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Microwave drying of boehmite sol intercalated smectites

K. G. K. WARRIER*, P. MUKUNDAN, S. K. GHOSH, S. SIVAKUMAR, A. D. DAMODARAN
Regional Research Laboratory (CSIR), Thiruvananthapuram 695 019, India

Monohydroxy aluminium oxide (boehmite) intercalated (cross-linked) smectites (SCLS) have been prepared from an aqueous suspension containing sodium mono-ion-exchanged bentonite (2 wt%) and boehmite (AlOOH) sol at pH 3.5 and at 32 °C. The SCLS has been separated by centrifugation and repeated washing. The intercalated smectite was dried in an oven at 60 °C over a period of 24 h and also in a microwave oven of 2.45 GHz frequency and 600 W power over a range of 3–15 min. Both samples have identical thermal and electrical properties. However, the microwave-dried samples have a distinctly higher surface area of 120 $m^2 g^{-1}$, stable up to 650 °C with a marginal reduction to 116 $m^2 g^{-1}$ compared with 94 $m^2 g^{-1}$ for the oven-dried sample. Similarly there was clear difference in the morphological features of the two samples, the air-dried sample having a close packed structure while the microwave one is delaminated and porous.

1. Introduction

Metal oxide pillared intercalated clays (PILC) or cross-linked smectites (CLS), having an expanded interlayer spacing as a result of intercalation of large molecules [1, 2], have received much recent attraction, because the large-sized molecules consist of hydroxy metal oligomers, which can be dehydroxylated to metal oxide cross-linked smectites or pillared clays. Although the actual mechanism of bonding in such expanded minerals [3] is still not clear, these materials have found prospective uses in heterogeneous catalysis and in petroleum refining [4]. Recent studies have shown that stable hydrous metal oxide sols have been effective as pillaring agents [5] with added advantages with respect to thermal stability [6]. In fact, many preparative and structural features are being investigated in detail in the area of metal oxide pillared clays. The various steps, such as the mono-ion exchange, intercalation, drying and dehydroxylation, have been reported with respect to aluminium oxide and zirconium oxide [7]. However, there are still many preparative parameters, such as smectite concentration [8], drying method [9, 10] and thermal stability, which need further investigation. One of the general difficulties in the synthesis of pillared smectites is the long drying time. Usually, the drying of smectites is done over a long period ranging from 10–30 h. Generally it becomes difficult to delaminate this under dispersion conditions in water, due to the non-slaky nature. Further, due to the highly close packed structure, thermal stability is also lowered. Microwave methods have recently found various applications in drying of ceramics [11] and the present work relates to the possibility of microwave drying of the pillared smectites to result in porous structures of high surface area and thermal stability.

2. Experimental procedure

The bentonite used was supplied by CDH Ltd, India, and all chemicals were of high-purity AR grade. Boehmite sol was prepared from aluminium nitrate by controlled precipitation [12] using ammonium hydroxide, and peptizing using nitric acid of AR grade (Merck, India). The bentonite separated to less than 1 μm fraction was first exchanged with sodium ions using a solution of 1 M NaCl. The sodium-exchanged mono-ionic bentonite (2 wt %) was then suspended in boehmite sol and stirred vigorously for 4–6 h at about 32 °C. The intercalated clay was separated by centrifuging the suspension and washing with water to remove the excess boehmite. The intercalated bentonite was then dried in an oven at 60 °C as usual, and another portion in a microwave oven over different time intervals. The intercalation was judged by X-ray diffraction (XRD; Rigaku, Japan) and the morphological features of the dried samples were examined under the SEM (Jeol 35C). The thermal stability was noted by taking thermogravimetry (TGA) measurements (Dupont, USA). The surface area was measured using the BET method (Micromeritrics 2000, USA). Dielectric measurements were taken using an 4192A LF Impedance Analyser (Hewlett Packard, USA).

3. Results and discussion

Intercalation of mono-ion-exchanged smectites from nano-dispersed hydroxy metal oxide sol has recently

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*Author to whom all correspondence should be addressed.

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emerged, with the added advantage of thermal stability [5, 6]. Monohydroxy aluminium oxide or boehmite is easy to prepare, is sufficiently stable and has a gradual thermal dehydroxylation. Boehmite molecules remain as charged moieties in the sol and are exchanged for the sodium ions in the mono-ion-exchanged smectites, expanding the initial interlayer spacing of 1.3 nm to as high as 1.9 nm, as seen from the XRD patterns presented in Fig. 1. The drying in the air oven, as usually practiced at 60 °C over a period of 24 h, resulted in a total weight loss of about 45 %. Another sample dried in a microwave oven, dried to constant weight at as early as 15 min. The drying curve is given in Fig. 2. It is interesting to note that both the samples dried through the air oven or the microwave oven have nearly the same loss of weight, which is also clear from the thermogravimetric curve presented in Fig. 3. The basic bentonite has two major decomposition peaks one at around 100 °C and the other at 480 °C with a total weight loss of about 12 %. On the other hand, the sample after intercalation is characterized by three peaks above 100 °C in both the oven-dried and microwave-dried samples. In addition, the weight loss curve follows a step-wise thermal dehydroxylation, indicating the identical nature of the sample. The boehmite clusters found at the interlayer space and subsequent gelation are probably the reason for the step-wise decomposition pattern. The total weight loss is also nearly the same. Primarily microwave decomposition is related to the dielectric loss factor and is connected with the free water molecules in the present system. The sol clusters in bonded form in the interlayers are not affected, and this could be the reason for the identical thermal decomposition. However, it appears that this decomposition of the free water has been extremely fast without damaging the intercalated structure of the smectite (Fig. 4).

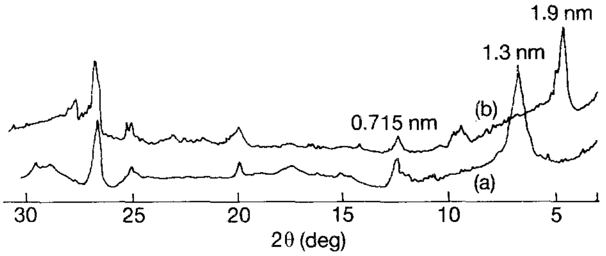

Figure 1 XRD patterns of (a) sodium-saturated and (b) intercalated montmorillonite.

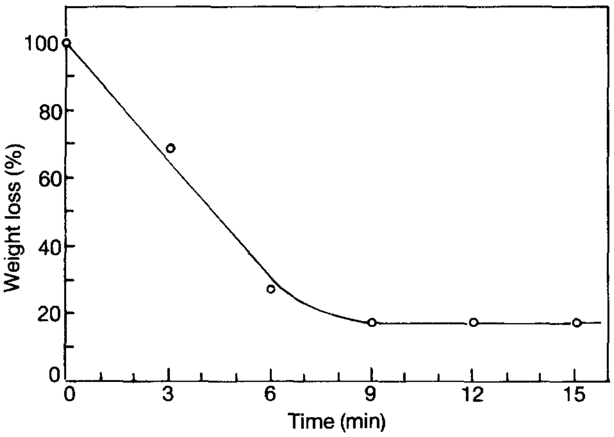

Figure 2 Drying of intercalated montmorillonite in a microwave oven.

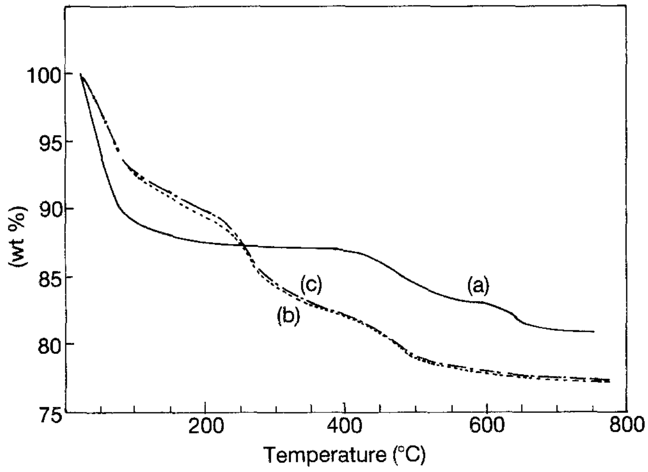

Figure 3 TGA curves of (a) raw, and intercalated (b) oven-dried, (c) microwave-dried montmorillonite.

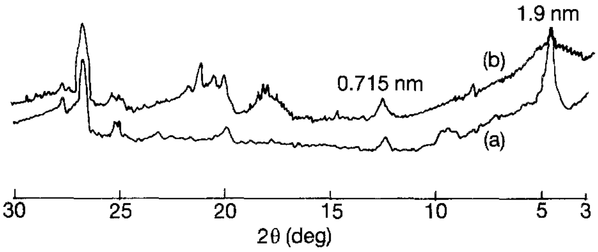

Figure 4 XRD patterns of intercalated bentonite, (a) oven-dried, and (b) microwave-dried.

The specific surface area of the starting bentonite was only 58 $m^2 g^{-1}$, which on intercalation and oven drying became 96 $m^2 g^{-1}$. This value, together with the increase in basal spacing from XRD data, shows the extent of intercalation. The microwave sample, on the other hand, had a specific surface area of 126 $m^2 g^{-1}$, much higher than the oven-dried one. Possibly the interparticle water molecules in bentonite evaporated at a fast rate, leaving micropores in the "house-of-cards" structure. The conventional method of oven drying at about 60 °C is sufficiently slow to allow the evaporation essentially to take place due to capillary action, and the bentonite layers become closely packed one over the other. This is true because the oven-dried pillared bentonite is hard and non-slaky, while the microwave-derived one is fragile and can be easily crushed to a fine powder.

The morphological features of the two samples are also distinctly different (Fig. 5). The oven-dried sample has a close-packed structure consisting of platy alumino silicate layers (Fig. 5a). The microwave-dried one has random packing with a certain amount of interparticle porosity and cracks, making it very fragile.

The dielectric constant measurements on the samples of bentonite before and after intercalation, drying and dehydroxylation, are presented in Fig. 6. In general, all the graphs show the frequency-dependent

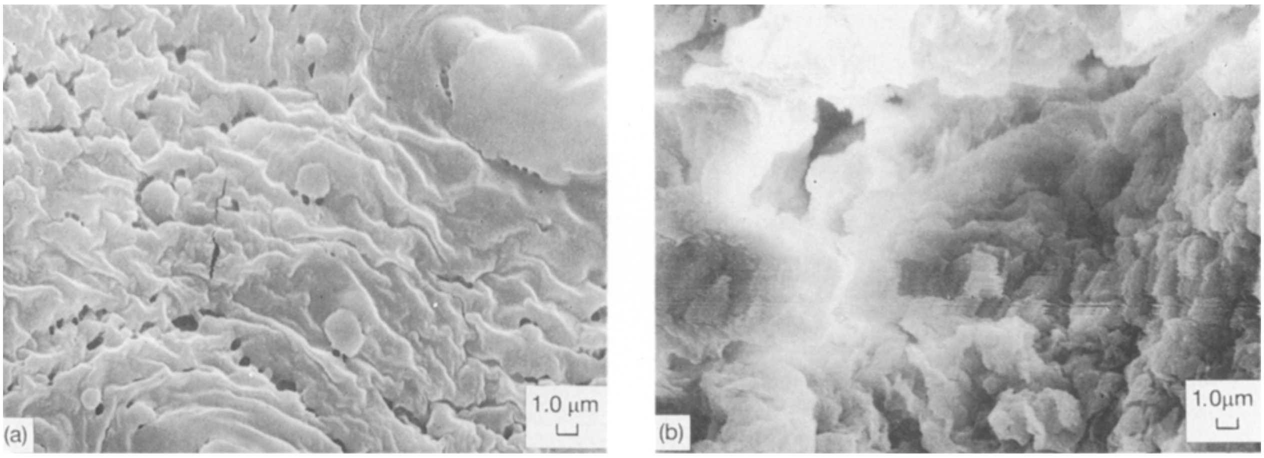

Figure 5 Scanning electron micrographs of (a) oven-dried and (b) microwave-dried pillared clays.

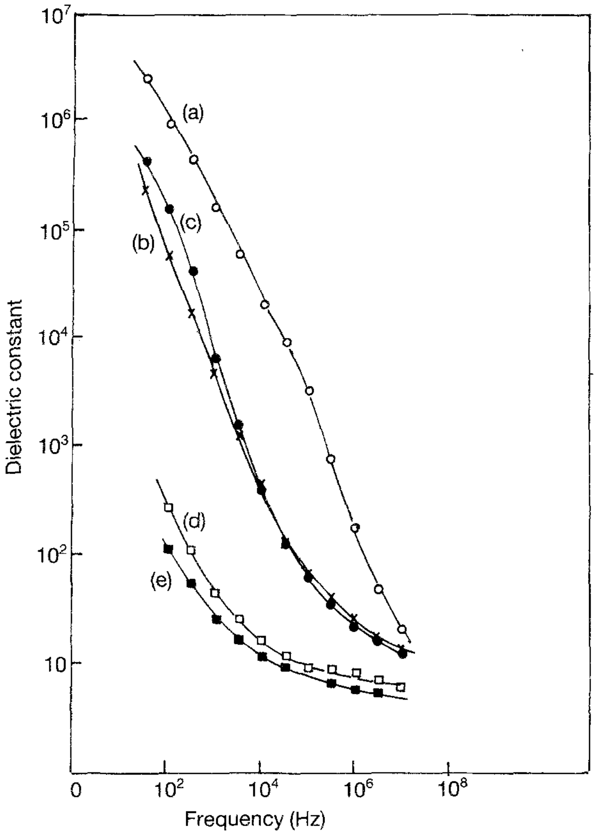

Figure 6 Variation of dielectric constant with frequency. (a) Raw montmorillonite, (b) intercalated oven-dried, (c) intercalated microwave-dried, (d) sample, (e) heated to 650 °C, (c) heated to 650 °C.

behaviour usually expected of these materials. As has been reported elsewhere [13], different types of hydroxyl groups and impurity ions, such as alkali metal ions, would play a significant role in controlling the electrical properties. Dipolar and space-charge polarization due to the presence of free charge carriers, result in a high dielectric constant. The dipolar effect decreases with loss of hydroxyls (on drying), and the space charge polarization effect decreases with increase in frequency. Both these factors are fairly frequency dependent; this appears to be true in the present case. The bentonite before intercalation has hydroxyl groups and exchanged sodium ions (charge carriers). On the other hand, the dried intercalated samples have much lower values because of the bonded intercalated groups and the relative absence of sodium ions. The dielectric constant follows a decreasing trend with increase of frequency as is usual, and graphs corresponding to the dried samples are identical. The dielectric constant decreases in value in the heat-treated samples at 650 °C due to the removal of the major charge carriers. Microwave drying is thus found to be a most interesting method for decreasing the drying time and increasing the specific surface area.

4. Conclusion

Intercalated smectites can be prepared from a boehmite sol medium and microwave drying can be effectively employed to derive high surface area, thermally stable, delaminated sol intercalated (SCLS) smectites. There is considerable reduction in drying time with a significant increase in surface area. However, the thermal decomposition and dielectric properties, as well as the intercalated structure, are identical. The present method, therefore, could be most suitable and novel in order to solve the major difficulties of drying the intercalated smectites without affecting any other properties.

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