

Characterization of acid activated montmorillonite and vermiculite clays by thermal desorption and differential scanning calorimetric techniques

J Ravichandran* & B Sivasankar[†]

Department of Chemical Engineering, Alagappa College of Technology

Received 24 February 1994; revised and accepted 20 September 1994

Montmorillonite and vermiculite clays, activated with hydrochloric acid solutions of different concentrations, have been characterized by thermal desorption and differential scanning calorimetric (DSC) techniques using ammonia and pyridine as probe molecules. The amount of adsorbed ammonia is found to be about twice the amount of pyridine on all the samples as determined by thermal desorption studies. DSC studies reveal the heterogeneity of acidic sites on the activated catalysts. DSC thermograms show the existence of three distinct acidic sites with different strength on the surface of the catalysts.

A method widely used for the determination of the acidity of solid surfaces^{1,2} depends on adsorption of bases either from the gas phase or from the liquid phase (non-aqueous solutions). Ammonia, pyridine or aliphatic amines are the bases most often used in such measurements³. When chemisorbed on surfaces possessing acid properties, amines can interact with acidic protons, electron acceptor sites and hydrogen from neutral or weakly acidic hydroxyl groups. Infrared spectroscopy⁴⁻⁶ has been widely applied for the determination of the nature of interactions between the adsorbed bases and the acid surfaces of the solid. TPD and DSC studies on adsorbed bases^{3,7-10} have been found useful for investigating the surface behaviour of clays. In the present work the DSC technique, which is more advantageous than many other techniques, has been used to study the nature of acidic sites and the acid strength distribution on acid activated montmorillonite and vermiculite clays.

Experimental

Montmorillonite and vermiculite clays were activated independently by refluxing with hydrochloric acid solutions of different concentrations in the range 0.1-3.0 M (200 ml each) with occasional shaking for about 4 h. The samples were cooled to room temperature, collected on a filter funnel and washed free of excess of acid with doubly distilled water. The samples were dried at 100-110°C for 12 h and calcined at 250°C for 2 h. Surface areas of acid treated as well as untreated clay samples were determined by nitrogen adsorption measurement at liquid nitrogen temperature using a Micromeritics pulse chemisorb-2700. The samples activated with 0.1, 0.2, 0.3, 0.4, 0.7, 1.0, 2.0 and 3.0 M HCl are denoted as M₁, M₂, M₃, M₄, M₅ and M₆ for montmorillonite and V₁, V₂, V₃, V₄, V₅, V₆, V₇ and V₈ for vermiculite.

The adsorption of pyridine and ammonia was carried out on modified clay samples as follows. The samples were degassed at 1×10^{-3} torr at 150°C. They were cooled to room temperature *in vacuo*. The bases were adsorbed by allowing their vapours to come into contact with the degassed samples. Excess of unadsorbed vapours and the bases physisorbed on the samples were removed by evacuation at 1×10^{-3} torr for several hours.

The desorption of adsorbed bases was studied by thermogravimetric analysis in the temperature range 30-600°C (Mettler TG-50 with TA-3000 micro system) and differential scanning calorimetry. Differential scanning calorimetric thermograms of samples were recorded on a Mettler DSC-20 unit with TA 3000 microprocessor. Pyridine/ammonia adsorbed catalyst samples were subjected to a temperature scan between 50 and 600°C at a heating rate of 20°C/min. A nullifying procedure^{3,10} was adopted. In this procedure the sample cell contained around 10 mg of base presorbed catalyst whereas the reference cell contained an equal weight of the corresponding base free catalyst. The measurements were carried out at atmospheric pressure and no purge gas was used.

Results and discussion

The variation of overall acidity (mM of ammonia or pyridine) of the acid activated montmorillonite and vermiculite as determined by thermal

[†]Department of Chemistry, College of Engineering, Anna University, Madras 600 025

Table 1—Differential scanning calorimetric (DSC) data on ammonia and pyridine desorption from acid treated montmorillonite and vermiculite samples

Catalyst	Surface area (m ² /g)	Peak temperature (°C)		ΔH (J/g)		Assignment
		Ammonia	Pyridine	Ammonia	Pyridine	
Montmorillonite based catalysts						
M ₂	129.6	124.7	120.4	85	76	WA
		303.9	308.0	10	13	LA
		407.2	478.2	105	135	BA
M ₄	161.5	118.2	137.4	149	106	WA
		313.2	313.2	26	38	LA
		511.9	512.1	37	118	BA
M ₅	188.3	112.0	117.2	90	79	WA
		300.3	303.0	20	27	LA
		523.3	525.2	9	15	BA
M ₆	185.3	121.8	130.2	69	88	WA
		301.1	308.4	41	25	LA
		551.9	530.3	11	23	BA
Vermiculite based catalysts						
V ₂	33.3	270	272	14	9	LA
V ₄	81.1	112	106.5	86	144	WA
		270	292.8	14	15	LA
V ₅	222.9	114	103.1	63	95	WA
		305	298.0	16	14	LA

WA—Pyridine and ammonia desorption from weak acid sites

LA—Pyridine and ammonia desorption from Lewis acid sites

BA—Pyridine and ammonia desorption from Brönsted acid sites

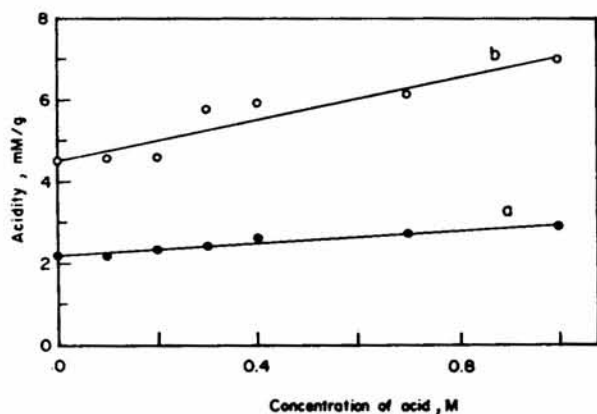


Fig. 1—Plot of acidity of montmorillonite vs concentration of acid [(a) pyridine and (b) ammonia]

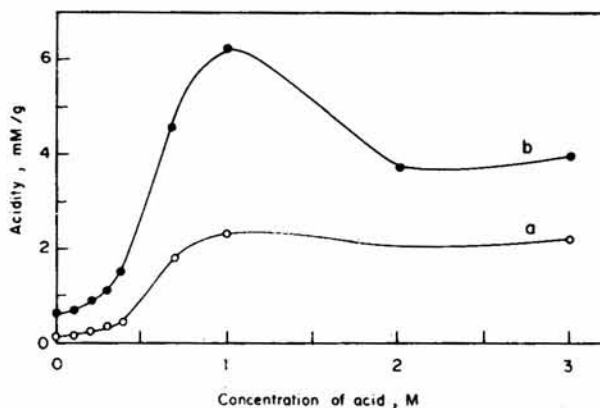


Fig. 2—Plot of acidity of vermiculite vs concentration of acid [(a) pyridine and (b) ammonia]

desorption of ammonia and pyridine is shown in Figs 1 and 2. It is clear from Fig. 1 that for montmorillonite the amounts of ammonia and pyridine adsorbed increase linearly with the increase in [HCl].

In the case of vermiculite (Fig. 2) the amounts

of ammonia and pyridine adsorbed increase gradually with increase in [HCl] used for treatment of the clay and attain maxima around 0.4, 0.7 and 1.0 M [HCl]. Treatment with [HCl] higher than 1.0 M apparently alters porous structure of vermiculite drastically and the acidity decreases.

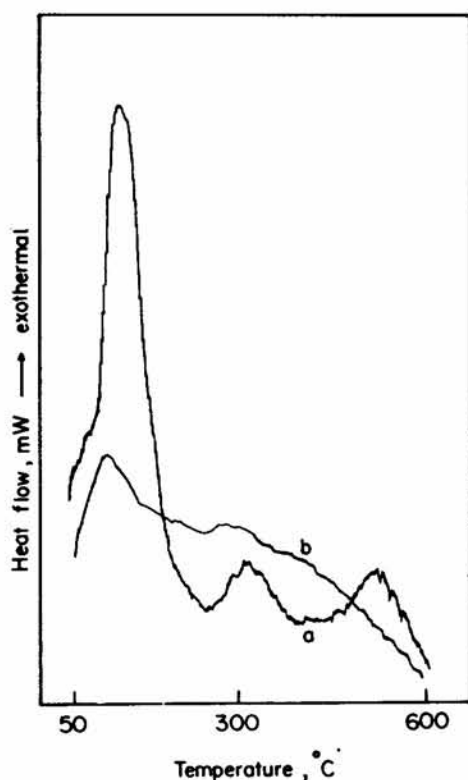


Fig. 3—DSC thermograms of pyridine desorbed from acid activated (a) montmorillonite (M_4) and (b) vermiculite (V_5)

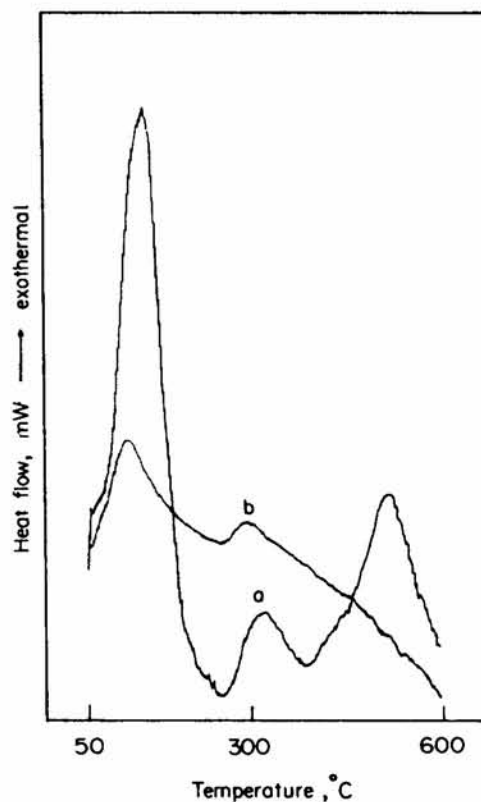


Fig. 4—DSC thermograms of ammonia desorbed from acid activated (a) montmorillonite (M_4) and (b) vermiculite (V_5)

It is also clear that the amount of ammonia adsorbed is about twice the amount of pyridine adsorbed on all the catalysts. This difference should be attributed to the difference in the sizes of the two adsorbate molecules. The entry of bigger pyridine molecules into the fine pores of acid activated samples is comparatively more difficult.

The surface area data of the activated samples are given in Table 1. Acid treatment of clays increases surface area gradually. The increase apparently depends on the concentration of acid but concentration of acids in the range 0.7 M to 3.0 M does not substantially increase the surface area.

Differential scanning calorimetric thermograms of pyridine desorption and ammonia desorption from the representative samples of acid treated montmorillonite (M_4) and vermiculite (V_5) are shown in Figs 3 and 4 respectively. The presence of three different types of acidic sites can be inferred. Heterogeneity of the surface acidity of acid activated montmorillonite sample is more clearly indicated by the appearance of three distinct peaks of pyridine and ammonia as compared to that in vermiculite sample. All the peaks are exothermic indicating that pyridine and ammonia have been chemisorbed on the samples.

The peak temperatures for pyridine have been found to be in the ranges 120-140, 300-313 and 478-525°C for montmorillonite samples and in the ranges 100-107, 272-298 and 438-463°C for vermiculite samples (Fig. 3). The peaks of desorption of ammonia (Fig. 4) also appear more or less in the same temperature ranges for the two types of clays. It is clear from the DSC thermograms that the mode of acid strength distribution is the same on both the clays, but their relative acid densities differ very much from each other.

The individual peak temperatures, the corresponding heats of desorption (ΔH values) of the bases and the assignments of the peaks to different acidic sites for the different activated samples of the two types of clays are given in Table 1.

Pyridine desorption occurs from weakly held sites in the lowest temperature range 120-140°C. It is apparent that the surface hydroxyl groups are not sufficiently acidic enough to protonate pyridine to form pyridinium ion. The pyridine molecules are probably held by these weakest acidic sites through hydrogen bonding^{11,12}. The presence of hydrogen bonded pyridine has also been confirmed by infrared spectral studies.

The peak in the intermediate temperature range 300-313°C has been attributed to the desorption of pyridine from lewis acid sites on montmorillonite samples. The peak temperatures of pyridine desorption of samples M₂, M₄, M₅ and M₆ and their corresponding ΔH values indicate that both the density of lewis acid sites and their strengths increase with increasing concentration of hydrochloric acid (upto 0.4 M). Above this concentration of acid, both the density and strength of lewis acids decrease.

The peak in the higher temperature range 478-525°C has been attributed to the desorption of pyridine from Bronsted acid sites³. The peak temperatures increase and the corresponding ΔH values of the samples (Table 1) decrease suggesting that the Brönsted acid strength increases whereas the Brönsted acid site density decreases with increasing acid concentration.

The desorption of pyridine in the higher temperature range 438-463°C (Fig. 3) and of ammonia (Fig. 4) is not observed as peaks in some thermograms of vermiculite samples (V₅). However, the occurrence of desorption is indicated by broad shoulders. From the DSC data (Table 1) the presence of weak acid sites, lewis acid sites and Brönsted acid sites has been inferred. From the comparison of the peak temperatures of the samples V₂, V₄ and V₅ the strength of lewis acid sites has been found to increase upto V₅. The density of lewis acid sites in these samples almost remains constant on all the catalysts.

The presence of weak, lewis and Brönsted acidic sites is further confirmed by desorption studies of ammonia. The DSC thermogram of ammonia desorption from samples M₄ of acid treated montmorillonite (Fig. 4, thermogram a) shows three distinct peaks.

The DSC thermogram of ammonia desorption from the representative samples of acid treated vermiculite is shown in Fig. 4 (thermogram b). The desorption of ammonia in the higher temperature range is not observed in the thermograms. However, the occurrence of desorption is indicated by a broad shoulder. From the DSC data, the presence of weak acid sites and lewis acid sites has been inferred.

References

- 1 Kojima M, Fletcher J C Q & O'Connor C T, *Appl Catal*, 28 (1986) 169.
- 2 Kijenski J & Baiker A, *Catalysis Today*, 5 (1989) 12.
- 3 Aboul-Gheit A K, *Thermochim Acta*, 132 (1988) 257.
- 4 Matsuda T, Asanuma M & Kikuchi E, *Appl Catal*, 38 (1988) 289.
- 5 Connell G & Dumesic J A, *J Catal*, 105 (1987) 285.
- 6 Borade R B, Adnot A & Kaliaguine S, *J chem Soc Faraday Trans*, 86 (1990) 3949.
- 7 Yan-Fei-Shen, An-Nan Ko & Paul Grange, *Appl Catal*, 67 (1990) 93.
- 8 Kojima M, Rautenbach M W & O'Connor C T, *J Catal*, 112 (1988) 495.
- 9 Aboul-Gheit A K, Hajjaji M A & Summan A M, *Thermochim Acta*, 118 (1987) 9.
- 10 Aboul-Gheit A K, *J Catal*, 113 (1988) 490.
- 11 Connell G & Dumesic J A, *J Catal*, 101 (1986) 103.
- 12 Connell G & Dumesic J A, *J Catal*, 102 (1986) 216.