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EFFECT OF THE EXCHANGE ION ON THE PROPERTIES OF BOEHMITE INTERCALATED MONTMORILLONITE

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Abstract—Boehmite intercalated montmorillonite has been prepared from ion exchanged montmorillonite by boiling an aqueous suspension of the reactants under reflux. The montmorillonite was first exchanged with either Na^+, Ca^{2+} or Ce^{3+} and was then intercalated with a boehmite sol. Various features of the intercalated materials such as specific surface area, extent of intercalation, thermal stability and changes in dielectric properties have been evaluated. The results show that high specific surface area and thermal stability can be obtained when montmorillonite is initially exchanged with Ce^{3+} and subsequently intercalated with the boehmite sol. The results also show that Ce^{3+} exchanged montmorillonite gives enhanced intercalation of boehmite.

Montmorillonite is a smectite aluminosilicate clay in which one octahedral sheet of alumina is sandwiched between two tetrahedral sheets of silica. The interlayer region between the aluminosilicate layers can be expanded by intercalating organic or inorganic compounds of suitable size. Large positively charged hydroxy polycations or sol particles can be intercalated into the layers of smectites and, on dehydroxylation, these can be converted into metal oxide cross-linked smectites or pillared clays.[1,2] The oxide pillars formed between the layers result in high surface areas and permanent micropores, and the materials can be used as petroleum cracking catalysts, as adsorbants and as desiccants.[3-5]

Large surface area and high thermal stability can be achieved by controlling the size and distribution of pillars between the layers. Although less is known about the structure and nature of bonding between the pillars and smectite layers,[6,7] recent studies have shown that a number of preparative parameters, such as exchange cations, pillaring medium, temperature, concentration, dehydration and dehydroxylation procedures,[8-12] influence the ultimate properties of the pillared clays.

Two significant difficulties which are involved in the intercalation reactions are the large volumes of smectite and the long drying periods required after intercalation. Intercalation under reflux[13] and under microwave irradiation are known to reduce the reaction time while maintaining high smectite concentration in the reaction mixture. It is also pertinent to note recent work which has shown that the use of hydroxy metal oxide sols containing nano size dispersions has resulted in pillared clays with larger specific surface areas and hydrothermal stabilities.[8,9]

The isomorphous substitution of ions in the interlayer of montmorillonite can considerably decrease the activation energy of the intercalation process.

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Hence the exchange cation may influence the extent of intercalation and also the arrangement of the metal oxide pillars. Sodium ions have frequently been used as the exchange ions, but a systematic study of the effect of the charge and size of the exchange cation with respect to the intercalating species has not been reported. The present work is an attempt to identify the possible influence of size and charge of exchange cations such as Na^+, Ca^{2+} and Ce^{3+} on the extent of boehmite intercalation in smectites and the nature of the resulting products.

EXPERIMENTAL

Montmorillonite with a cation exchange capacity of 34.4 meq/100 g and a basal spacing of 13.9 Å, containing 23.9% by weight of Al_2O_3, 48.6% SiO_2, 5.58% Fe_2O_3, 2.52% Na_2O, 4.09% MgO and traces of calcium was supplied by M/s Loba India, Bombay. The boehmite sol was prepared from aluminium nitrate by controlled precipitation and peptization.[14] Montmorillonite was fractionated from a suspension to give particles less than 1 μm in size and was ion exchanged with sodium, calcium and cerium by treatment with 0.1 M solutions of NaCl, $CaCl_2$ and $Ce(NO_3)_3 \cdot 6H_2O$ respectively. The mixtures were shaken for 6 h, separated by centrifugation and repeatedly washed with distilled water. Washing was discontinued when no cations could be detected in the washings measured by an atomic absorption technique. The exchanged montmorillonite (10 g) was suspended in double-distilled water (100 cm^3) and treated under reflux with stable boehmite sol containing 0.25 g aluminium per g montmorillonite for 2 h. The mixture was allowed to stand at 30°C for 12 h. The intercalated montmorillonite was separated by centrifugation and washed with double-distilled water to remove excess boehmite sol and dried in air at 60°C for 24 h. The intercalated samples were heated to 500, 800 and 850°C over periods of 4 h at a heating rate of 10°C min^{-1}. The interlayer spacings were calculated from X-ray powder diffraction patterns recorded with a Rigaku D/Max-1C Model 5 X-ray diffractometer using nickel filtered Cu-K_α radiation in the 2θ range 3–8°. Specific surface areas were measured by the nitrogen adsorption BET method using a Micromeritics, Gemini Model 2360 surface area analyser at liquid nitrogen temperature between the relative pressures (P/P_o) 0.05–0.3 after degassing the samples at 300°C for about 3 h. Thermal analyses were performed with a Shimadzu Model 50 H, TGA and DTA at a heating rate of 10°C min^{-1} in flowing nitrogen. The dielectric properties of 10 mm pellets of the samples were measured by a Hewlett–Packard Impedance Analyser Model 4192A LF in the frequency range 50 Hz to 10 MHz.

RESULTS AND DISCUSSION

The X-ray diffraction patterns (XRD) of the boehmite intercalated Na^+, Ca^{2+} and Ce^{3+} exchanged montmorillonite (designated as NaM, CaM and CeM, respectively) are presented in Fig. 1.

The XRD pattern of pure montmorillonite gives an interlayer spacing of 13 Å, which increased to 20.08 Å after intercalation. The interlayer spacings of the intercalated materials decreased to *ca* 17 Å after heat treatment at 800°C, indicating the collapse of the structure. The *d*-spacings decreased by 5.98% (NaM), 11.8% (CaM) and 4.2% (CeM) after heating at 500°C, indicating the differences in the nature of pillared structures and the preferential stability of CeM. The variation in *d*-spacing of the boehmite intercalated clays with thermal behaviour shows that the thermal stability of the material is influenced by the nature of the initial exchange ion. This is supported by the specific surface area measurements (Table 1), which decrease in all the materials after dehydroxylation. However, CeM showed the highest surface areas at all temperatures of dehydroxylation. The data in Table 1 also demonstrate the dependence of surface area on the

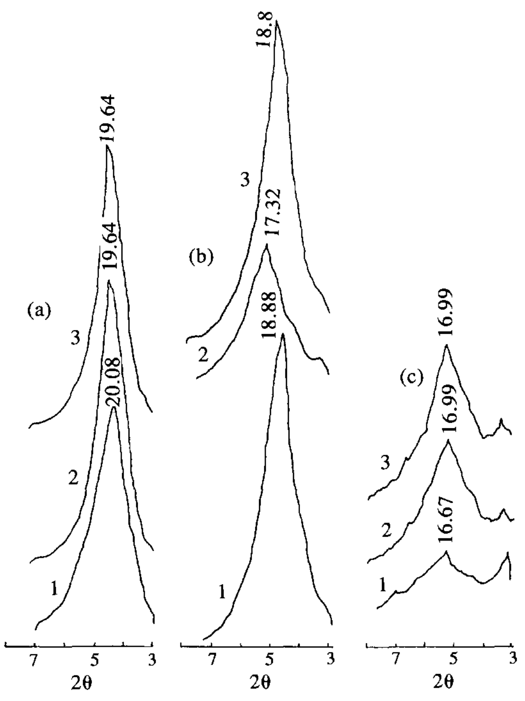

Fig. 1. X-Ray powder diffraction pattern of samples. (1) NaM; (2) CaM; (3) CeM. Temperatures: (a) 32°C; (b) 500°C; (c) 700°C from the (001) plane.

Table 1. Specific surface area of boehmite intercalated montmorillonites heated at temperatures between 300 and 850°C

Samples	Specific surface area (m^2 g^{-1})			
	300°C	500°C	800°C	850°C
Montmorillonite	77	76	8	n.d.[a]
NaM	213	173	92	61
CaM	293	226	145	52
CeM	300	242	190	50

[a] n.d., not determined.

increasing size and charge of the initially exchanged ion.

Analysis of the boehmite intercalated montmorillonite for alumina content showed that NaM, CaM and CeM contained 36.72%, 33.11% and 32.39% alumina, respectively. Hence the number of millimoles of aluminium intercalated per gram of clay is lowest in CeM, which results from an ordered low pillar population[15] between the layers when Ce^{3+} is the exchange cation.

TGA (Fig. 2) showed near identical decomposition patterns for all the boehmite intercalated montmorillonites. The major weight loss below 120°C may be associated with the removal of water. Above this temperature, the weight loss is due to the removal of chemically adsorbed[16] water and structural dehydroxylation. Between 120 and 420°C, the weight loss of NaM is 9.93% compared to 8.63% and 8.52% for CaM and CeM, respectively. Montmorillonite undergoes major dehydroxylation at *ca* 500°C and in the boehmite intercalated montmorillonite this extends to 700°C, consistent with the gradual decrease in the basal spacings observed in the XRD patterns. In the high temperature range, NaM shows a higher weight loss than CaM and CeM, which is consistent with the relatively high drop in *d*-spacing and hence results in reduction of specific surface area. In the case of CeM, the weight loss and decrease in *d*-spacing are less than the others and this explains the higher specific surface area at high temperature.

The DTA curve presented for montmorillonite (Fig. 3a) shows an endotherm at *ca* 516°C which is associated with dehydroxylation. The broad exotherm between 675 and 900°C indicates that the thermal stability is affected by the gradual collapse of the interlayers, which begins at around 675°C. In the intercalated compounds, the endotherm is lowered by about 15°C, possibly due to the lower dehydroxylation temperature of boehmite.[17] The DTA curve for CeM (Fig. 3d) follows that of pure

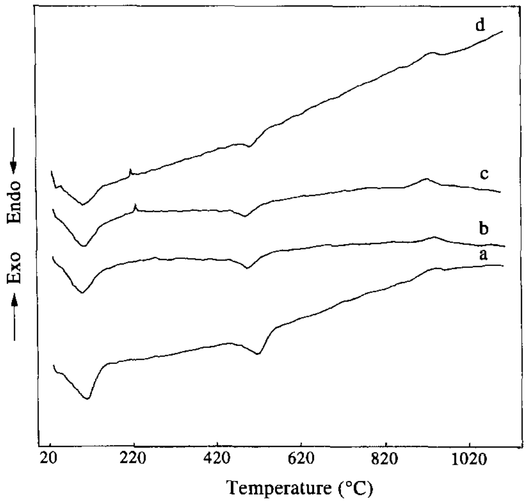

Fig. 3. Differential thermal analysis curves of montmorillonite (a), NaM (b), CaM (c) and CeM (d).

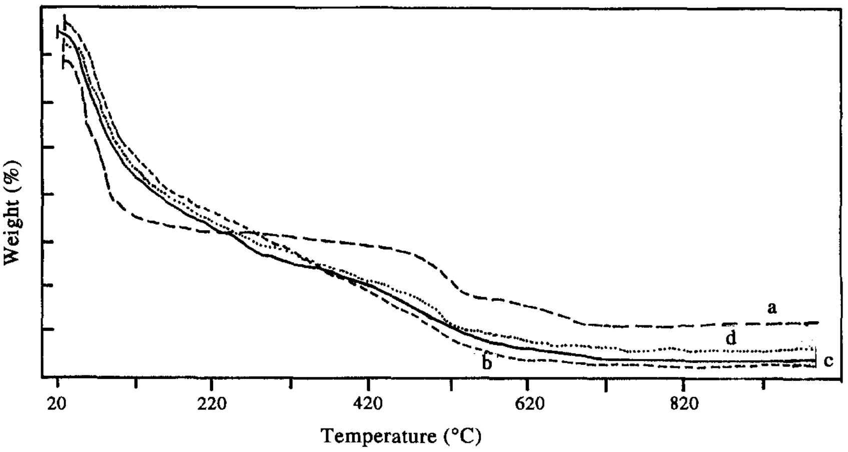

Fig. 2. TGA curves of montmorillonite (a), NaM (b), CaM (c) and CeM (d).

montmorillonite except the broad exothermic change in the range 675–900°C, indicating the stability effect of alumina acting as a prop in CeM and demonstrating the retention of the layered structure of montmorillonite after intercalation. This trend is seen to a lesser extent in NaM and CaM. These observations, together with the specific surface areas of all materials at 800°C, indicate that CeM is more stable than the other boehmite intercalated montmorillonites.

The dielectric properties of montmorillonite after exchange, intercalation and thermal dehydroxylation are shown in Fig. 4. As expected, the dielectric properties of the exchanged montmorillonite are high due to the dipolar effects of hydroxyl groups contributing to space charge polarization. A general decrease in the dielectric constants with increasing frequency is also observed in all samples. The order of dielectric constants in the exchanged montmorillonites is Ca > Ce > Na. This reflects the large number of sodium ions which take part in the exchange reaction. After intercalation, this order is found to be Ca > Na > Ce. However, the dielectric constant values of materials heated at 500°C followed the trend Na > Ce > Ca, although the values for cerium and calcium exchanged samples are similar. These lower values of dielectric constant compared with that of the sodium exchanged one indicate the presence of stable alumina pillars.

The thermal stability of boehmite intercalated montmorillonite is enhanced at temperatures up to 800°C by aluminium oxide acting as a prop. Boehmite intercalated montmorillonite obtained from Ce^{3+} exchanged montmorillonite has a maximum specific surface area of 300 $m^2\,g^{-1}$, which decreases to 190 $m^2\,g^{-1}$ after heating to 800°C. The specific surface area of boehmite intercalated Na^+ exchanged montmorillonite decreases from 213 to 92 $m^2\,g^{-1}$ under identical conditions. The results indicate that the replacement of Ce^{3+} by boehmite gives a better orientation of pillars between the montmorillonite layers.

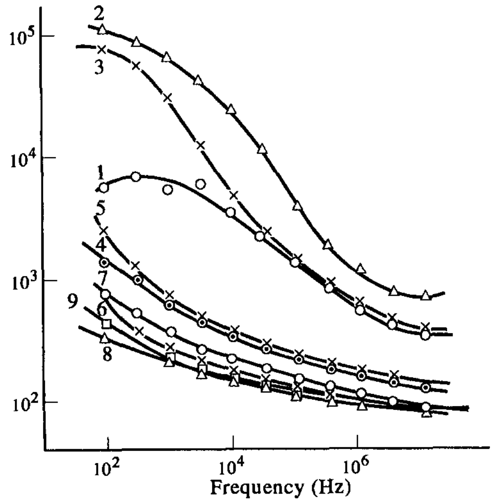

Fig. 4. Dielectric constant (ε) vs frequency curves of : (1) Na-montmorillonite; (2) Ca-montmorillonite; (3) Ce-montmorillonite; (4) NaM; (5) CaM; (6) CeM; (7) NaM (500°C); (8) CaM (500°C); (9) CeM (500°C).

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