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Dependence of concentration of montmorillonite and boehmite sol on the properties of Al-PILC

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Abstract—Al-pillared montmorillonite has been prepared by the intercalation of boehmite (AlOOH) sol by a novel method involving refluxing the montmorillonite–boehmite mixtures. Al/g montmorillonite ratio in the range 0.25 to 20 has been used for the preparation of a variety of pillared compounds. Results indicate that a minimum amount of Al is required (> 5 m mol Al/ g montmorillonite) for obtaining thermally stable pillared montmorillonite. Specific surface area values in the range of 212–180 m^2/g and basal spacing 20.6–16.4 Å after calcination of the intercalated species at 700°C over a period of 4 h was obtained in the various experiments. The possibility of obtaining desired pillar population with different Al/montmorillonite ratio is also highlighted. Further, changing the concentration of montmorillonite suspension in the range 1–40 wt% in the intercalation reactions while keeping the intercalant concentration constant, it was possible to obtain a range of properties with respect to the surface area and thermal stability. The reflux method of intercalation adopted in the present work could achieve specific surface area as high as 146 m^2/g at 700°C in the reaction containing a concentrated suspension of montmorillonite as high as 40 wt%. Samples were characterised by X-ray diffraction, N_2 adsorption BET method and chemical analysis. These results are novel since the earlier studies on intercalation have shown very low solid content in the precursor mixtures. The combined effect of delamination of montmorillonite and intercalation at the interlayers are expected to contribute better properties in reflux method. © 1997 Elsevier Science Ltd

Keywords: montmorillonite; boehmite; intercalation; pillared clay; surface area; thermal stability.

High surface area pillared clays (PILC) obtained by the exchange of interlayer cations in smectite type aluminosilicates by large inorganic polycations [1] have generated great interest in heterogeneous catalysis [2]. A large number of ceramic oxides such as Al_2O_3, ZrO_2, Fe_2O_3, Cr_2O_3, and TiO_2 [3–7] has been successfully incorporated in different types of smectites such as montmorillonite, saponite, beidellite and hectorite. The ability of these materials to retain high surface area at high temperature of calcination determine their role as effective catalyst in many high temperature synthesis reactions, particularly in petroleum cracking [8]. Generally such materials are synthesised by contacting a dilute aqueous suspension of the smectite with a hydrolysed salt solution at room temperature [1]. Much work has been reported to improve the textural properties of these materials by modifying the nature of pillar precursor, preparation and dehydroxylation methods. The nature of distribution of pillars and the pillar density in between the layers determine the ultimate thermal stability of PILC [9]. Preparative environments such as temperature of pillaring, concentration of smectite suspension, extent of intercalated metal oxide and nature of exchange cations [10,11] do influence the distribution of pillars in PILC. Hydroxy metal cations in nanosize colloidal form have been used as pillar precursors for the preparation of Al_2O_3, TiO_2, SiO_2–TiO_2 pillared smectites [12–14]. Boehmite sol has been found to have advantages over the hydroxy oligomeric aluminium solution as intercalant [12] in terms of increased surface area and thermal stability. Earlier we have reported the reflux method for intercalation with boehmite sol for Al-pillared montmorillonite with these advantages [15]. The necessity of an optimum amount of aluminium for an effective intercalation, with respect to increased thermal stability of pillared montmorillonite, has also been indicated recently in the case of hydroxy aluminium solution intercalant [16]. Further, the pillared smectites are most often prepared from a dilute clay suspension of 1–2 wt%, which

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involves large volumes of reactant mixture, making handling difficult. The present work is aimed at understanding these two significant aspects such as the effect of critical concentration of Al/g montmorillonite, where boehmite sol is the intercalant, and also the possibility of using a much higher solid content of montmorillonite when the intercalation is done through the reflux method.

EXPERIMENTAL

Montmorillonite used in this work, supplied by Loba Chem. India, has a cation exchange capacity 80 meq/100 g and contains 48.6 wt% SiO_2, 23.6% Al_2O_3, 5.58% Fe_2O_3, 2.52% Na_2O, 4.09% MgO and traces of calcium. The as-received montmorillonite was converted to a cerium exchanged one by treating it with 0.1 M cerium nitrate solution under constant stirring over a period of 6 h followed by centrifugal separation and repeated washing. Boehmite sol was prepared by the controlled precipitation of a 10% aluminium nitrate solution at 90°C with the addition of 1 : 1 25% NH_4OH solution as already reported elsewhere [17]. The precipitate was washed free of nitrate ion and then peptised with 1 : 1 HNO_3 acid. The concentrated sol was diluted with distilled water and the pH was maintained at 5.4 by adding HNO_3. The transparent sol obtained was aged for 14 days and was estimated for Al_2O_3 content. The stock sol used in the intercalation was 0.3 M with respect to the aluminium concentration.

A calculated amount of boehmite sol containing 0.25 mmol Al/g montmorillonite was mixed with 10 g Ce-montmorillonite suspended in double-distilled water. The total volume of the reaction mixture was maintained at 1 litre by adding required amounts of double distilled water. This reaction mixture was refluxed over a period of 2 h. Similar batches were prepared with varying amounts of boehmite sol in order to get Al/montmorillonite ratios of 0.5, 1.25, 5, 7, 10, 15 and 20 mmol Al/g montmorillonite. All these samples were separated by centrifugation and repeated washing with distilled water, and dried in an oven at 60°C over a period of 12 h. Part of these samples were calcined at 500°C and 700°C in a muffle furnace separately over a period of 4 h. Another set of experiments were carried out with varying concentration of montmorillonite suspension. A calculated amount of boehmite sol containing 10 mmol Al/g montmorillonite was mixed with 1 wt% Ce-montmorillonite suspension. The reaction mixture was refluxed over a period of 2 h. Similar batches were prepared with varying concentration of montmorillonite suspension (wt%) such as 5, 10, 20 and 40 using the same amount of boehmite sol. The samples are named as A, B, C, D, and E according to the wt% of montmorillonite suspension used for intercalation as 1, 5, 10, 20 and 40 respectively. All these samples were separated by centrifugation and washed repeatedly five times with distilled water and dried at 60°C over a period of 12 h followed by calcination at 500°C and 700°C for about 4 h. The X-ray diffraction patterns of the powder samples were taken from a Rigaku D/Max IC, Japan, X-ray diffractometer using nickel filtered CuK_α radiation. Specific surface areas of the samples were measured by the adsorption of N_2 on powder samples by the BET method in a Micromeritics Gemini 2360 (USA) surface area analyser. All samples were degassed at 300°C in flowing nitrogen over a period of 3 h in a separate degassing unit prior to the N_2 adsorption. The surface area values were calculated between the relative pressure (P/P_0) 0.05 to 0.3. Chemical analyses of the samples with respect to the Al_2O_3 content were determined by the ethylene diamine tetra acetic acid (EDTA) complexometric titration method.

RESULTS AND DISCUSSION

Effect of Al/montmorillonite ratio

Table 1 shows the *d*(001) values of the montmorillonite pillared with boehmite at different Al/montmorillonite ratios. The basal spacing of such samples after drying at 60°C shows variation from 16.07 to 20.55 Å. This considerable enhancement compared to initial *d*(001) value 13.9 Å in montmorillonite is due to the intercalation of boehmite species. The *d*-values are in the range of Keggin ion intercalated montmorillonite reported earlier [3]. Further, the presence of Keggin ion in boehmite sol as has been reported earlier [18] was confirmed from ^{27}Al NMR of boehmite sol, in this work, as presented in Fig. 1. The characteristic peak at 63.37 ppm corresponds to tetrahedral aluminium in the Al_{13} species and the intensity of the peak indicates the higher concentration of Al_{13} in the sol. There is a gradual increase in *d*(001) values after intercalation with increasing Al/montmorillonite ratio. However the values are nearly the same between the samples prepared with

Table 1. *d*(001)-spacing (Å) as a function of temperature for the Al-pillared montmorillonite prepared with different Al/montmorillonite ratios

Al/montmorillonite ratio	*d*(001)-spacing of Al-PILC[a]		
	60°C	500°C	700°C
0.25	16.07	15.2	—
0.50	17.67	15.8	—
1.25	17.60	15.6	—
2.50	17.67	16.2	—
5.00	19.91	18.8	16.7
7.00	20.08	18.7	16.7
10.00	20.55	18.9	16.4
20.00	20.55	18.9	16.4

[a] Error minimised to + 0.05%.

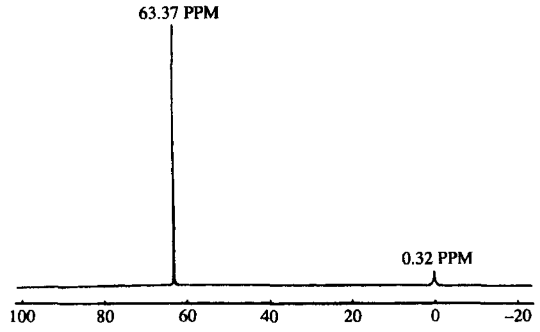

Fig. 1. ^{27}Al MAS NMR of boehmite sol.

different Al/montmorillonite ratio in the range of 5 to 20 mmol Al/g montmorillonite. After calcination of such compounds at 500°C over a period of 4 h the $d(001)$ values decrease in all the cases, as expected. On heating at 700°C, these samples were able to hold a $d(001)$ value of 16.7–16.4 Å, showing the thermal stability of the intercalated complex. The samples with Al/montmorillonite ratios less than 5 mmol/g were characterised by broad diffraction patterns. It appears that the use of intercalant having a ratio of 5 mmol Al/g montmorillonite is favourable for the absolute concentration of Al_{13} species in boehmite sol and this may be large enough to result in well intercalated composition with uniform distribution of pillars [9]. Below this ratio the amount of Al_{13} species present in the sol may not be adequate for a pillar population necessary to hold the interlamellar space open at high temperature. The percentage Al_2O_3 incorporated in the pillared materials was calculated by the difference in % Al_2O_3 between the montmorillonite sample before (23.6 wt%) and after intercalation. The intake of alumina in these samples prepared with different Al/montmorillonite ratios varies from 3.98% to 15.52%. At 300°C the pillared samples have specific surface areas 133 to 212 m^2/g (Table 2). Higher surface area values are obtained with Al/montmorillonite ratio above 2.5 mmol Al/g clay. However, at higher temperature of calcination the surface area increases with the increase of Al/montmorillonite ratio. The highest surface area of 183 m^2/g was obtained for the pillared material prepared by using 20 mmol Al/montmorillonite even after calcination at 700°C. A 3.98% loading of Al_2O_3 in montmorillonite resulted in a material with specific surface area of 94 m^2/g and d-value 15.2 Å at 500°C, whereas 8.82% loading of Al_2O_3 in montmorillonite was able to give a surface area of 129 m^2/g at 700°C. Similarly 12.52% incorporation of Al_2O_3 resulted in a pillared montmorillonite with surface area of 180 m^2/g and d-value 16.7 Å at 700°C. Any further increase in the amount of Al_2O_3 does not show appreciable difference in the surface area values. The variation in the surface area and $d(001)$ spacing with % Al_2O_3 intercalated may be correlated with the pillar population [9] in the interlamellar region of pillared montmorillonite. An optimum amount of Al_2O_3 may be required to have adequate pillar population in order to keep the layers open which leads to high surface area, $d(001)$ spacing and hence higher porosity and thermal stability. This point, however, has been indicated earlier where conventional preparation of Al-PILC used hydrolysed aluminium salt solution as the intercalant [19].

Effect of montmorillonite concentration

Table 3 provides the $d(001)$ values and specific surface area corresponding to boehmite intercalated montmorillonite from different wt% of montmorillonite suspension. The $d(001)$ diffraction peaks become broader with an increase in the concentration of montmorillonite suspension keeping the $d(001)$ values almost identical. Intense and sharp reflection patterns indicate a better homogeneous distribution of pillars in the interlayer region of smectite clays [1]. A broad diffraction pattern is indicated for the lack of homogeneous pillar distribution. Sample A shows sharp intense peak at 21.55 Å. Very large dilution of the clay suspension results in effective delamination of the montmorillonite layers and therefore facilitates the formation of well-defined pillars oriented around

Table 2. Surface area values (m^2/g) of Al-PILC prepared with different Al/montmorillonite ratios

Al/montmorillonite ratio	Surface area (m^2/g) 300°C	500°C	700°C
0.25	133	94	nd
0.50	148	93	nd
1.25	154	95	nd
2.50	183	138	129
5.00	208	195	155
7.00	212	213	164
10.00	201	212	169
15.00	210	203	180
20.00	204	208	183

Table 3. $d(001)$-value and surface area of Al-PILC prepared with different wt% montmorillonite suspensions

Sample	Wt% montmorillonite suspension	$d(001)$-values (Å)^a 60°C	500°C	700°C	Surface area (m^2/g) 500°C	700°C
A	1	21.55	18.41	16.37	268	177
B	5	21.04	18.03	16.99	260	180
C	10	20.55	18.08	16.37	262	175
D	20	20.05	18.03	16.37	235	166
E	40	20.05	18.12	16.36	208	146

^{a}Error minimised to + 0.05%.

the exchange sites homogeneously. The surface area values show considerable variation with difference in the wt% of montmorillonite, especially at higher concentrations. Sample A shows 268 m^2/g at 500°C which decreased to 177 m^2/g after heating to 700°C for 4 h. The lowest surface area values are obtained for sample E. Between sample A and C the surface area values were nearly identical at around 180 m^2/g at 700°C. This may be due to the homogeneous distribution of pillars in these samples. Whereas samples D and E have lower surface area than the other samples, indicating lower thermal stability due to the lack of homogeneity in the distribution of pillars as also evidenced from the broad X-ray diffraction patterns. However, the reasonably higher surface area of 146 m^2/g at 700°C obtained for the sample E shows the effectiveness of the reflux method of pillaring using a concentrated montmorillonite suspension as high as 40 wt%, which was not attempted earlier and is quite impracticable in a conventional synthesis route. The higher temperature involved in the reflux pillaring may be very effective in achieving excellent delamination [20] of montmorillonite layers even in concentrated suspension and thus facilitate the formation of well-ordered pillars leading to higher surface area values. Therefore, the reflux method of pillaring may be an effective and novel technique to prepare pillared montmorillonite with a higher wt% montmorillonite suspension.

CONCLUSION

The amount of Al/g montmorillonite and the concentration of montmorillonite suspension used in the intercalation of Ce-montmorillonite using boehmite sol considerably influence the properties of the resultant PILC through the difference in the pillar density as well as orientation of pillars. A desired pillar population may be obtained with controlled Al/montmorillonite ratio and the existence of a minimum amount of Al required to get a thermally stable material is highlighted. An optimum Al/montmorillonite ratio between 10–15 mmol Al/g montmorillonite was able to provide a pillared material with surface area 212–180 m^2/g and $d(001)$ spacing 20.5–16.4 Å. The homogeneity in the orientation of pillars between the montmorillonite layers can be achieved with a very dilute suspension of the montmorillonite in conventional methods of synthesis already reported. On the other hand, the reflux method employed in this work, for boehmite sol intercalated Al-pillared montmorillonite, has shown the possibility of carrying out the intercalation with concentrated clay suspension as high as 40 wt%. The reason for this advantage has been explained based on the enhanced delamination of the montmorillonite layers in exposing large number of exchange sites.

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