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Preparation of acidic forms of montmorillonite clay via solid-state ion-exchange reactions

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A solid-state procedure has been developed which enables Al^{3+} and Fe^{3+} ion-exchanged montmorillonite to be prepared via co-grinding of the clay with the appropriate metal nitrate at room temperature. Pyridine adsorption/infrared spectroscopic studies indicate that montmorillonite treated in this manner contains Brønsted and Lewis acid sites in significant quantities, suggesting that these easily prepared materials may be of interest as acid catalysts.

Keywords: Montmorillonite; clay; acid; ion exchange; solid-state

1. Introduction

Solid-state reactions between zeolitic and other crystalline phases are currently attracting interest as a means of modifying zeolitic catalysts. A number of reports have described the introduction of alkaline earth, rare earth and transition metal cations in A, X, Y, ZSM-5 and mordenite zeolites by means of solid-state ion-exchange reactions [1]. Additionally, solid-state reactions have recently been employed for the formation of organic host–guest complexes [2], the intercalation of polar organic molecules into smectite clay [3,4] and, most remarkably, the formation of organoammonium montmorillonites by room-temperature ion exchange between dehydrated sodium montmorillonite ($MM{-}Na^+$) and solid organoammonium halides [5]:

$$MM{-}Na^+ + NR_4Cl \rightarrow MM{-}NR_4^+ + NaCl. \qquad (1)$$

Intrigued by this report we have investigated whether this methodology can be extended to cations other than organoammonium ions, such as high valent metal ions. For metal ion-exchanged clays, Brønsted acidity arises principally from the dissociation of adsorbed water as described by the equation

$$M(OH_2)_n^{m+} \rightleftharpoons M(OH)(OH_2)_{n-1}^{(m-1)+} + H^+. \qquad (2)$$

In general, therefore, the greater the polarising power of the metal ion, the more Brønsted acidic the clay is [6,7]. For this reason, clays ion-exchanged with metal ions such as Al^{3+} and Fe^{3+} are of interest as solid acids; indeed, a large body of literature exists concerning the acid catalysis of organic reactions using high valent metal ion-exchanged clays [8–13]. However, large scale preparation of ion-exchanged clay minerals in aqueous media is hampered by the tendency of aqueous clay suspensions to form intractable gels at clay concentrations higher than ≈ 20 g/ℓ (necessitating the use of large volumes of water), and the inherent difficulties involved in the filtration of clay suspensions on a large scale. In this regard solid-state ion-exchange reactions would appear to represent an attractive alternative.

2. Experimental

2.1. MATERIALS

Sodium montmorillonite was prepared via purification of bentonite (BDH) using standard procedures [14]. The measured cation exchange capacity (CEC) of the clay was 82 meq/100 g. $Al(NO_3)_3 \cdot 9H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ were obtained from J.T. Baker Chemicals and were used as received. The aqueous preparation of Al^{3+}-montmorillonite was performed according to the method of Adams et al. [15].

2.2. PHYSICAL MEASUREMENTS

Routine X-ray diffraction (XRD) measurements were performed in air with a Philips PW 1820 powder diffractometer using Cu K_α radiation. In situ monitoring of heated samples was accomplished using a Philips 1050 diffractometer equipped with an Anton Paar heating system. For the latter measurements a flow of dry nitrogen was maintained over the samples. For pyridine adsorption/infrared spectroscopic measurements thin self-supporting wafers were prepared using 25–30 mg of vacuum-dried material (10^{-2} mbar, room temperature, 24 h). These were placed in a stainless steel IR cell evacuated to a pressure of $\approx 10^{-6}$ mbar and further dried for 15 min at 120°C. Pyridine was then admitted to the IR cell (15 min at 120°C) and, after evacuation at the same temperature to remove physisorbed pyridine, the IR spectrum was recorded. Concentrations of Brønsted and Lewis acid sites were determined by integration of the 1545 and 1455 cm^{-1} bands of the adsorbed pyridine, respectively.

2.3. PROCEDURE FOR SOLID-STATE ION-EXCHANGE REACTIONS

Typically, oven-dried $MM{-}Na^+$ (2.00 g, 1.64 meq) was mechanically ground (Retsch grinding apparatus employing 1 cm diameter corundum spheres) with

Table 1
Results of ion exchange experiments using sodium montmorillonite

Substrate	Substrate m.p. (°C)	Method [a]	Na salt formed (XRD)
$Al(NO_3)_3 \cdot 9H_2O$	73.5	co-grinding	yes
		sonication	yes
$Fe(NO_3)_3 \cdot 9H_2O$	47.2	co-grinding	yes
		sonication	yes
$AlCl_3$	183 [b]	co-grinding	no
$Al(OEt)_3$	134	co-grinding	no
$Fe(citrate) \cdot 5H_2O$	> 100 [c]	co-grinding	no

[a] Co-grinding refers to co-grinding of reactants; sonication refers to separate grinding of reactants, followed by mixing and sonication.

[b] Sublimes at 178°C.

[c] Decomposes.

1.64 meq of the metal salt for 30 min in air. The product mixture was dried under vacuum (10^{-2} mbar, room temperature, 24 h) and subsequently analysed using X-ray powder diffraction.

3. Results and discussion

Ion-exchange reactions were conducted using sodium montmorillonite (MM–Na^+) as the source clay and various salts of Al(III) and Fe(III), chosen on the basis of their low lattice energy/melting point. The results are summarised in table 1. For both $Al(NO_3)_3 \cdot 9H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$, ion exchange is found to occur by the equation

$$\text{MM–Na}^+ + \tfrac{1}{3}\text{M(NO}_3)_3 \rightarrow \text{MM–}\tfrac{1}{3}\text{M}^{3+} + \text{NaNO}_3 \quad (\text{M} = \text{Al, Fe}), \qquad (3)$$

as evidenced by the presence of a reflection in the diffractograms of the products at $2\theta = 29.4°$, characteristic of $NaNO_3$ (fig. 1a). Furthermore, reflections due to the starting metal nitrate salts are not observed in the product diffractograms, suggesting that a high degree of ion exchange is achieved. Unfortunately, confirmation of this by comparison of bulk and surface Al and Fe concentrations (as determined by X-ray fluorescence spectroscopy and X-ray photoelectron spectroscopy respectively) is not possible due to the high background concentrations of these elements in naturally occurring clays of this type.

In the case of $AlCl_3$, $Al(OEt)_3$ and $Fe(citrate) \cdot 5H_2O$ no ion exchange is observed using the above procedure, presumably as a consequence of the higher lattice energies of these compounds relative to the metal nitrates.

Two alternative methods for performing solid-state ion-exchange reactions were also examined. In the first, the two components (clay + metal nitrate) were

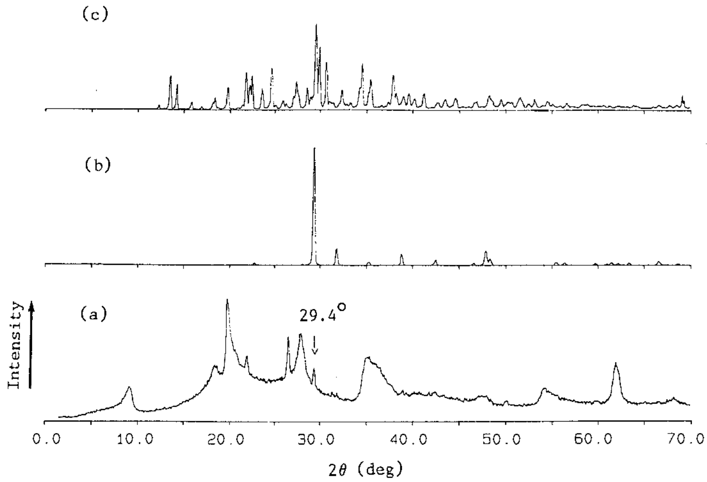

Fig. 1. X-ray powder diffractogram of (a) product of solid-state ion-exchange reaction between MM–Na^+ and $Al(NO_3)_3 \cdot 9H_2O$, (b) $NaNO_3$, and (c) $Al(NO_3)_3 \cdot 9H_2O$.

ground separately, mixed at room temperature (using a Magi-mix) and then subjected to sonication for 30 min. Using this procedure, ion exchange was observed for both the aluminium and iron nitrates, X-ray diffractograms of the products being identical to those obtained via co-grinding of the components. In a variation on this procedure, separately ground MM–Na^+ and $Al(NO_3)_3 \cdot 9H_2O$, after mixing, were heated at 100°C for 2 h. However, in situ monitoring of the reaction mixture by XRD revealed the absence of any peaks due to $NaNO_3$, from which it may be concluded that either no ion exchange occurred or that the $NaNO_3$ crystallites which did form were too small to be detectable using XRD (i.e. < 30 Å).

With regard to the mechanism of the ion-exchange process in these reactions, while grinding of the clay and exchanging species is necessary in order to effect the exchange reaction, particle sizes resulting from such grinding are generally not less than ≈ 1 μm. This requires that macroscopic transport of the exchanging ions occurs across the particle interface. Additionally, it is evident that these reactions are successful only when the reacting species possesses a sufficiently low lattice energy. On the basis of these observations one can speculate that ion exchange occurs as a result of localised warming during the grinding (or sonication) process. If local temperatures approach the melting point of the exchanging species, surface diffusion of the exchanging cations may result. Since these reactions are very exothermic (as exemplified by the large difference in lattice energies between the $NaNO_3$ formed and the starting metal nitrates), it is not unreasonable to suppose that, once initiated, they are self-sustaining. Water present in the hydrated metal nitrates should further assist transport of the ions across the macroscopic distances involved.

Despite recent interest in solid-state ion-exchange reactions as a means of modifying zeolites, very little mechanistic information is available. Two mechanisms appear feasible for such ion-exchange reactions in zeolites and clays [1]: in the first, the crystalline phase (i.e. metal nitrate salt) dissociates to some extent into its constituent ions which then migrate separately, in a manner similar to that of a conventional solution exchange. Alternatively, neutral molecules of the salt may become separated from the larger crystallites and migrate as such to the ion-exchange sites in the clay (or zeolite).

In order to ascertain whether high valent metal ion-exchanged clays prepared by solid-state reactions do indeed possess acidic properties, a pyridine adsorption/IR study was carried out on an Al^{3+}-exchanged clay prepared by the co-grinding procedure. For comparison, a number of other samples were also examined, comprising the MM–Na^+ starting material, Al^{3+}-exchanged montmorillonite prepared by aqueous ion exchange, a sample prepared by separate grinding of MM–Na^+ and $Al(NO_3)_3 \cdot 9H_2O$ followed by mixing and heating (for which the presence of $NaNO_3$ was not detected by XRD), and finally a sample consisting of a non-acidic silica gel physically mixed with $Al(NO_3)_3 \cdot 9H_2O$ (at the same aluminium concentration as the solid-state reaction mixture). Since the Brønsted and Lewis acidity of a clay is in part determined by its water content, samples were first subjected to a pre-drying procedure and then dried in situ under high vacuum (see section 2 above). Approximate concentrations of Brønsted and Lewis acid sites were determined by integration of the 1545 and 1455 cm^{-1} bands of adsorbed pyridine in combination with recently determined integrated molar extinction coefficients [16].

Table 2 summarises the results of the acidity measurements. Striking are the increases in the numbers of Brønsted and Lewis acid sites which result from replacement of the Na^+ ions in MM–Na^+ with Al^{3+}, both via the aqueous

Table 2
Acidity of ion-exchanged montmorillonite as measured by pyridine adsorption/infrared spectroscopy

Clay	[Brønsted sites] (micromol/g) [a]	[Lewis sites] (micromol/g) [a]
MM–Na^+	5 (5)	<15 (<15)
MM–Al^{3+} (aqueous exchange)	95 (160)	35 (60)
MM–Al^{3+} (solid-state exchange with grinding)	45 (65)	50 (75)
MM–$Na^+/Al(NO_3)_3 \cdot 9H_2O$ (solid-state exchange with heating)	50 (65)	15 (20)
silica gel + $Al(NO_3)_3 \cdot 9H_2O$ (physical mixture)	3	3

[a] Figures in parentheses refer to acid site concentrations corrected for the sample path length via referencing to the silica overtones (2000–1600 cm^{-1}) of the clay lattice.

exchange and via the solid-state procedure. Whilst the material prepared by aqueous exchange contains the highest concentration of Brønsted sites, the solid-state material is found to possess the highest concentration of Lewis sites. The fact that the properties of the two clays differ considerably presumably reflects the nature of the cationic aluminium species present, resulting from differing degrees of hydrolysis of the Al^{3+} ions. Significant Brønsted acidity is also detected in the clay sample prepared by mixing and heating (2 h at 100°C) of $MM\text{-}Na^+$ with $Al(NO_3)_3 \cdot 9H_2O$, although the concentration of Lewis sites present is very low. During preparation of this material the presence of NO_2 was detected, arising from the thermal decomposition of the $Al(NO_3)_3 \cdot 9H_2O$. We therefore speculate that Brønsted acidity in this sample arises from the action of HNO_3 (formed in situ) on the clay lattice [8].

In contrast to the Al^{3+}-exchanged clays, the sample of $Al(NO_3)_3 \cdot 9H_2O$ physically mixed with silica gel (previously found to contain no acidic sites) shows minimal acidity, providing strong evidence that Lewis and Brønsted acidity in the solid-state clay sample arises from the presence of aluminium ions located on the ion-exchange sites of the clay.

4. Conclusions and final comments

It has been shown that the sodium form of montmorillonite clay may be ion-exchanged with Al^{3+} and Fe^{3+} ions at room temperature via a solid-state procedure utilising the corresponding nitrate salts. Montmorillonite treated in this manner is found to contain Brønsted and Lewis acid sites in significant quantities, suggesting that these easily prepared materials may be of interest as acid catalysts. Lewis acidic clays are of particular interest as catalysts for Friedel–Crafts acylation and alkylation reactions [17,18].

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