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Intercalation of Al oligomers into Ca^{2+}-montmorillonite using ultrasonics

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Enhanced thermal stability and textural properties can be induced into pillared interlayered clays when aluminium oligomers are intercalated into the Ca^{2+} form of montmorillonite clay using ultrasonics within 20 min at ambient temperature.

Smectite type clays, negatively charged layered silicates with exchangeable charge-balancing cations, upon interaction with water undergo topotactic solid-state reaction. This reversible swelling process occurs due to the hydration of the cations which exist in the van der Waals' region. Thus, expanded adjacent lamellae can be held apart by inserting a robust metal oxide between the layers. This newly formed material, a pillared interlayered clay (PILC) or cross-linked smectite (CLS),[1,2] offers higher surface area, thermal stability and increased acidity. These materials find applications as molecular sieves, adsorbents, desiccants, sensors, solid electrolytes and solid acid catalysts.[3]

The first use of an alumina pillared clay as a cracking catalyst was reported by Vaughan *et al.*,[4] and the catalytic activity was found to be comparable with commercial zeolite catalysts. However, critical evaluation of PILCs against Y-zeolite in cracking of heavier hydrocarbons has shown that pillared clays have lower thermal stability (<1073 K) and hydrothermal stability (the structure collapses around 1023 K with 100% steam). Catalyst deactivation is faster due to the formation of coke, although it yields a higher octane fuel.[5] However, with the search for cheaper catalytic processes to produce higher octane fuel and the recommendation of two-stage steaming below 923 K,[6] PILCs have once again become an alternative to existing commercial catalysts.

Preparation of PILCs is rather complex, since several factors (intercalation of the pillaring species, drying method, thermal treatment for dehydroxylation and calcination) govern the structural, textural and catalytic properties of the final material.[2] Efforts are being made to reduce the preparation time of PILCs, in particular the intercalation process which normally takes 3–20 h. Several advanced techniques such as the use of microwave radiation[7] or ultrasonic agitation[8] have been employed for drying or intercalation. Sivakumar *et al.*[8] reported that upon ultrasonication, the entire intercalation process can be completed within 20 min at ambient temperature. However, intercalation of boehmite sol into Na^{+}-montmorillonite resulted in a delaminated phase with a 'house-of-cards' structure,[9] which has lower microporosity and a wide pore size range compared to the pillared phase. It is known that Na-montmorillonite clay swells macroscopically to a larger extent than the Ca^{2+} form.[10] Because of the neutral behaviour of the silicate layers and associated monovalent ion, the layers become completely dispersed and basal spacing is no longer observed. On the other hand, divalent cation clays disperse in the form of small areas consisting of several stacked layers retaining the basal spacing. Hence, it appears that ultrasonication enhances the delamination of the Na^{+} clay.

Here we report our studies on the effect of ultrasonication time and the concentration of aluminium oligomer on the structural and textural properties of alumina pillared clays.

A commercial Ca^{2+}-montmorillonite [cation exchange capacity (c.e.c.) = 75 mequiv g^{-1}, surface area = 78 $m^2\ g^{-1}$ and chemical analysis (mass%: $SiO_2 = 69.1$, $Al_2O_3 = 18.7$, $Fe_2O_3 = 4.4$, $TiO_2 = 0.37$, $MgO = 4.19$, $CaO = 2.93$, $K_2O = 0.25$ and $Na_2O = 0.07$)] was used. The clay was further purified by sedimentation techniques in order to remove large particles; particles below 2 μm in size were used as the host material. A solution of chlorohydrol powder (Reheis Chemicals, USA) was used for Al intercalation. In a typical experimental procedure, to an aqueous suspension of 5 g of clay and 50 ml water, an aqueous solution of chlorohydrol powder (9.1 g dissolved in 50 ml water) was added to give a ratio of 20 mequiv Al^{3+} (g clay)$^{-1}$. The mixture was immediately subjected to ultrasonication (Sheshin, Japan; operating frequency 50 kHz) for 20 min at ambient temperature (300 K). The product was filtered, washed several times with conductivity water till the filtrate was free from chlorides ($AgNO_3$ test), then dried at room temperature under vacuum. These intercalated materials were heated to 773 K in a programmable furnace, at 10 K min^{-1} and further calcined for 6 h. The sample was designated as 20PILC20. The samples [with 5% clay suspension and 20 mequiv Al^{+3} (g clay)$^{-1}$] prepared with different ultrasonication times, *viz.* 10, 20, 40 and 60 min, are designated as 20PILC10, 20PILC20, 20PILC40 and 20PILC60, respectively, and the samples prepared with different Al^{3+} (g clay)$^{-1}$ ratios, *viz.* 10, 20, 30 and 40 Al^{3+} (g clay)$^{-1}$ under ultrasonication for 20 min are designated as 10PILC20, 20PILC20, 30PILC20, 40PILC20, respectively. For comparison, both Ca^{2+} and Na^{+} forms of the same clay were treated ultrasonically for 20 min. One

Table 1 Effect of ultrasonication time on the final pillared clay

sample	t/min	d_{001}/nm	Al_2O_3 incorporation (mass%)	S_{BET}/$m^2\ g^{-1}$	micropore vol./ml g^{-1}
20PILC10	10	1.83	14.42	119.2	0.04
20PILC20	20	1.9236	16.47	281.5	0.11
20PILC40	40	1.834	19.18	211.6	0.076
20PILC60	60	1.76	23.66	265.5	0.057
PILC-CON		1.806	15.14	174.7	0.065

sample of alumina pillared clay was prepared by the conventional method of treating an Al oligomeric solution with clay at 353 K for 6 h under magnetic stirring; this sample is designated as PILC-CON. All the samples were characterized by powder X-ray diffraction (Rigaku D MaxIII VC, using Ni-filtered Cu-Kα radiation). Chemical analyses of the samples were carried out by XRF (Rigaku 3070 X-ray wavelength dispersive spectrometer), surface area and micropore volume were determined by the N_2 adsorption isotherm method at liquid N_2 temperature using an Omnisorp 100 CX (Coulter) instrument after degassing the sample at 523 K for 6 h.

Acceleration of the diffusion process is known to be enhanced by ultrasonication, through the effects of cavitation, micro-agitation, microstreaming, radiation pressure and changing temperature gradient.[11] Further, an important criterion for successful intercalation is the expansion of the stacked layers along the *c* axis. This in turn is governed by the forces of attraction present between the negatively charged layers and the charge compensating cations present within the van der Waals' region. Though it is known that the Na^+ clay swells to a greater extent in water, it should be noted that the intercalation process commonly employed is through mechanical stirring for elongated periods. When the Na^+ exchanged clay was subjected to ultrasonication (20 min, 300 K), it was delaminated and lamellae in the final product (PILC) could not be achieved. We therefore used the Ca^{2+} form of the clay which retains the layered structure more strongly than the Na^+ form and can withstand the ultrasonic treatment. When Ca^{2+}-montmorillonite was treated ultrasonically (20 min, 300 K) the layered clay structure was observed to be intact with no change in the d_{001}-spacing; this confirms that ultrasonication does not contribute to the clay swelling. In the conventional process, the intercalation is faster and uniform when the clay is in its swollen form. The time to swell the clay can be up to 2 months.[12] In the present ultrasonication method, the swelling process seems to be absent.

Table 1 shows the effect of ultrasonication time on the extent of aluminium incorporation and the observed *d*-spacing value and surface area achieved. After 10 min, the intercalation process is incomplete as indicated by the lower Al_2O_3 incorporation and lower *d*-value (20PILC10). Ultrasonication for 20 min resulted in the optimum *d*-spacing and highest surface area with the optimum micropore volume. However, 20PILC40 shows a reduction in the intensity of the (001) reflection suggesting that partial delamination has occurred, even though it exhibits higher Al_2O_3 incorporation. The XRD pattern of 20PILC60 has no visible (001) reflection, which confirms that the layered structure of the clay has been completely destroyed. Under such conditions, the interactions of pillaring species with the layers will be maximised, which will not impart any constraint to Al incorporation; hence the maximum Al_2O_3 incorporation is observed in 20PILC60. The effect of ultrasonication time on the alumina uptake and d_{001}-spacing is shown in Fig. 1.

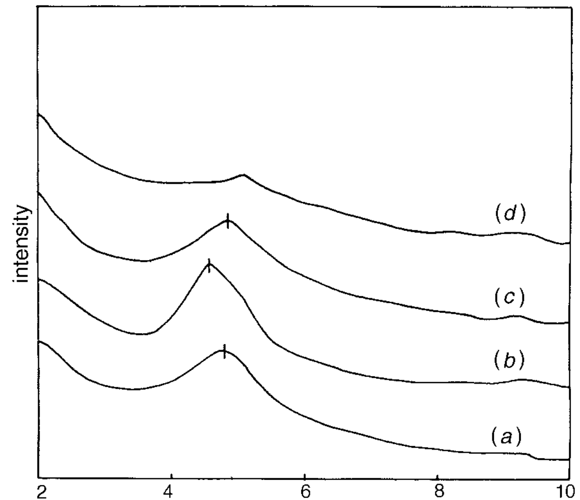

Fig. 1 X-Ray diffractograms of samples prepared with ultrasonication times of (*a*) 10, (*b*) 20, (*c*) 40 and (*d*) 60 min

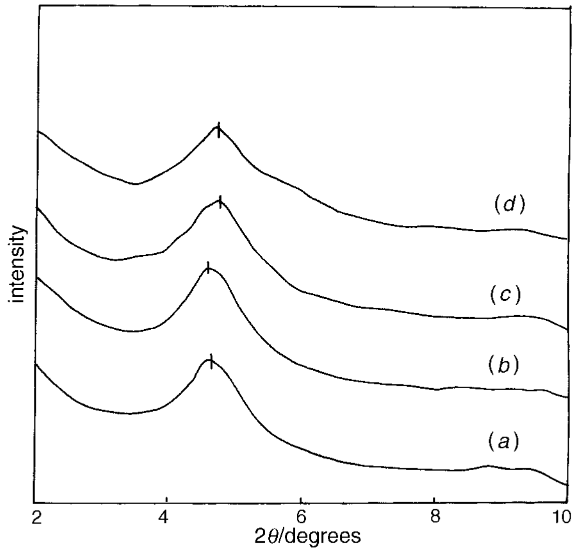

Fig. 2 X-Ray diffractograms of samples prepared by varying Al^{3+} content: (*a*) 10, (*b*) 20, (*c*) 30 and (*d*) 40 mequiv Al^{3+} (g clay)$^{-1}$

In order to study the effect of Ca^{2+}–clay layers, different concentrations of Al oligomers were intercalated. It was believed that if Ca^{2+} holds the clay sheet strongly it will impart diffusional restrictions on the concentrated intercalating species. 20PILC20 showed the maximum *d*-spacing, whereas 10PILC20 shows a lower *d*-value with reduced intensity, probably due to the formation of an insufficient number of pillars. However, the maximum Al_2O_3 insertion due to diluted pillaring species was observed for 10PILC20. On increasing the concentration of pillaring species, samples 30PILC20 and 40PILC20 showed decreasing Al_2O_3 incorporation due to molecular association of the Al oligomers, retarding diffusion into the layers. This is illustrated in the XRD patterns (Table 2 and Fig. 2). In the dilute solution extensive depolymerization occurs due to rehydrolysis of the polycation, a highly

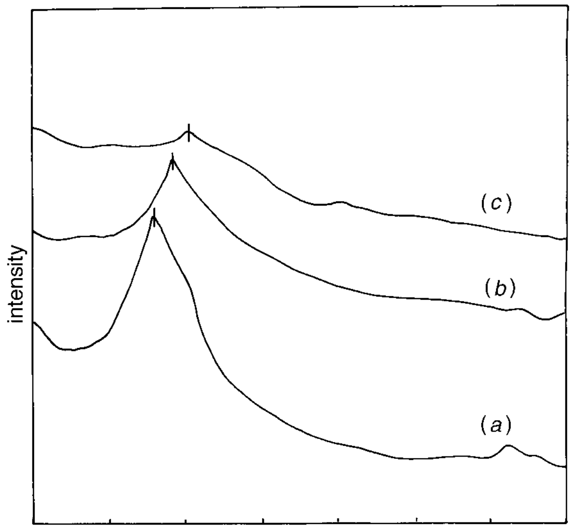

Fig. 3 X-Ray diffractograms of 20PILC20 calcined at different temperatures: (*a*) 773, (*b*) 973 and (*c*) 1173 K

Table 2 Effect of concentration of Al oligomer on the final pillared clay

sample	Al^{3+}/mequiv $(g\ clay)^{-1}$	d_{001}/nm	Al_2O_3 incorporation (mass%)	$S_{BET}/m^2\ g^{-1}$	micropore vol./ml g^{-1}
10PILC20	10	1.895	17.88	170	0.063
20PILC20	20	1.9326	16.47	281	0.11
30PILC20	30	1.874	13.55	233	0.083
40PILC20	40	1.867	10.35	226	0.082

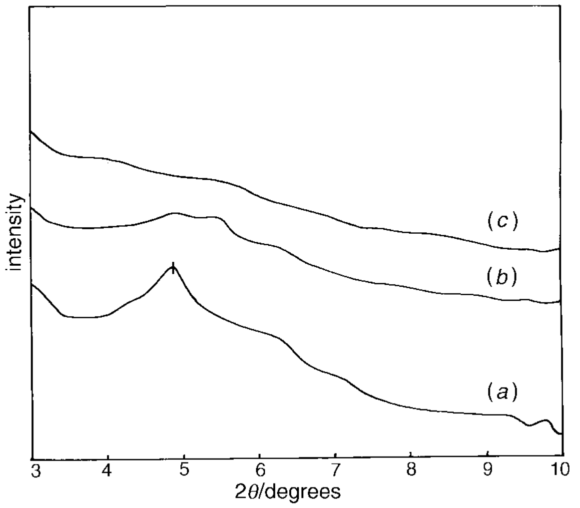

Fig. 4 X-Ray diffractograms of conventionally prepared pillared clays calcined at different temperatures: (*a*) 773, (*b*) 973 and (*c*) 1173 K

concentrated solution is also ineffective because of the very slow hydrolysis. These results are consistent with those of Harris.[13]

Since the sample 20PILC20, prepared by treating 20 mequiv Al^{3+} (g $clay^{-1}$) for 20 min under ultrasonic agitation, showed optimum *d*-spacing and surface area, its thermal stability was compared with that of a conventionally prepared pillared clay (Fig. 3 and 4). In the conventionally prepared pillared clay, the lamellar structure is lost around 973 K, whereas 20PILC20 is stable to 1073 K. The observed higher thermal stability can be explained on the basis of uniform distribution of the pillars within the layers.

In conclusion, the use of ultrasonication can be effective for the preparation of Al-pillared clays using the Ca^{2+} form of montmorillonite. Ultrasonication reduces the time for intercalation without any thermal treatment at elevated temperatures. The process yields a final alumina pillared clay material which upon calcination exhibits properties similar to those of zeolites with large surface area and high thermal stability. It is evident from the study that 20 mequiv $Al^{3+}(g\ clay)^{-1}$ and ultrasonic agitation for 20 min at ambient temperature are the optimal parameters. The process is easy to scale up for commercial applications.

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