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Delamination Through Sonication for Hydroxy Metal Oxide Sol Intercalation of Montmorillonite

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Abstract: Boehmite intercalated alumina pillared montmorillonite has been prepared from a 10% aqueous suspension of the sodium exchanged montmorillonite in as short a period as 20 min through ultrasonication at 32°C. This technique has resulted in Al-PILC having specific surface area 165 m^2/g and *d*-spacing 17 Å, stable up to 700°C. The delamination of the alumino silicate layers through the sonication technique enhances the extent of intercalation as well as the stability, in addition to reducing considerably the time of reaction practiced at present for the synthesis of pillared montmorillonites. Further, the delamination is effective in suspensions of high solid content. The samples were characterised by chemical analysis, XRD, surface area (BET), TGA, DTA and SEM. The properties were compared to a sample prepared after 30 h of intercalation at 32°C using boehmite species as intercalant.

INTRODUCTION

Thermally stable intercalated alumino silicates are a new class of microporous materials obtained by the irreversible exchange of large inorganic polymers in between the layers of alumino silicates and subsequent dehydroxylation. The metal oxide formed in between the layers acts as prop to open the structure and provide permanent porosity to the material. Such metal oxide cross-linked alumino silicates (smectites) are termed as CLS.[1] A variety of inorganic oxides such as Al_2O_3, Fe_2O_3, TiO_2, Cr_2O_3 and ZrO_2 have been reported as intercalating species.[2–4] The high specific surface area, permanent and controlled porosity and acidity of these materials have shown potential as a catalyst or catalyst support in many organic reactions as well as in petroleum cracking.[5] Pillared smectites have also been identified as excellent adsorbents, dessicants, chemical sensors and solid electrolytes.[6] On the other hand, the low thermal stability of these materials limits their application in high temperature reactions and cracking. Earlier work has reported that the surface area, porosity and thermal stability of these materials depend to a large extent on many factors such as type of pillaring agents, exchange cations, temperature of intercalation reaction and nature of dehydroxylation.[7,8] Usually, the pillaring process consists of first exchanging the smectite with a mono ion, then intercalating with the desired pillaring species from an aqueous medium, followed by drying and dehydroxylation. Recent research work, reported for enhancing thermal stability of such pillared smectites, is on the use of hydrated metal oxide nano size dispersions such as sols.[9] High temperature intercalation results in enhanced thermal stability. Further, different dehydroxylation methods were suggested to increase the thermal stability and porosity of these materials such as microwave drying, freeze drying and super critical drying.[10,11]

The intercalation reactions are usually done in very dilute aqueous suspensions (1%) of mono ion exchanged montmorillonite in order to effect a higher order of delamination. Ultrasonication of a suspension of smectite can be more effective for

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delamination and the present work is on the preparation of alumina pillared montmorillonite under sonication condition, through intercalation of boehmite sol from a 10% suspension of the sodium exchanged montmorillonite.

EXPERIMENTAL

The montmorillonite supplied by Loba-Chem. India, having cation exchange capacity 34 meq/100 g, basal spacing 13·9 Å and specific surface area 77 m^2/g, was taken as the alumino silicate source. The as-received montmorillonite was converted to a sodium-exchanged one by treating with 0·1 M NaCl under constant shaking over a period of 6 h followed by centrifugal separation and repeated washing. A 10% aqueous suspension of the sodium exchanged montmorillonite was mixed with a calculated amount of (0·25 g Al/g clay) stable boehmite sol.[12] The mixture was immediately subjected to ultrasonication using Vibronics-Ultrasonic Processor (Model VPL. P 1, 120 W) Vibronics Pvt. Ltd, Bombay, India, for 2 min at 32°C. Similar batches were prepared with varying times of 5, 10, 15 and 20 min. All the samples were separated by centrifugation and washed repeatedly to remove the excess boehmite sol. The samples were dried in an air oven at 60°C over a period of 24 h . These dried samples were dehydroxylated separately at 500°C and 700°C for about 4 h at a heating rate of 10°/min. The samples were named as SM. 2, 5, 10, 15 and 20. Another boehmite intercalated sample prepared by the usual method, reported elsewhere, represented as UM, has been used for comparison. The basal spacings were calculated from X-ray diffractograms taken in a Rigaku, Japan, diffractometer using nickel filtered CuKα radiation. The specific surface area of the samples was measured by BET technique by the adsorption of nitrogen using Micromeritics (Gemini 2360) surface area analyser after degassing the samples at 300°C for about 3 h. Thermal analyses of the samples were conducted using Shimadzu TG 50 H and DTA 50 H instruments in nitrogen atmosphere at a heating rate of 10°/min. Surface morphology of these materials were taken from a JEOL 35C scanning electron microscope.

RESULTS AND DISCUSSION

The smectites lose their long range structural order in slurries, termed delamination, which is a unique property of the layer structures and is responsible for the house of card structures associated with porosity and high specific surface area.

Table 1. BET specific surface area of samples after heating at different temperatures (in m^2/g)

Sample	300°C	700°C
Montmorillonite	77	45
SM. 2	110	79
SM. 5	140	76
SM. 10	167	160
SM. 15	162	158
SM. 20	180	166
UM	160	118

The effect of delamination can be enhanced through dilution or mechanical agitation. Further, ultrasonic energy can also be used for delamination. In the present investigation, the specific surface area of montmorillonite after sonication increases to 85 m^2/g from the initial value of 77 m^2/g. Table 1 provides the specific surface area of different samples at 300°C and 700°C. The montmorillonite with initial specific surface area of 77 m^2/g increased to 160 m^2/g after intercalating under the usual method (UM), where the time of intercalation was 30 h. The specific surface area was lowest in SM. 2 and highest in SM. 20. The other samples were in between. On dehydroxylation at 700°C, the specific surface area reduction in percentage was about 40–45 in SM. 2 and 5, while in other samples, it was only about 2–10. Sonication leads to a better delamination of the alumino silicate layers, which may enhance the available space in between the silicate layers to hold the boehmite species at the proper reaction sites. This leads to a more ordered cross-linking, and thus imparts microporosity to the material, resulting in high specific surface area values for SM.10, 15 and 20. The low specific surface area and large reduction in the *d*-values at high temperatures in the case of SM. 2 and 5 are due to insufficient delamination. A comparison of the specific surface area of SM. 20 with UM shows that there is a 26% reduction in UM at 700°C, which could be due to the relatively poor pillars in between the layers.

The chemical analysis data of samples with respect to Al_2O_3 content presented in Table 2 show

Table 2. Chemical analysis data

Sample	%Al_2O_3
Montmorillonite	23·6
SM. 2	29.9
SM. 5	31·9
SM. 10	31·9
SM. 15	32·2
SM. 20	31·9
UM	34·2

Table 3. Basal spacing of samples in Angstrom units as a function of temperature

Sample	32°C	500°C	700°C
Montmorillonite	13·90	11·60	9·90
SM. 2	21·04	18·04	17·67
SM. 5	21·08	18·04	16·36
SM. 10	21·04	17·67	16·36
SM. 15	21·88	17·33	16·36
SM. 20	21·08	18·33	16·67
UM	20·08	18·40	16·36

that the amount of Al_2O_3 increases from 23·69% to 31·90% in SM. 20, which indicates the effective intercalation of boehmite in a small interval of reaction time.

The basal spacing of all the samples calculated from the XRD patterns are presented in Table 3. The *d*-spacing of all the samples increases from 13·9 Å to 20–21 Å, which shows the effective intercalation of the hydrous alumina species as evidenced from the Al_2O_3 content. Even though the *d*-spacing decreases on dehydroxylation, it retains a value of 16·67 Å at 700°C, and is quite comparable to that of UM. The reduction in the value of basal spacing was 22% in SM. 2 and 5 while it was only 16% in SM. 20 and 22% in UM. High specific surface area associated with similar *d*-spacing in SM. 20 indicates the possibility of formation of a house of card structure and possible formation of well ordered pillars.

The TGA curves (Fig. 1) of SM. 2 and SM. 20 show a higher volatile content of about 25%. The major decomposition below 400°C is due to the removal of adsorbed and chemically bonded water and that above 400°C is due to the dehydroxylation of the intercalated species . The ordered intercalation in SM. 20 is shown by a distinct decomposition pattern. The DTA curves of SM. 2 and SM. 20 are presented in Fig. 2. The two endothermic peaks obtained at around 100°C and 500°C are characteristic of dehydration and dehydroxylation, respectively. The energy required for the dehydroxylation as calculated from the area under the respective peaks at 500°C for the sample SM. 20 was 115% higher than that for SM. 2 . This indicates the possibility of hydrous alumina intercalant being held in an ordered manner as a result of the delamination by sonication.

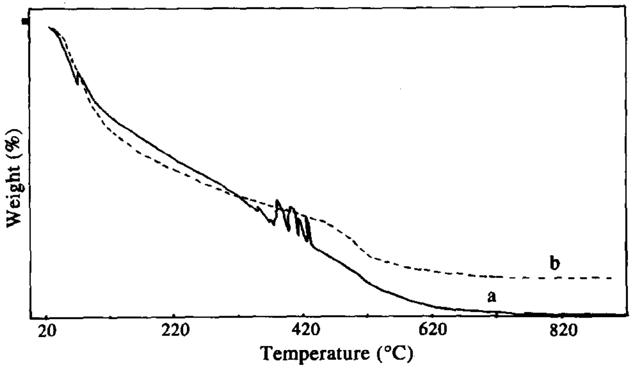

Fig. 1. TGA curves of (a) SM. 2, (b) SM. 20.

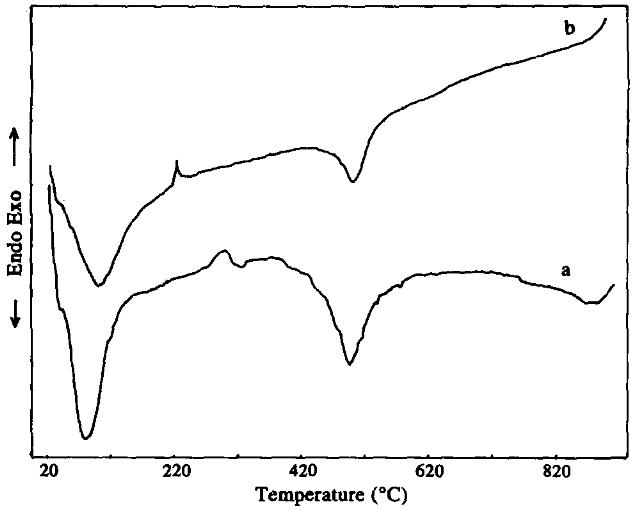

Fig. 2. DTA patterns of (a) SM. 2, (b) SM. 20.

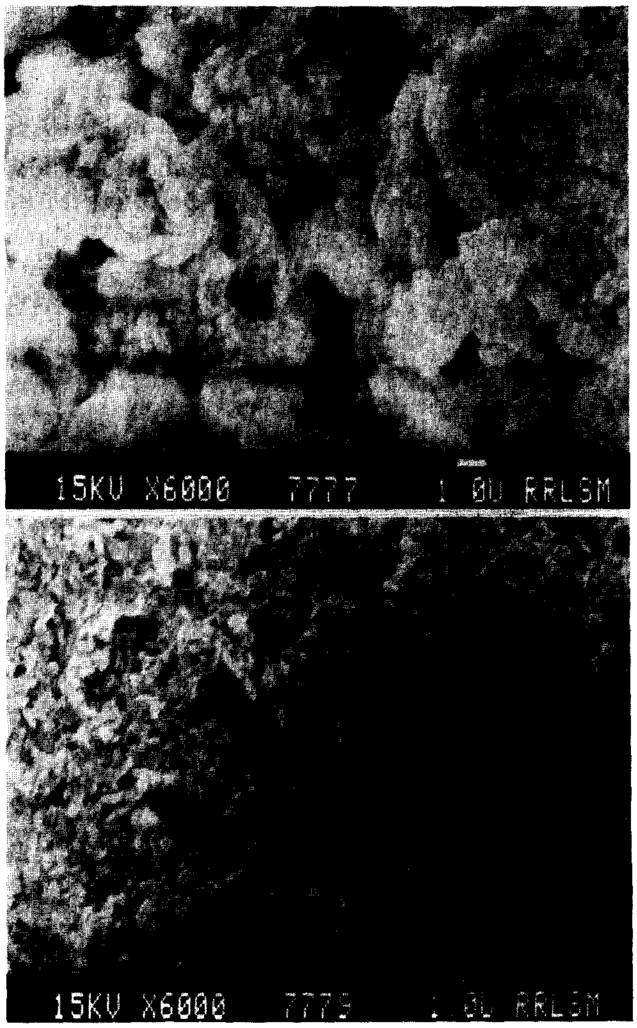

Fig. 3. Scanning electron micrographs of (a) montmorillonite, (b) pillared montmorillonite.

The morphological features of montmorillonite observed under the SEM before and after pillaring (Fig. 3) are distinct. Although the sample before pillaring has formed clusters containing occasionally oriented layered flakes [Fig. 3(a)], the pillared one appears to have clusters containing irregularly shaped particles [Fig 3(b)]. This probably happens because of the change in surface charge of the particles as a result of pillaring, thus losing the property of layer orientation.

CONCLUSION

The intercalation of smectite using boehmite under delaminated conditions has shown a considerable advantage with respect to time of intercalation and the smectite concentration. A suspension containing 10% weight of smectite could be used for intercalation after as little as 20 min of sonication, and yields reasonably high values of *d*-spacing (16·67 Å), specific surface area (165 m^2/g) and thermal stability. This novel technique has shown added advantages over the conventional method where long reaction time and low smectite concentration are employed.

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