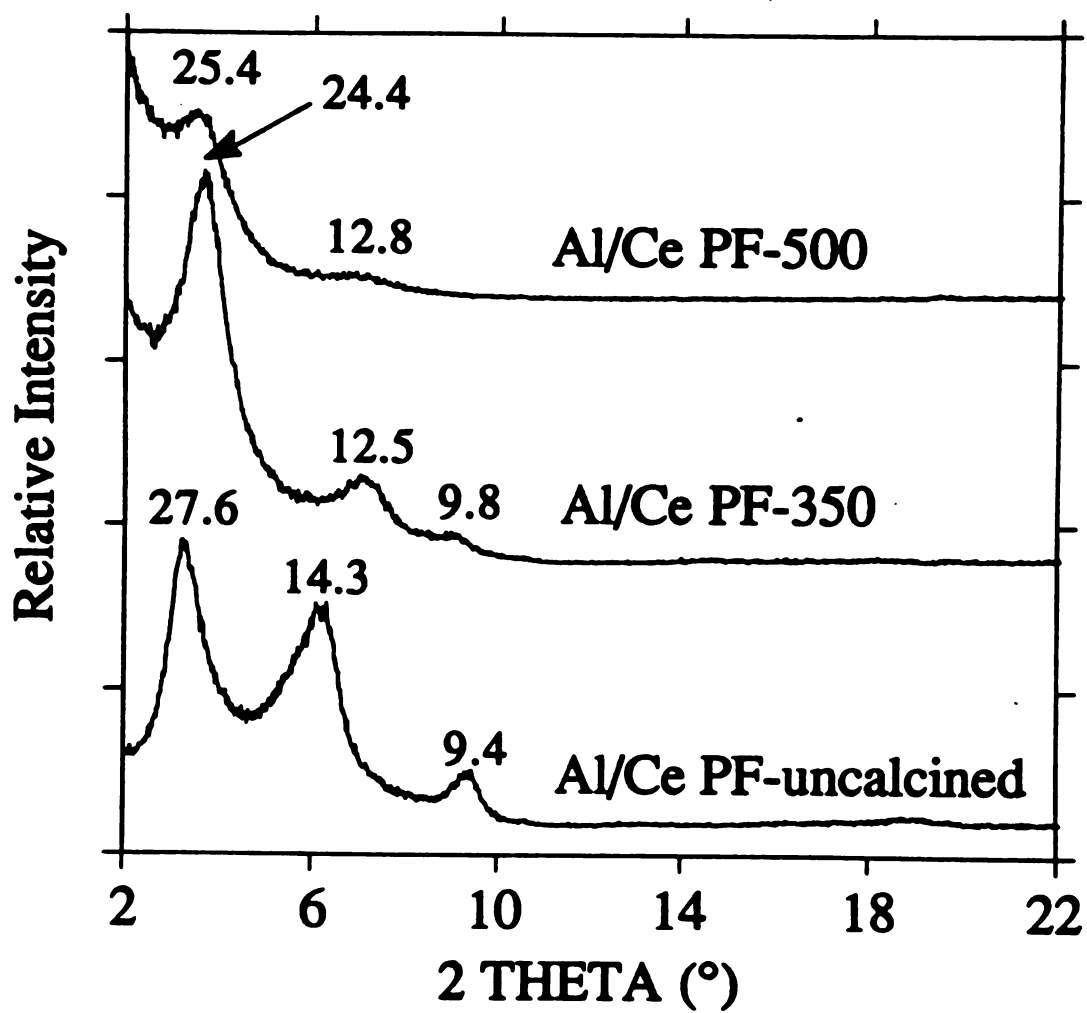
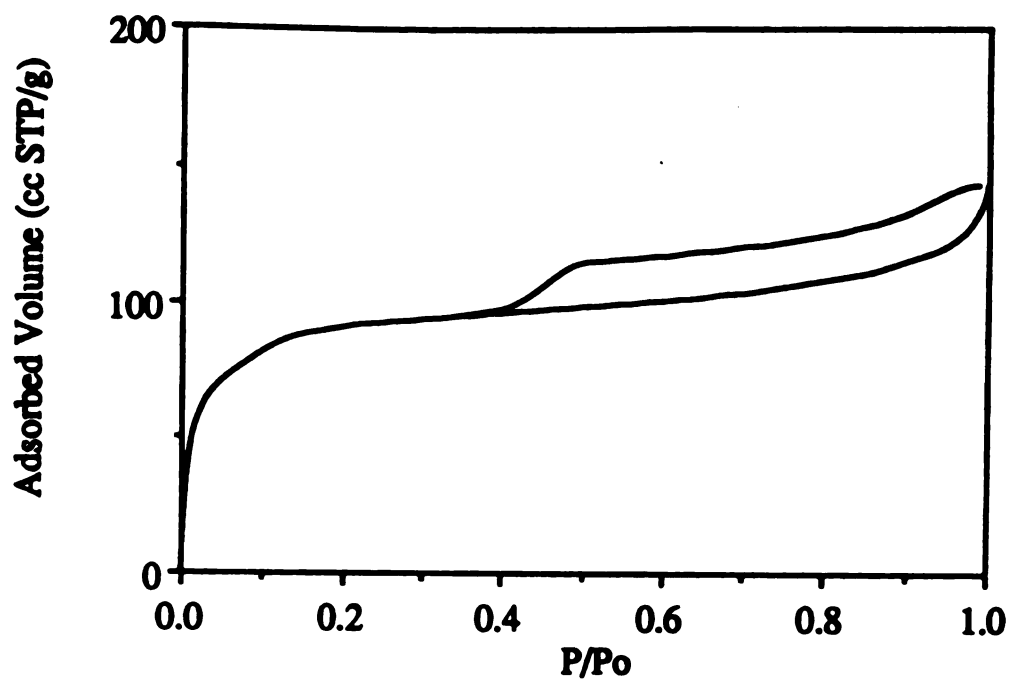


Figure 51. X-ray diffraction pattern of Al/Ce PF-uncalcined, Al/Ce PF-350 and Al/Ce PF-500.

Al/Ce PF-350



Al/Ce PF-500

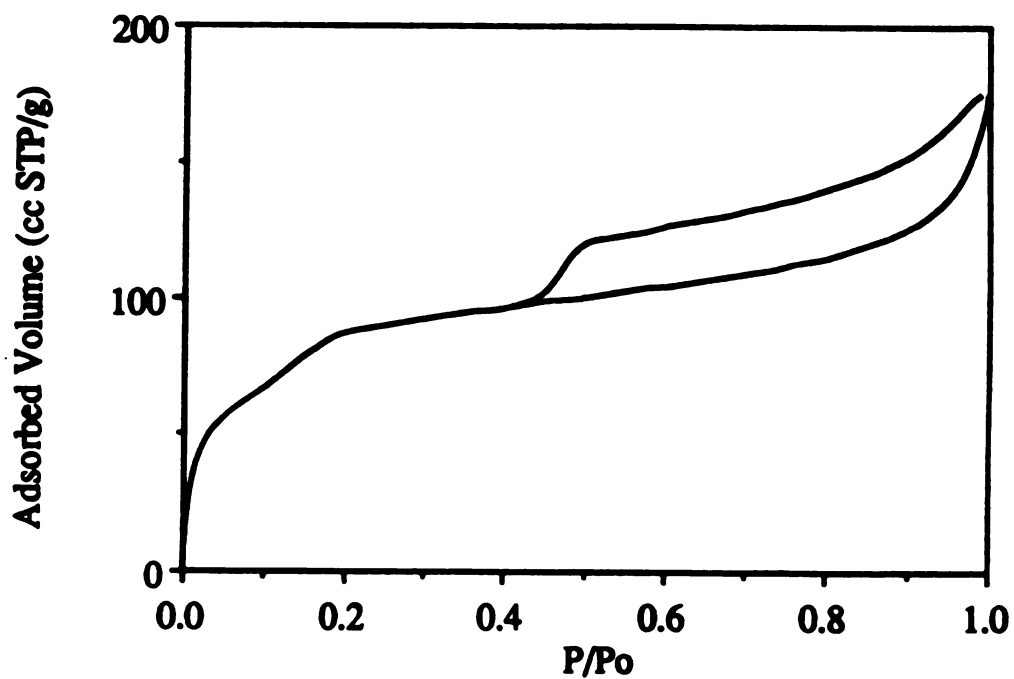


Figure 50. N_2 adsorption-desorption isotherms for Al/Ce-350 and Al/Ce-500

In order to better locate the position of the step in the isotherm, the derivative with respect to P/P° in log scale was plotted (Figure 52). Kresge et al.²² proposed a mathematical relationship between the position of the adsorption peak and the pore size, for argon adsorption. As we carried out nitrogen adsorption, we can only apply this relationship with extreme caution. The larger peak obtained in Figure 52 corresponds to pores of 19 Å ($\log P/P^\circ = -0.95$) for Al/Ce PF-350 and 21 Å ($\log P/P^\circ = -0.84$) for Al/Ce PF-500. It is not surprising that the pore sizes differ from the pore sizes obtained from X-ray (15 and 16 Å for Al/Ce PF 350 and 500, respectively), since the Ar equation was applied for N₂ data. It is, however, noticeable that a similar pore size difference was observed by both techniques. The smaller peak corresponds to pores of 10 Å diameter. It is not clear if this corresponds to real pores or if, as proposed by Kresge et al., it reflects adsorption on the walls of the pores.

The t-plot analysis cannot be carried out in this case in the same way as with microporous solids. Especially, the microporous surface area obtained from the micropore volume by assuming that each N₂ molecule in the micropores is adsorbed on the surface is too high. Thus, in supermicropores, multilayer adsorption occurs to a certain extent and it is difficult to calculate the microporous surface area from the microporous volume. Pore volume analysis from the desorption isotherm was nevertheless possible with a slit shape pore model.²³ Results from t-plot analysis, desorption analysis and BET analysis are gathered in Table 31.

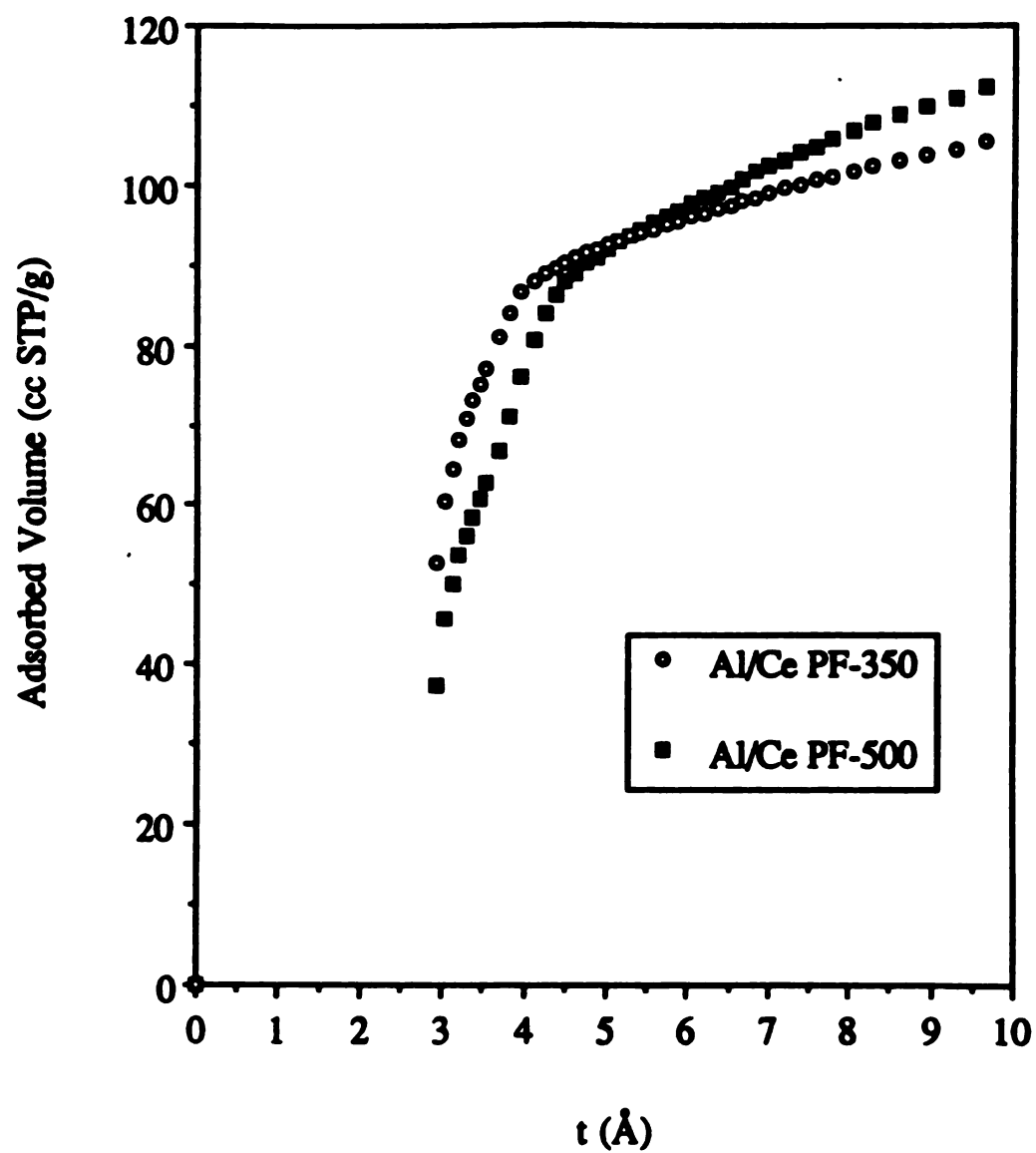


Figure 51. t -plot of N₂ adsorption isotherm for Al/Ce-350 and Al/Ce-500.

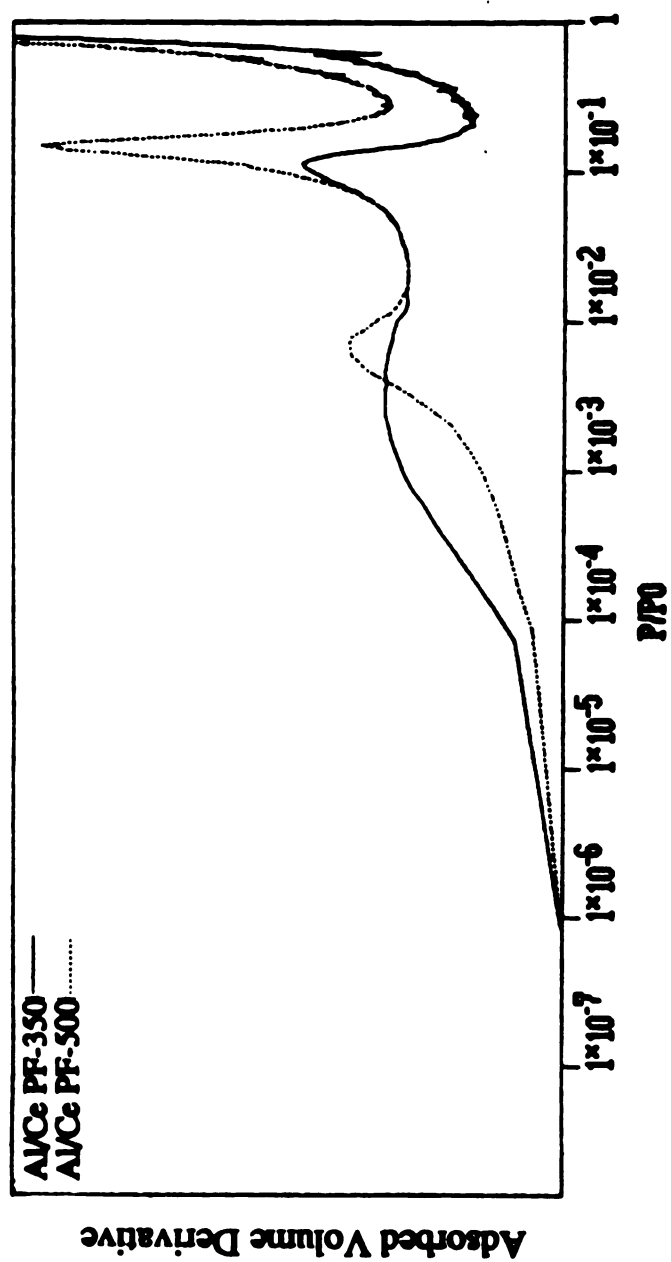


Figure 52. Differential adsorbed volume versus P/P° in log scale for Al/Ce-350 and Al/Ce-500.

Table 31. N₂ adsorption-desorption isotherms analysis for Al/Ce pillared fluorohectorite.

Method		Al/CePF-350	Al/CePF-500
BET	Total surface area (m ² /g)	345	290
t-plot	Total surface area (m ² /g)	337	274
	Microporous volume (cc/g)	0.12	0.11
	Mesoporous surface area (m ² /g)	45	71
Desorption Analysis	Total pore volume (cc/g)	0.22	0.26
	Microporous Volume (cc/g)	0.11	0.10
	Mesoporous surface area (m ² /g)	61	85
	Mesoporous volume (D>30Å)	0.05	0.10
	% Pore volume (D>30Å)	38	23

In contrast with alumina pillared fluorohectorite (see Chapter 3), the Al/Ce pillared fluorohectorite exhibited less than 40% of their pore volume in large mesopores.

The acidity of Al/Ce PF-350 and 500 was studied by NH₃ TPD. The first peak, corresponding to NH₃ desorption, is presented in Figure 53.

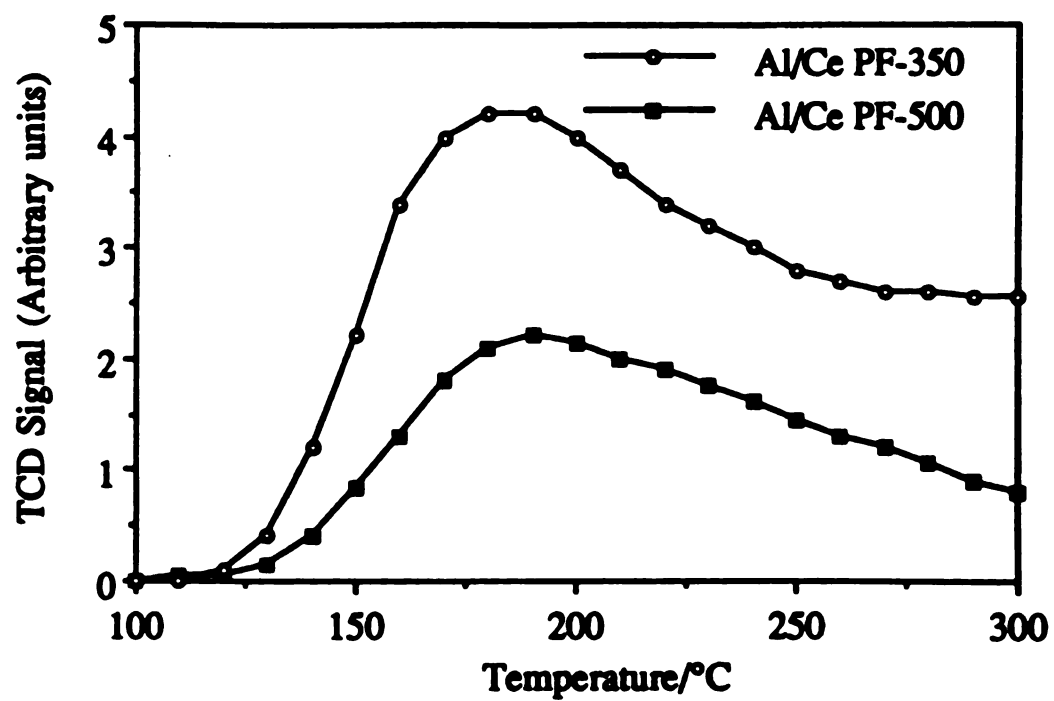


Figure 53. NH_3 TPD profiles for Al/Ce PF-350 and Al/Ce PF-500.

The peaks NH_3 -TPD peaks observed with the Al/Ce pillared fluorohectorite were very similar to those observed with alumina pillared fluorohectorite (see Chapter 5). Thus, the amount of NH_3 bonded to Al/Ce PF-350 is about twice that for Al/Ce PF-500. ^{27}Al , ^{29}Si and ^{19}F MAS-NMR measurements for Al/Ce PF-350 and 500 were also very similar to those observed with APF-350 and 500, respectively. The same chemistry most probably occurs in Al/Ce pillared fluorohectorite and in alumina pillared fluorohectorite upon calcination. The role of cerium in the pillars structure could not be understood.

2 Evolution of product selectivity with basal spacing

The catalytic properties of supergallery Al/Ce pillared clays were studied in the same conditions as those of alumina pillared clays. We also included in this study a surfactant-modified alumina pillared Wyoming montmorillonite (SMAPWM), kindly supplied by L.J. Michot. This modified pillared clay exhibit a d_{001} basal spacing of 15.3 Å and was fully characterized by Michot and Pinnavaia.²⁴ The results are presented in Table 32. Also included in Table 32 are selectivity obtained with relevant alumina pillared clays, for comparison purposes. No unquestionable influence of the basal spacing on selectivity was observed. Thus, even though Al/CePF-500 seems to afford a higher yield of ortho isomer compared to APF-500, no such difference is observed between Al/CePF-350 and APF-350. The higher ortho alkylation yield with Al/CePF-500 might be related to the higher mesoporous surface area in this material. Also, SMAPWM and APWM exhibit similar monoalkylated product selectivity.

Table 32. Influence of basal spacing on product selectivity.^a

Catalyst	d ₀₀₁ (Å)	weight (g)	Conversion (%)	Monoalkyl (%)	ortho	meta	para
Al/CePF-500	25.5	0.2	16	83	32	28	39
APF-500	17.9	0.2	23	85	21	36	43
Al/CePF-350	24.4	0.2	81	44	19	38	43
APF-350	18.2	0.18	92	27	20	38	42
Al/CePF-350	24.4	0.05	15	81	16	40	44
APF-350	18.2	0.035	15	90	17	39	44
APWM	18.7	0.6	91	34	13	46	41
SMA PWM	15.3	0.2	89	32	15	53	32

a: The reaction conditions were as follows: 30g biphenyl, 140 psi propene, 250°C, 20 hours reaction time.

E. Conclusion

We observed a relationship between the ratio of microporous surface area to mesoporous surface area and the yield of ortho alkylation. Thus, mesoporous catalysts exhibit higher ortho alkylation yields than microporous catalysts. We propose that this is the consequence of a competition between thermodynamic and kinetic control. For mesoporous materials, kinetic control is favored because of easier diffusion and this results in higher ortho alkylation yields. The basal spacing and, thus, the micropores size have at best a minor influence on the product distribution. It is conceivable that larger molecules than biphenyl could undergo shape selective effects in the pillared clay micropores. However, such effects might be overshadowed by the catalytic activity of acid sites outside the

micropores. Due to their low crystallinity, pillared clays are probably not susceptible to exhibit very impressive shape selective properties. They remain, however, very interesting materials for their catalytic activity. In particular, mesoporosity can be controlled in pillared clays and this is very helpful in liquid phase reactions where diffusion control is strong.

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