PHYSICOCHEMICAL PROPERTIES OF MONTMORILLONITE INTERLAYERED WITH CATIONIC OXYALUMINUM PILLARS

M. L. OCCELLI AND R. M. TINDWA

Gulf Research & Development Company, P.O. Drawer 2038
Pittsburgh, Pennsylvania 15230

Abstract—By ion exchanging expandable clay minerals with large, cationic oxyaluminum polymers, "pillars" were introduced that permanently prop open the clay layers. On the basis of thermal, infrared spectroscopic, adsorption, and X-ray powder diffraction (XRD) analysis, the interlayering of commercial sodium bentonite with aluminum chlorohydroxide, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{+7}$, polymers appears to have produced an expanded clay with a surface area of 200–300 m^2/g. The pillared product contained both Brönsted and Lewis acid sites. XRD and differential scanning calorimetry measurements indicated that the micropore structure of this interlayered clay is stable to 540°C. Between 540° and 760°C, the pillared clay collapsed with a corresponding decrease in surface area (to 55 m^2/g) and catalytic cracking activity for a Kuwait gas oil having a 260°–426°C boiling range.

Key Words—Catalysis, Interlayering, Molecular sieve, Montmorillonite, Oxyaluminum, Pillar.

INTRODUCTION

Since their introduction in the early 1950s, molecular sieves have developed into an estimated $250,000,000 business providing catalysts and adsorbents for the chemical and petrochemical industry (Flanigen, 1980). During the past 25 years, more than 100 species of zeolites have been synthesized, yet only a few (e.g., types A, X, Y, ZSM-5, mordenite, erionite) have found a significant industrial application (Breck, 1980). Among these, NaY alone represents more than 95% of the total worldwide zeolite usage. The open, three-dimensional framework structure, the large pore size (~8.0 Å), and the high thermal and hydrothermal stability of zeolites with the faujasite structure contribute significantly to the wide use of these materials in the preparation of petroleum cracking catalysts. The limited range of pore size (2 to 8 Å), however, limits the utility of zeolites as catalysts for the conversion of high molecular weight hydrocarbons of the type found in synthetic and heavy oils.

A new class of molecular sieve-like materials with a pore-size range (6 to 40 Å) larger than faujasite-type zeolites has been synthesized by interlayering expandable clay minerals with large cations. Loeppert *et al.* (1979) prepared expanded smectites using bipyridyl and 1,10-phenanthroline complexes stable to 550°C. Barrer (1978) reviewed the interlayering of smectites with polar organic molecules. Highly stable, high surface-area material can best be prepared by crosslinking layers of expanding layered silicates with oligomeric molecules derived from the hydrolysis of polyvalent cations, such as Al^{+3} and Zr^{+4} (Yamanaka and Brindley, 1979; Brindley and Sempels, 1977; Lahav *et al.*, 1978; Shabtai *et al.*, 1980).

Vaughan and Lussier (1980) showed that the interlayering of montmorillonite with hydroxy-aluminum oligomers generates materials that can be used in conventional petrochemical processes, such as catalytic cracking and hydrocracking. On the basis of their sorptive properties, these interlayered montmorillonites appear to behave like two-dimensional molecular sieves, sorbing 1,3,5-trimethylbenzene (kinetic diameter = 7.6 Å) but not perfluorobutylamine (10.4 Å). The present paper further explores the relationship between zeolites and interlayered clays, and reports on the correlation that exists between the chemical and physical properties of an interlayered clay and its catalytic activity.

EXPERIMENTAL

Montmorillonite

The bentonite used is a crushed rock containing ≥90% Na-montmorillonite and minor amounts of feldspar, biotite, and gypsum impurities and was obtained from the American Colloid Company (Volclay Yellow-Tan Grade, 325 mesh). This type of Na-bentonite was studied by Yamanaka and Brindley (1979) and Vaughan and Lussier (1980). The chemical composition (Table 1) provided by the supplier is typical of this material.

Infrared, X-ray powder diffraction, and thermal analysis

Infrared (IR) spectra were obtained using a Nicolet 7000 FT-IR spectrometer. Samples were pressed at 1500 atm into self-supporting wafers approximately one inch in diameter. The wafers were then mounted in an optical cell, evacuated at ~0.01 torr, and degassed by

22

Table 1. Typical chemical analysis of Upton (Wyoming) Na-bentonite (Volclay, Yellow-Tan Grade).[1]

	Wt. %[2]
SiO_3	63.02
Al_2O_3	21.08
Fe_2O_3	3.25
FeO	0.35
MgO	2.67
$Na_2O + K_2O$	2.57
CaO	0.67
H_2O	5.64
Trace elements	0.72

[1] Provided by the American Colloidal Company.
[2] Moisture free.

Table 2. Chlorhydrol® 50% solution.[1]

	Sample results
Al_2O_3	23.4%
Cl	8.19%
Al:Cl atomic ratio	1.98:1.0
Sulfate (SO_4)	<0.25
Heavy metals (as Pb)	<10 ppm
Fe	40 ppm
As_2O_3	<1 ppm
pH	4.25
Specific gravity at 25°C	1.337
Description of solution	Colorless

[1] From Reheis Chemicals Company.

heating for 3 hr at 400°C. After cooling the wafers to room temperature, pyridine was adsorbed in the samples. X-ray powder diffraction (XRD) measurements were obtained using a Picker X-ray diffractometer at a scan rate of 1°2θ/min and monochromatic CuKα radiation. Differential scanning calorimetry (DSC) measurements and thermal gravimetric analyses (TGA) were obtained with a DuPont 1090 thermogravimetric analyzer using nitrogen as a purge gas and heating rates of 20°C/min and 5°C/min, respectively.

Interlayering cation

Dissolved Al^{+3} readily hydrates in water to $Al(H_2O)_6^{+3}$. The high charge on the Al^{+3} ion weakens the O–H bond of the coordinated water, allowing proton dissociation to occur with ease (Bailar, 1956). Upon losing one H^+, a 1/3 basic aluminum cation dimer $[Al_2(OH)_2(H_2O)_8]^{+4}$ is obtained.[1] As the pH is increased, the dimers condense to form chain structures until a stable 2/3 basic aluminum salt $[Al_6(OH)_{12}(H_2O)_{12}]^{+6}$ is formed (Treadwell and Lien, 1931; Hsu and Bates, 1964). As the basicity of the solution is increased further, these six-member ring oligomers coalesce producing a stable 5/6 basic aluminum cation, such as $[(Al_{28}(OH)_{70}(H_2O)_{28}]^{+14}$ (Denk and Alt, 1952; Hem and Roberson, 1967). In the present experiments, a 5/6 basic aluminum chloride (ACH) salt marketed by Reheis Chemical Company under the tradename of Chlorhydrol® was used (see Table 2). The structure of this salt has not been completely determined, however, Johansson (1960) proposed that $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{+7}$ is present, a cation that consists of a four-coordinated aluminum ion surrounded by 12 AlO_4-octahedra joined together by common edges.

Interlayered montmorillonite

Sodium montmorillonite was ion exchanged with hydroxy aluminum oligomers by first slurrying the clay in

[1] The nomenclature of the basic aluminum cations is explained in Denk and Alt (1952).

water and then adding the polymer. After stirring for 1 hr at 90°C, the exchange was essentially complete. The slurry was filtered, washed, and oven-dried at 120°C overnight. The addition of 150 meq of polymer per 100 g of Na-bentonite typically increased the surface area of the clay from 50 m^2/g to ~280 m^2/g and generated an expanded clay with a basal spacing of 18.2 Å. If the interlayered clay is spray-dried in slurry form, the surface area of the final product is 350–390 m^2/g (Vaughan and Lussier, 1980).

Surface area and surface stability

The Barrett-Joyner-Halenda (Barrett *et al.*, 1950) method was used to calculate pore size distribution from nitrogen adsorption isotherms. The value of adsorbed gas, V, at 64 relative pressures P/P_0 in the interval $0.046 \leq P/P_0 \leq 0.967$ has been used. In Figure 1, some of the nitrogen sorption data are plotted using Langmuir and BET isotherms. Only the Langmuir isotherm gave a linear plot, indicating that the high surface area of the aluminum Chlorhydrol (ACH) bentonite is due to the microporous structure of the interlayered space. Surface stability was investigated by noting the effects of heat treatment on the d(001) spacing by TGA and DSC analysis. As shown in Figure 2, the XRD basal spacing of ACH-bentonite monotonically decreased with temperature. The change was minimal below 540°C; between 540°C and 650°C, the basal spacing decreased from 17.6 to 16.9 Å; and above 760°C, no evidence for an expanded structure remained.

The TGA curve in Figure 3 shows that ~50% of the water lost was surface water and that at 150°C water associated with the ACH-bentonite micropore structure began to be removed. Between 150° and 500°C, 0.067 g H_2O/g clay was lost. At 500°C, there is a cumulative loss of 0.16 g H_2O/g clay which seems to correlate well with the total pore volume of the clay of 0.18 cm^3/g determined by N_2 sorption. The inflection point at 500°C represents the beginning of the loss of hydroxyl water associated with both the basic clay structure and the ACH pillars. Between 500° and 700°C, an
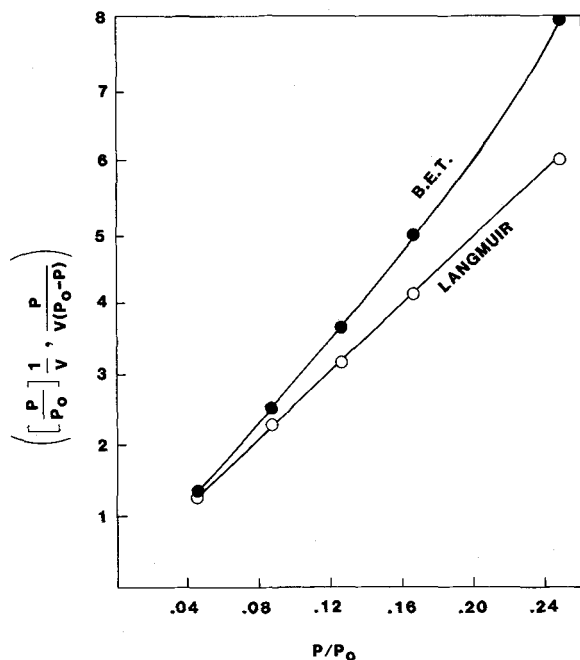
Figure 1. Nitrogen sorption representation using Langmuir (P/P_0V vs. P/P_0) and BET ($P/(P_0 - P)V$ vs. P/P_0) isotherms. Prior to testing, the interlayered bentonite was heated overnight at 260°C.

additional 0.03 g H_2O/g clay was lost. There was no weight change above 700°C.

By comparison, the Na-bentonite used has a pore volume of ~0.08 cm^3/g and a cumulative loss of 0.14 g H_2O/g clay. As can be seen in Figure 3, only 0.014 g H_2O/g of Na-bentonite was lost between 150° and 500°C. Because the pillars did not dehydroxylate over this temperature range, an ACH-bentonite structure with a surface area of 280 m^2/g must contain ~0.053 g of "zeolitic" water per gram of interlayered clay. The variation in surface area as a function of the activation temperature has been plotted on the same graph. Note the range of stability up to 540°C. Above 540°C, the pillars began to decompose, and the surface area shows a strong dependence on temperature. At 750°C, the surface area was reduced to its original value prior to interlayering. The DSC curve (Figure 4) shows that an endothermic reaction took place between 100° and 500°C corresponding to water loss from the clay surface and interlayered space. At 500°C, a second endotherm is present corresponding to the beginning of the collapse of the interlayered structure.

These results are in agreement with published data on clays pillared with inorganic oxides. In fact, Yamanaka and Brindley (1979) reported that by exchange reactions with tetrameric hydroxy cations, $[(Zr_4(OH)_{14} \cdot nH_2O)]^{+2}$, Na-montmorillonites with surface areas as high as 300–400 m^2/g, stable to 500°C, can be obtained. Similarly, Vaughan et al. (1979) noted that
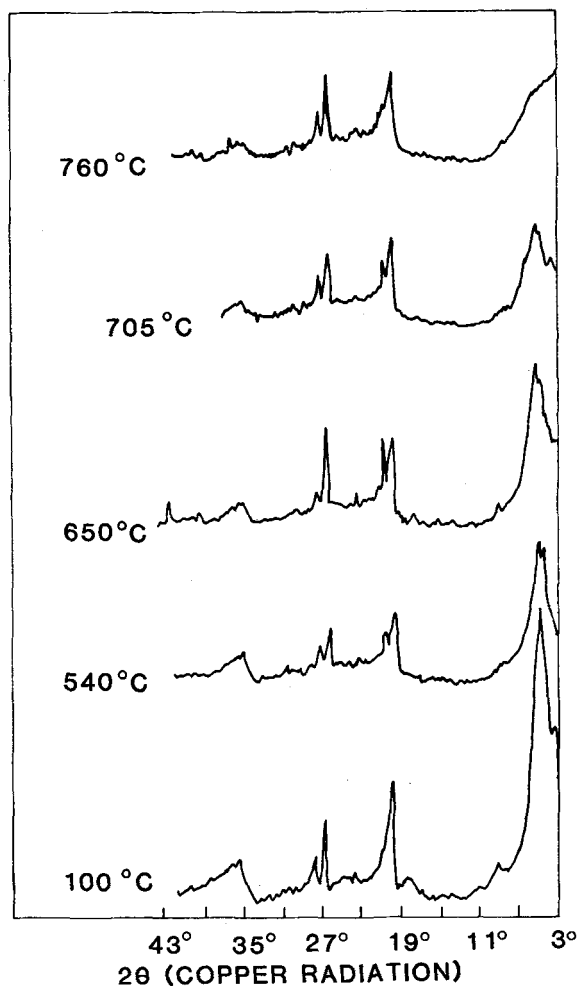

Figure 2. X-ray powder diffraction patterns of ACH-bentonite samples heat-treated for 4 hr at different temperatures.

by interlayering unbeneficiated Na-bentonite with chlorohydroxide polymers, clays with surface areas of 250–350 m^2/g and basal spacings between 17.0 and 18.8 Å can be formed.

Surface acidity

Spectroscopic studies of adsorbed bases are well established and are useful techniques for investigating the surface acidity of heterogeneous catalysts (Svoboda and Kunze, 1966). Parry (1963) showed that specific adsorption bands in the vibrational spectrum of chemisorbed pyridine in the 1400 and 1700 cm^{-1} region can distinguish between Lewis and Brönsted acidity. Ward (1968) and Kiviat and Petrakis (1973) showed how to determine the relative numbers of these sites. On the basis of ammonia and pyridine adsorption data, Wright et al. (1972) noted the presence of Lewis and Brönsted acidity in synthetic mica/montmorillonite.

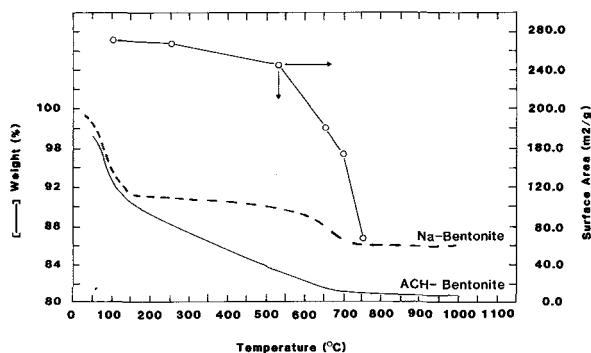Infrared spectra obtained by evacuating the pyridine-

Figure 3. Thermogravimetric analysis of ACH-bentonite showing the correlation between weight and surface area losses.

loaded wafers at three different temperatures (Figure 5) indicate that the ACH-bentonite contained both Lewis and Brönsted acid sites. The presence of pyridine co-ordinated via its nitrogen lone-pair electrons to an empty p-orbital can be seen by the bands at 1445 and 1600 cm^{-1}. The band at 1540 cm^{-1} and the strong band at 1490 cm^{-1} are indicative of pyridinium ion formed by reaction with surface protons. The band at 1540 cm^{-1} is typical of the bonding of the N$^+$–H group (Wright et al., 1972). The band at ~1582 cm^{-1} has been assigned instead to physically adsorbed pyridine. By evacuating the pyridine-loaded sample at 150°C, the "Lewis-acid" bands increased in frequency to 1452 and 1620 cm^{-1},

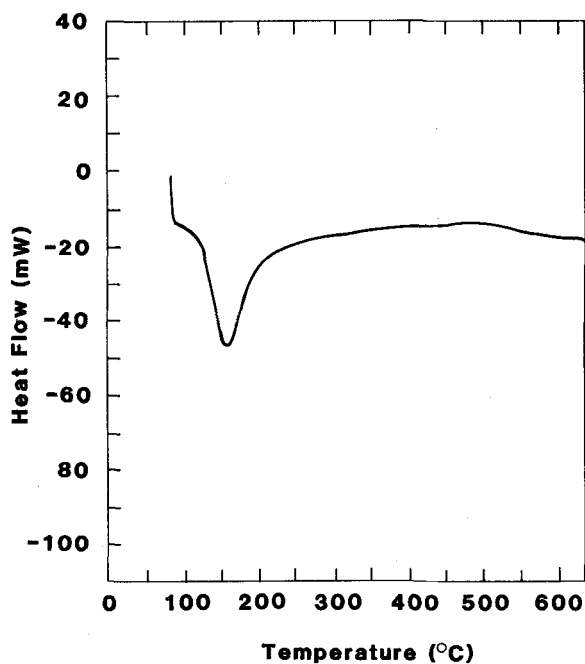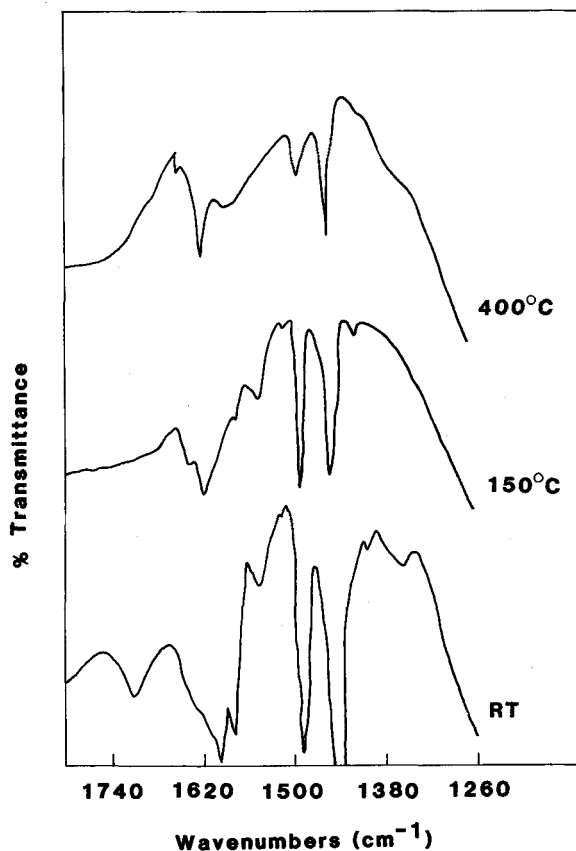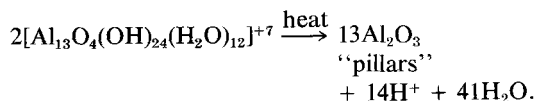Figure 5. Infrared spectrum of pyridine adsorbed on ACH-bentonite. The sample was heated in vacuum at 400°C prior to sorbate loading.

while the "Brönsted bands" shifted to 1544 cm^{-1}. The unchanged intensity of the band at 1490 cm^{-1} is consistent with the presence of both types of acid sites. Co-ordinately bonded pyridine, as well as some pyridinium ions, were still present on a sample calcined at 400°C (Figure 5). However, the intensities of the bands at 1457 and 1624 cm^{-1} seem to indicate that surface acidity of the calcined material was mostly of the Lewis type.

The spectra of ACH-bentonite in the O–H stretching region shows the presence of a doublet indicating the existence of two types of hydroxyls (Figure 6). The band at 3650 cm^{-1} is due to the stretching frequency of structural OH. The band at 3700 cm^{-1} is likely associated with the ACH-pillars because it disappeared upon pyridine adsorption (Figure 6). Protic acidity may be responsible for the observed instability of inorganic pillars at high temperature, i.e., when pillars are formed by dehydration of the interlayering polymeric cation (Vaughan and Lussier, 1980), protons are generated as follows:
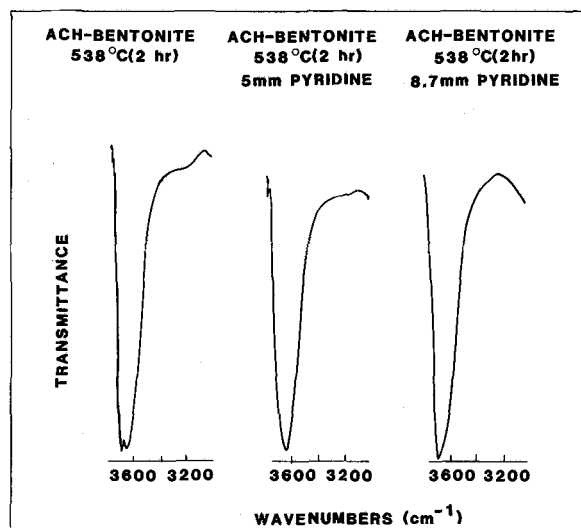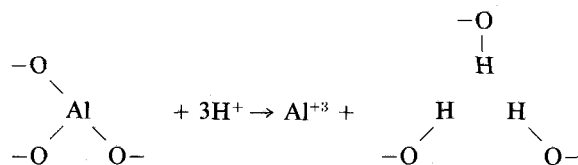
$$2[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{+7} \xrightarrow{heat} 13Al_2O_3$$
$$\text{"pillars"}$$
$$+ 14H^+ + 41H_2O.$$

Figure 4. Differential scanning calorimetric analysis of ACH-bentonite.

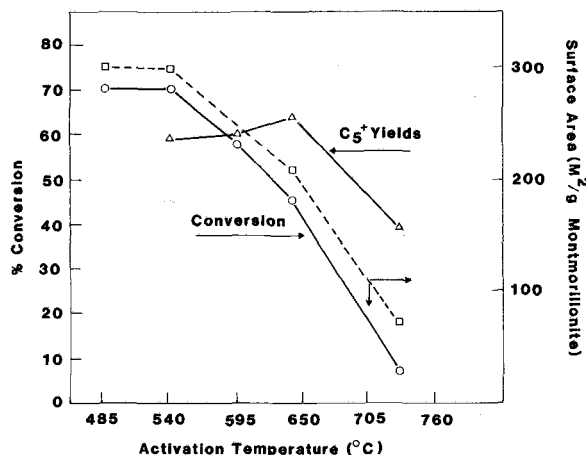Figure 6. Hydroxyl absorption bands of ACH-bentonite before and after pyridine loading.

Figure 7. Thermal effects on the surface area and catalytic properties of Na-montmorillonite interlayered with aluminum chlorohydroxide cations.

At high temperature the protons are capable of leaching Al^{+3} from the pillars much in the same way that acids leach Al^{+3} from a zeolite structure:

$$\begin{array}{c}-O \\ \backslash \\ Al \\ / \quad \backslash \\ -O \quad O-\end{array} \quad + \; 3H^{+} \rightarrow Al^{+3} \; + \quad \begin{array}{c}-O \\ | \\ H \\ \\ H \quad\quad H \\ / \quad\quad \backslash \\ -O \quad\quad O-\end{array}$$

When this reaction occurs, the pillars first decrease in size and then, as aluminum removal continues, collapse.

Catalytic properties

Catalytic evaluation was performed using a microactivity test (MAT) similar to the one described by Ciapetta and Anderson (1967). The weight hourly space velocity was 15, with an 80-sec catalyst-contact time at 480°C. A catalyst-to-oil ratio of 2.5 was used. The charge stock was a Kuwait gas oil having a 260°–426°C boiling range. The results in Figure 7 show that the ACH-bentonite retained its high conversion ability and activity up to 540°C. Its catalytic activity is comparable to that of a clay-based commercial cracking catalyst containing about 15% of a zeolite of the faujasite type:

	Conversion (volume %)	Gasoline (volume %)
ACH-bentonite	74.2	44.0
Commercial cracking catalyst	70.6	47.7

Prior to testing, the catalysts were heated at 540°C for 10 hr with 10% steam. However, although the activity of the commercial catalyst was practically independent of the pretreatment temperature below 760°C, between 540° and 650°C a progressive collapse of the pillared structure occurred with a corresponding decrease in surface area and cracking activity. Similar conversion results on a West Texas gas oil were published by Vaughan *et al.* (1979), and Shabtai *et al.* (1980) discussed the catalytic activity of interlayered clays for cumene and 1-isopropylnaphthalene dealkylation.

CONCLUSIONS

By interlayering commercial Na-bentonite with aluminum chlorohydroxide polymers, $[Al_{13}O_4(OH)_{24} \cdot (H_2O)_{12}]^{+7}$, an expanded clay with a surface area of 200–300 m²/g containing both Brönsted and Lewis acid sites was obtained. At high temperatures (under vacuum), acidity was found to be mostly of the Lewis type. However, under actual cracking conditions, the interconversion of Brönstead to Lewis acid sites may not be as extensive, because it will probably be controlled by reactor temperatures and feed compositions.

Nitrogen adsorption on the pillared structures can be represented by Langmuir isotherms showing that the high surface area of the expanded clay is due predominantly to micropores in the interlayered space. XRD and DSC data show that this structure is essentially stable to 540°C. When tested for microactivity under mild pretreatment conditions, the interlayered clays were as active as a commercial cracking catalyst containing zeolite of the faujasite type. However, when the cracking activity was evaluated under typical pilot plant conditions, the interlayered clay lost its high surface area and most of its catalytic activity. This behavior was not observed in the commercial catalyst.

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Резюме—При помощи ионообменных расширяющихся глинистых минералов с большими катионными оксиалюминовыми полимерами были введены ''столбы,'' которые постоянно поддерживают открытыми глинистые слои. На основе данных по термическому и адсорбционному анализах, инфракрасной спектроскопии и порошковой рентгеновской дифффракции (XRD), прослойка промышленного бентонита с хлоргидроокисей алюминия, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{+7}$, кажется, что полимеры образовали расширенную глину с площад поверхности 200–300 м²/г. ''Столбовый'' продукт содержал кислотные места Бренстеда и Льюиса. Измерения по XRD и дифференциальной сканирующей калориметрии указывают, что микропористая структура прослойковой глины является стабильной до 540°C. [Е.С.]

Resümee—Wenn expandierbare Tonminerale mit großen, kationischen Oxyaluminium-Polymeren ausgetauscht werden, werden ''Pillars'' eingebaut, die die Tonlagen permanent aufspreizen. Aufgrund thermischer und infrarotspektroskopischer, Adsorptions- und Röntgenpulverdiffraktions (XRD)-Analysen scheint die Wechsellagerung von käuflichem Na-Bentonit mit Aluminiumchlorohydroxid, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{+7}$, -Polymeren zur Bildung eines expandierbaren Tons zu führen, der eine Oberfläche von 200 – 300 m²/g hat. Das ''Pillar''-Produkt enthielt sowohl Brönsted- als auch Lewis-Säureplätze. XRD- und differentialkalorimetrische Messungen deuteten darauf hin, daß die Struktur der Mikroporen dieser Wechsellagerungstone bis 540°C stabil ist. Zwischen 540° und 760°C brach der ''Pillar''-Ton zusammen, was zu einer entsprechenden Abnahme der Oberfläche (auf 55 m²/g) führt und zu einer Abnahme der Fähigkeit zum katalytischen Cracken von Gasöl aus Kuwait, das einen Siedebereich zwischen 260° und 420°C hat. [U.W.]

Résumé—Par l'échange d'ions entre des minéraux argileux expansibles et de larges polymères cationiques oxyaluminium, des ''pilliers'' ont été introduits qui maintiennent ouverts de manière permanente les couches argileuses. Basé sur des analyses thermiques, de spectroscopie infrarouge, d'adsorption, et de diffraction de rayons-X (XRD), le placement en couches alternatives de bentonite de sodium commerciale et de polymères chlorohydroxide d'aluminium, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{+7}$, semble avoir produit une argile dilatée ayant une aire de surface égale à 200–300 m²/g. Le produit à pilliers contenait à la fois des sites acides Brönsted et Lewis. Des mesures XRD et de calorimétrie differentielle ont indiqué que la structure micropore de cette argile à couches alternatives est stable jusqu'a 540°C. Entre 540° et 760°C, l'argile à pilliers s'est effondrée entraînant une diminution correspondante de l'aire de surface (à 55 m²/g) et une activité catalytique/craquante pour un petrole à essence du Kuwait ayant une étendue de températures d'ébullition de 260°–426°C. [D.J.]