

## PROPERTIES AND CATALYTIC ACTIVITY OF ACID-MODIFIED MONTMORILLONITE AND VERMICULITE

J. RAVICHANDRAN<sup>1</sup> AND B. SIVASANKAR<sup>2</sup>

<sup>1</sup> Department of Chemical Engineering, Anna University, Madras - 600 025, India

<sup>2</sup> Department of Chemistry, Anna University, Madras - 600 025, India

**Abstract**—The acidic properties of acid-modified montmorillonite and vermiculite were determined by pyridine and ammonia adsorption to correlate with the alkylating and dehydrating activity of the activated samples. Treatment of the minerals with different concentrations of hydrochloric acid results in the variation of overall acidity and density of acidic sites. Infrared (IR) spectral and differential scanning calorimetric analyses have revealed the presence of Bronsted and Lewis acid sites on the activated samples. The catalytic activity towards the above reaction has been correlated to the acid strength and density of Lewis acid sites. Treatment of montmorillonite with hydrochloric acid in the range of 0.1 and 0.3 *M* and vermiculite with 0.2 to 0.3 *M* seemed to be suitable for the conversion of methanol into olefin-rich hydrocarbons. Acid-activated montmorillonite catalyzed the isopropylation of benzene to a maximum extent of 16%, whereas acid-activated vermiculite gave a maximum conversion of only 4%.

**Key Words**—Acidity, Benzene, Catalyst Characterization, Hydrocarbons, Isopropylation, Methanol Dehydration, Montmorillonite, Vermiculite.

### INTRODUCTION

Modified smectites exhibit attractive properties as solid acids (Pinnavaia 1983). These modified clay minerals have attracted considerable attention as acid catalysts for petroleum refining (Occelli 1983) and other acid-catalyzed reactions (Occelli et al. 1985; Burch and Warburton 1986). Hydroxyl groups on the surface of the layer aluminosilicates are very important with respect to the use of these solids in catalysis or adsorption.

Treatment of clays with acid has been reported to replace exchangeable cations with H ions and leaching Al and other cations out of both tetrahedral and octahedral sites, but leaving the SiO<sub>4</sub> groups largely intact (Theocharis et al. 1988). The present study was undertaken to modify montmorillonite and vermiculite by treatment with hydrochloric acid. Acid treatment produces an increase in surface area and acidity. The nature, strength and density of acidic sites on activated samples have been investigated by IR spectroscopy and differential scanning calorimetry using pyridine and ammonia as probe molecules. The dehydration of methanol and alkylation of benzene (cumene synthesis) were carried out as test reactions for the acid-activated clay minerals. The effect of temperature and concentration of the acid used for the preparation of the catalyst also have significant influence on the catalytic activity.

### EXPERIMENTAL

Montmorillonite (Fluka) and vermiculite (Tamil Nadu, Minerals, India) were treated with hydrochloric acid solutions at different concentrations in the range of 0.1 to 3 *M* (30 g clay/L). The suspensions were maintained at 100 °C with stirring for 4 h. The samples were cooled to room temperature, collected over a fil-

ter funnel and washed with double distilled water until free of excess acid. The samples were dried at 100 to 120 °C for 12 h and calcined at 250 °C for 2 h. The samples activated with 0.1, 0.2, 0.3, 0.4, 0.7, 1.0, 2.0 and 3.0 *M* hydrochloric acid are denoted as M<sub>1</sub>, M<sub>2</sub>, M<sub>3</sub>, M<sub>4</sub>, M<sub>5</sub> and M<sub>6</sub> for montmorillonite (no 2.0 or 3.0 *M* samples) and V<sub>1</sub>, V<sub>2</sub>, V<sub>3</sub>, V<sub>4</sub>, V<sub>5</sub>, V<sub>6</sub>, V<sub>7</sub> and V<sub>8</sub> for vermiculite, respectively.

### Characterization

The untreated and acid-activated samples were analyzed for their chemical composition by ARL 3410 inductively coupled plasma (ICP). Surface area of the acid-activated as well as untreated samples was determined by nitrogen adsorption at liquid nitrogen temperature using a Micromeritics Pulse Chemisorb 2700.

The structure of the catalyst was confirmed by IR spectral studies with a Perkin-Elmer 983 G spectrophotometer, using the KBr mull technique.

### Determination of Acidity

Acidity of the samples was determined by *n*-butylamine titration as well as by adsorption of pyridine and ammonia as probe molecules (Aboul Gheit 1988). The amount of pyridine and ammonia adsorbed were obtained by thermogravimetric analysis (TGA) using a Mettler TA-3000 system. The natures of acid sites were characterized on the basis of IR spectral data of pyridine and ammonia presorbed activated samples. The nature, strength and density of acidic sites were confirmed by differential scanning calorimetric (DSC) studies of pyridine and ammonia presorbed activated samples using Mettler DSC 20 with a TA 3000 micro-processor.

Table 1. Surface area of montmorillonite and vermiculite before and after treatment with HCl.

HCl (M)	Sample	Surface area m <sup>2</sup> /g	Sample	Surface area m <sup>2</sup> /g
Montmorillonite		Vermiculite		
0.0	M <sub>0</sub>	19.0	V <sub>0</sub>	3.5
0.1	M <sub>1</sub>	98.7	V <sub>1</sub>	9.6
0.2	M <sub>2</sub>	129.7	V <sub>2</sub>	33.3
0.3	M <sub>3</sub>	138.8	V <sub>3</sub>	49.1
0.4	M <sub>4</sub>	161.5	V <sub>4</sub>	81.1
0.7	M <sub>5</sub>	188.3	V <sub>5</sub>	222.9
1.0	M <sub>6</sub>	185.0	V <sub>6</sub>	275.0
2.0	—	—	V <sub>7</sub>	270.4
3.0	—	—	V <sub>8</sub>	270.8

### Catalytic Activity

The catalytic activity of the activated montmorillonite and vermiculite was tested using a flow reactor by the following 2 reactions.

#### Dehydration of Methanol

The catalytic activity tests were performed between 300 and 400 °C. About 0.2 g of the catalyst was packed into the Pyrex glass reactor (1 cm diameter and 25 cm length) and held in position with the help of quartz wool plugs. Two mL/h of continuous supply of the reactant was maintained by a calibrated syringe model infusion pump. Glass beads packed on the inlet side of the reactor served for preheating the reactant. The catalyst bed temperature was maintained at desired temperature by means of a heating chord surrounding the reactor controlled by a digital temperature controller-cum-indicator. Temperature measurements were made by a chromel–alumel thermocouple placed inside a thermowell immersed in the catalyst bed. The gas mixture from the reactor was allowed to pass through a condenser and collected. Gaseous products were collected in a gas burette. The products were analyzed with a Hewlett Packard-5890 gas chromatograph, using the Porapak-Q column.

#### Alkylation of Benzene (Cumene Synthesis)

Acid-catalyzed isopropylation of benzene was studied as a model of alkylation reaction. The alkylation activity of acid-activated montmorillonite was investigated with different compositions of benzene and isopropanol in the temperature range between 150 and 300 °C. The catalyst used was 0.2 g and the flow rate was 1.5 mL/h. The liquid products were analyzed using the Carbowax-20M column.

## RESULTS AND DISCUSSION

The chemical composition of the acid-treated clays revealed that the treatment of montmorillonite and vermiculite with hydrochloric acid at different concentrations in the range of 0.1 to 1 M has Al content of 15.6 to 3.3%.

Table 2. Infrared absorption frequencies of acid-treated montmorillonite, vermiculite and silica.

Assignment	Wave number (cm <sup>-1</sup> )		
	Montmorillonite	Vermiculite	SiO <sub>2</sub>
$\nu(\text{Si-O})$	1100 <sub>sh</sub>	1070 <sub>sh</sub>	1210 <sub>sh</sub>
	1040 <sub>vs,b</sub>	1020 <sub>vs,b</sub>	1090 <sub>vs,b</sub>
	985 <sub>sh</sub>		965 <sub>w</sub> 800 <sub>s</sub>
$\nu(\text{Si-O}), \nu(\text{Al-O})$	810 <sub>sh</sub>	810 <sub>m</sub>	
	$\nu(\text{Al-O}), \nu(\text{Si-O}), \nu(\text{Al-O-Si})$	720 <sub>w</sub>	725 <sub>w</sub> 680 <sub>w</sub> 650 <sub>sh</sub> 670 <sub>w</sub>
$\nu(\text{Mg-O})$	530 <sub>m</sub>		
$\nu(\text{Si-O})$	460 <sub>s</sub>	450 <sub>s,b</sub>	465 <sub>s</sub>

Key: sh = shoulder; vs = very strong; b = broad; w = weak; s = strong; and m = medium.

The surface area of the different acid-activated montmorillonite and vermiculite is given in Table 1. Surface area has been found to increase for acid-treated clays and the increase depended on the acid concentration. Treatment with higher concentration of acid than 0.7 M has not resulted in substantial increase in the surface area of montmorillonite, whereas surface area of vermiculite steadily increased with HCl concentration upto 1.0 M.

The IR absorption spectra of montmorillonite and vermiculite show 2 characteristic regions (Hair 1967; Farmer 1974; Suquet et al. 1991): 1) the 3750 to 3500 cm<sup>-1</sup> region and 2) the 1150 to 400 cm<sup>-1</sup> region.

The absorption bands in the region of 3750 to 3500 cm<sup>-1</sup> have been assigned to the surface structural hydroxyl groups of the layered aluminosilicates as well as of adsorbed water.

The IR absorption bands in the 1150 to 400 cm<sup>-1</sup> region are relatively more informative about the structural characteristics of clay minerals and are attributed to lattice vibration (Hair 1967; Farmer 1974; Suquet et al. 1991).

The acid attack on the clay mineral results in the dissociation of a part of the absorption bands of acid-activated montmorillonite and vermiculite (with lower concentrations of HCl), which do not show much variation from those of untreated clay minerals.

The IR absorption spectra data on activated montmorillonite (M<sub>2</sub>) and vermiculite (V<sub>2</sub>) are shown in Table 2 along with that of silica.

The IR absorption band observed around 820 cm<sup>-1</sup> has been identified as sensitive to the nature of octahedral cations by Farmer (1974) and Suquet et al. (1991). The absorption band observed at 810 cm<sup>-1</sup> in the present study increases in intensity with treatment of higher concentrations of hydrochloric acid. The intensity of this band compares with that of pure silica when the concentration of HCl is greater than 1 M.

The acidity of catalyst samples was determined by *n*-butylamine titration in aqueous medium and also by

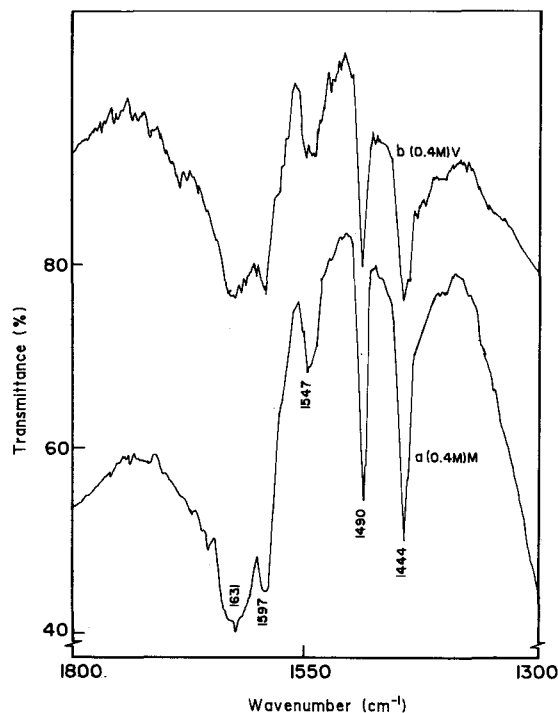


Figure 1. IR spectra of pyridine adsorbed on a) 0.4 *M* acid-activated montmorillonite; and b) 0.4 *M* acid-activated vermiculite.

thermal desorption of adsorbed pyridine and ammonia using TGA. The overall acidity increases linearly up to 1 *M* hydrochloric acid (Ravichandran and Sivasankar 1995). The IR spectra of pyridine-adsorbed samples clearly indicated the presence of both Lewis and Bronsted acid sites. The IR bands recorded for pyridine adsorbed on the representative samples of acid-treated montmorillonite and vermiculite are shown in Figure 1. The presence of Lewis acid sites is indicated by IR absorption bands at 1631, 1490 and 1445  $\text{cm}^{-1}$ . The absorption bands of 1631, 1597, 1547 and 1490  $\text{cm}^{-1}$  indicate the presence of Bronsted acid sites. The presence of hydrogen-bonded pyridine is indicated by IR absorption bands at 1490 and 1440  $\text{cm}^{-1}$ . In addition, an overlap of the vibration band of pyridine adsorbed on Lewis acid sites, Bronsted acid sites and hydrogen-bonded pyridine occurs in the region. The presence of Bronsted and Lewis acidic sites on acid-activated vermiculite has been indicated by IR spectral data (Figure 1). An interesting observation is that the intensities of the absorption bands at  $\approx 1540$ , 1490 and 1630  $\text{cm}^{-1}$  generally decreased with increasing concentration of the acid greater than 1 *M* used for activation. The absorption band at 1540  $\text{cm}^{-1}$  assigned exclusively for Bronsted acidity disappears completely for vermiculite activated by 2-*M* and higher concentration of hydrochloric acid.

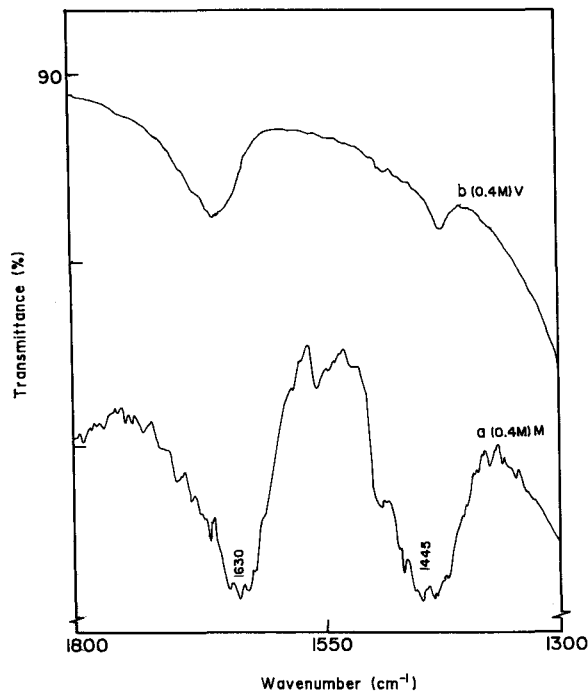


Figure 2. IR spectra of ammonia adsorbed on a) 0.4 *M* acid-activated montmorillonite; and b) 0.4 *M* acid-activated vermiculite.

The presence of Lewis and Bronsted acid sites are further confirmed by IR studies of ammonia-adsorbed catalysts. Two absorption bands have been observed at 1445 and 1630  $\text{cm}^{-1}$  (Figure 2). The band at 1630  $\text{cm}^{-1}$  is attributed to the bending vibration of ammonia coordinatively linked to a Lewis center. The absorption band in the region at 1445  $\text{cm}^{-1}$  is assigned to the characteristic vibration of the  $\text{NH}_4^+$  ion, indicating the presence of Bronsted acidic sites (Hair 1967).

The DSC effects due to base desorption from the acid sites alone appear in the thermograms using nullifying technique (Aboul Gheit 1987; Ravichandran and Sivasankar 1995). The presence of Lewis and Bronsted acidic sites can be inferred from the desorption peaks of pyridine at 313 and 530  $^{\circ}\text{C}$ , respectively. The desorption peak at 120  $^{\circ}\text{C}$  has been assigned to the presence of H-bonded pyridine. The individual peak temperatures, the corresponding  $\Delta\text{H}$  values and assignments for the different samples are given in Table 3.

#### Dehydration of Methanol

The conversion of methanol into hydrocarbons is of industrial importance, as methanol is a potential feedstock. The dehydration of methanol catalyzed by acidic solids to hydrocarbons offers a viable route for the production of olefins (Ebeid et al. 1992). The effect of temperature on catalytic activity for acid-activated montmorillonite and vermiculite was investigated in

Table 3. Acidity and DSC data on pyridine desorption from acid-treated montmorillonite and vermiculite.

HCl (M)	Sample	Acidity mmol pyridine/g	Peak temperature (°C)	$\Delta H$ J/g	Assignment
Montmorillonite					
0.2	M <sub>2</sub>	2.39	120.4	76	HA
			308.0	13	LA
			478.2	135	BA
0.4	M <sub>4</sub>	2.63	137.4	106	HA
			313.2	38	LA
			512.1	119	BA
0.7	M <sub>5</sub>	2.72	117.2	79	HA
			303.0	27	LA
			525.2	15	BA
1.0	M <sub>6</sub>	2.90	130.2	88	HA
			308.4	25	LA
			530.3	33	BA
Vermiculite					
0.2	V <sub>2</sub>	0.20	272.0	9	LA
0.4	V <sub>4</sub>	0.36	106.5	144	HA
			292.8	15	LA
0.7	V <sub>5</sub>	1.81	103.1	95	HA
			298.0	14	LA

Key: HA = pyridine desorption from weak acid sites, LA = pyridine desorption from Lewis acid sites and BA = pyridine desorption from Bronsted acid sites.

the temperature range between 300 and 400 °C. The volume of hydrocarbons obtained from methanol dehydration was found to increase with temperature. The dehydration of methanol produced a mixture of C<sub>1</sub>–C<sub>4</sub> hydrocarbons. With increase in temperature, the formation of olefinic compounds was found to decrease. Higher temperatures and higher acidities favored the formation of paraffinic hydrocarbons on acid-activated montmorillonite samples.

The volume of hydrocarbons obtained for dehydration of methanol as a function of acidity (mmol pyridine/g catalyst) at 400 °C is shown in Figure 3 for

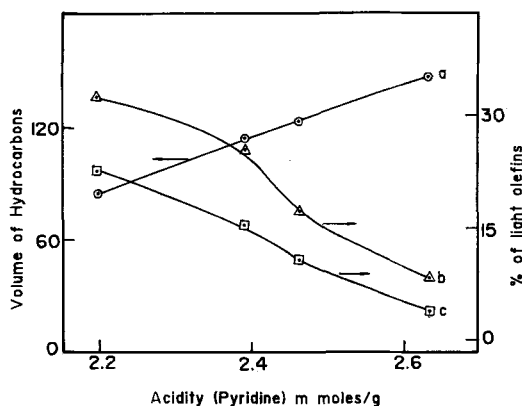


Figure 3. Plot of volume of hydrocarbons and % of light olefins obtained vs. acidity for methanol dehydration on acid-treated montmorillonite a) 60 min; b) 60 min; and c) 120 min.

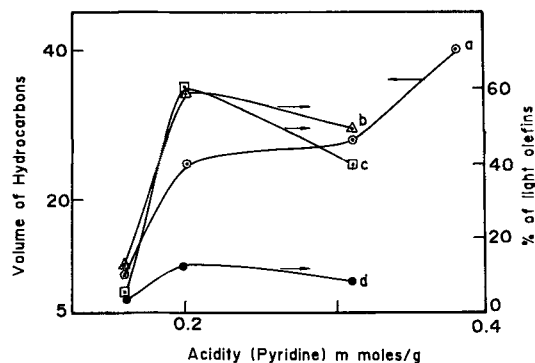


Figure 4. Plot of volume of hydrocarbons and % of light olefins obtained vs. acidity for methanol dehydration on acid-treated vermiculite a) 60 min; b) 60 min; c) 120 min; and d) 180 min.

montmorillonite and Figure 4 for vermiculite. In the case of montmorillonite, the highest degree of conversion has been observed for the catalyst M<sub>4</sub> with acidity 2.63 mmol pyridine/g. In the case of vermiculite, maximum volume of hydrocarbons obtained has been observed for the catalyst V<sub>4</sub> with acidity 0.36 mmol pyridine/g.

The variation of percentage of light olefins as a function of acidity at 350 °C is shown in Figure 3 for montmorillonite and Figure 4 for vermiculite. The percentage of light olefins obtained was initially found to be 32% on M<sub>1</sub> and it decreases with increasing acidity of the catalyst to about 8% for M<sub>4</sub>. Treatment of montmorillonite with hydrochloric acid concentration in the range between 0.1 and 0.3 having acidity values of 2.20 to 2.46 mmol pyridine/g seemed to be suitable for the conversion of methanol into olefin-rich hydrocarbons. Samples with higher acidity in the range of 2.63 to 2.90 mmol pyridine/g did not give any unsaturated hydrocarbons. In the case of vermiculite, the maximum percentage of unsaturated hydrocarbons was 59% for the catalyst V<sub>2</sub>. Treatment of vermiculite with 0.2 to 0.3 M hydrochloric acid having acidity values of 0.20 to 0.31 mmol pyridine/g was apparently suitable for the production of olefin-rich hydrocarbons.

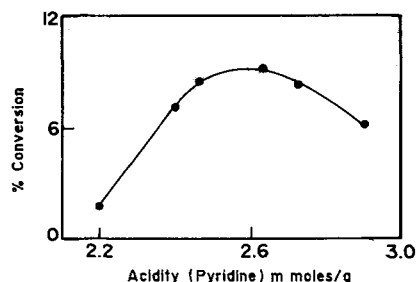


Figure 5. Plot of % conversion vs. acidity for isopropylation of benzene on acid-treated montmorillonite (90 min).

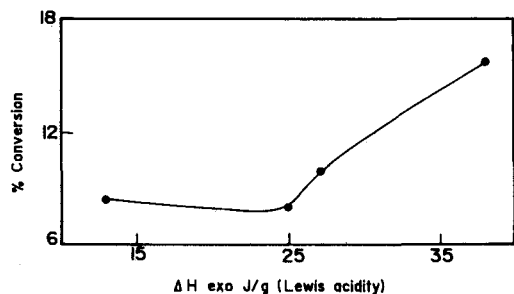


Figure 6. Plot of % conversion vs.  $\Delta H$  exo (Lewis acidity) for isopropylation of benzene on acid-treated montmorillonite (30 min).

### Alkylation of Benzene

Acid-catalyzed isopropylation of benzene was studied as a model of alkylation reaction. The alkylation activity of acid-activated montmorillonite and vermiculite was investigated with different compositions of benzene and isopropanol in the temperature range between 150 and 300 °C. The optimum molar ratio for the maximum isopropylation of benzene was 7:1 benzene to isopropyl alcohol. Maximum conversion was found at 250 °C.

The overall conversion of benzene as a function of acidity for various acid-activated montmorillonites is shown in Figure 5. The higher (15.8%) was observed for the catalyst  $M_4$  with acidity 2.63 mmol pyridine/g. The isopropylation of benzene as a function of density of Lewis acid sites for various acid-treated montmorillonites is shown in Figure 6. The higher conversion (15.8%) was observed for the catalyst  $M_4$  which has the maximum density (38 J/g) of Lewis acid sites among the various acid-activated montmorillonite samples.

In the case of vermiculite, the overall conversion of benzene was found to be less than 4%. This may be attributed to the very low density of Lewis acid sites as indicated by DSC data. Maximum conversion was found for the sample  $V_4$ , which has the maximum density of Lewis acid sites.

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