Synthesis and characterisation of alumina pillared Texas montmorillonite and determination of the effective Keggin ion charge

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Controlled calcination of Texas montmorillonite has allowed production of a range of materials of cation exchange capacity from ≈ 70 mequiv./100 g dry clay to virtually zero. Pillaring of these with Chlorhydrol precursor solution has then provided a family of materials of pillar density ranging from about one per six unit cells to zero. The analytical technique based on isomorphous metal dilution (IMD) that follows pillaring is validated. The results provide a consistent value for the precursor (Keggin) ion charge, in the conditions normally used, of 3.15 ± 0.10 rather than the "formal" value of 7. An approach to the attainment of pillar densities consistent with the introduction of shape/size selectivity on pillared layered materials is outlined.

Keywords: Montmorillonites; layered materials; pillared layered materials; synthesis; pillar precursor charge; pillar density

1. Introduction

Where a pillar precursor is introduced into a layered host by ion-exchange the number of precursor ions that can enter the inter-lamellar region (per unit weight of host) is fixed by the cation exchange capacity (CEC) of the host and the precursor ion charge. Since calcination of the host provides a route to production in a controlled way of a family of materials differing only in CEC (see, e.g., ref. [1]) we have proposed [2] that this then allows production of a family of pillared materials differing only in pillar density. We described also [2] how detailed chemical analysis of (octahedrally) isomorphously substituted metals such as Mg, which is substantially more reliable than that of Si or Al, then permits calculation of pillar density since the weight of, e.g., Mg per unit weight of host diminishes in linear proportion to the weight of pillars introduced. We designated this approach, isomorphous metal dilution (IMD), and explained how the charge on the precursor ion can then be determined.

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We describe here appropriate experiments involving alumina pillaring of Texas montmorillonite which confirm both propositions.

2. Experimental

The Texas montmorillonite (English China clays) used has been the subject of detailed study in our laboratory on a number of occasions and the stoichiometric formula ascertained [3] as $[Si_8Al_{3.51}Mg_{0.42}Fe(II)_{0.07}]O_{20}(OH)_4$, exactly as found in the present study (see later). The pillar precursor employed was the Keggin ion, normally formulated as $[Al_{13}O_4(OH)_{24+y}(H_2O)_{12-y}]^{(7-y)+}$, derived from the commercial product Chlorhydrol.

Material preparation. 500 g of the montmorillonite was subjected to repeated sedimentation with rejection of top and bottom fractions followed by centrifugation. It was then NH_4^+-exchanged by suspension in M NH_4Cl solution, separated and re-exchanged twice more. The residual solid was washed repeatedly with de-ionized water until chloride free, dried at 60°C in air, ground and then sieved to pass 106 μm. The material was then divided into approximately 50 g lots and the CECs of each lot determined by the micro-Kjeldahl method following water content measurement by TGA [3,4]. The final values taken were the average of a number of measurements, and were reproducible to not worse than 1 mequiv./100 g dry clay. Finally, the separate lots were calcined in a Carbolite muffle furnace for 7 h at an appropriate temperature in the range 50–650°C to achieve charge reduction.

Pillaring of the individual lots was achieved using the most widely used and recommended recipe for Chlorhydrol. 50 g of clay were suspended in 2 dm^3 of de-ionized water while 143 g of Chlorhydrol was dispersed in a further 2 dm^3. The two dispersions were brought to 80°C and held there for 1 h, a procedure accepted to fully depolymerise the Chlorhydrol. The contents of the two containers were then slowly mixed with vigorous stirring at 80°C over a further period of 1 h. The whole was allowed to age overnight and then separated, dried and ground as described earlier. Finally, each sample was, in turn, calcined in a quartz crucible for 20 h at 500°C, at which temperature the pillars are bonded to both sheets.

Chemical analysis. About 0.1 g of a PILC was dissolved in a mixture of 10 ml 40% (v/v) HF and 10 ml of 70% $HClO_4$ in a platinum crucible. After evaporation to dryness, the solid was redissolved in 5 ml of $HClO_4$ and this was then diluted to 50 ml with de-ionized water. For Mg analysis, 2 ml of this solution was further diluted to 50 ml by addition of a La^{3+} (10^4 mg ml^{-1}) releasing agent solution. This reagent was omitted for the Fe analyses. The solutions were then analysed by AAS; the details have been given elsewhere [3,4].

3. Results

The formula weight of the montmorillonite as specified is 720. At the highest CEC encountered, the inter-lamellar NH_4^+ adds only 7, and so can be ignored in the light of the experimental accuracy attainable and the fact that decomposition to liberate NH_3 occurs so readily on heating.

Table 1 lists the experimental data obtained with clays calcined at temperatures between 150 and 650°C. In common with all other work with smectites we observed a fall in CEC of about 5 units on drying up to 150°C. This is generally attributed to removal of external exchange sites, a proposition supported by the virtually exact balance of CEC of the 150°C dried material and the charge deficit calculated from Mg and Fe analysis.

As the montmorillonite formula presented earlier demands, we see that the maximum layer charge found here is 0.49. Further, there is consistency in the Mg/Fe analyses since the ratio [Mg]/[Fe] over the whole range of pillared clays is 6.1 ± 0.1. These results give confidence in the quality of the analytical data and those derived therefrom.

4. Conclusions

The excellent linearity of the relationship between the Mg concentration of the pillared clays and the CEC of the original clay and the essential independence of the calculated Keggin ion charge (Z) of the original CEC provide conclusive evidence of (1) the validity of the isomorphous metal dilution technique and (2) the simpli-

Table 1
Experimental results

Calcination temp (°C)	CEC (mequiv./ 100 g)	Layer charge	Mg (mg ion/ 100 g)	Fe (mg ion/ 100 g)	Formula weight [a]	Pillar density [b]	Z [c]
150	68.5	0.493	50.5	8.3	826	0.161	3.06
200	67.3	0.484	50.8	8.3	821	0.153	3.16
250	63.7	0.459	51.2	8.4	814	0.142	3.23
300	60.1	0.433	51.6	8.6	810	0.136	3.18
350	53.1	0.382	52.5	8.9	794	0.112	3.18
400	31.2	0.22	54.2	8.9	769	0.074	3.04
500	15.2	0.109	56.1	9.3	743	0.035	3.11
659	3.6	0.026	57.5	9.5	725	0.008	3.25

[a] A plot of Mg against CEC is linear giving an intercept of 57.9, hence the calculated formula weight $= (57.9/[Mg]) \times 720$.

[b] The formula weight of the alumina pillar must be close to 660, hence pillar density $= (\text{formula weight} - 720)/660$.

[c] The precursor ion charge is given by $Z = \text{layer charge}/\text{pillar density}$.

city and applicability of the calcination approach to the control of pillar density. Our earlier propositions are thus fully confirmed and a reliable route to the study of the relation between pillar density and the physical and chemical properties of pillared layered materials is opened up.

We pointed out some time ago [5] that alumina pillaring data then available indicated that, in the conditions pertaining to the usual procedures, the Keggin ion charge must be much less than the assumed formal value of 7+. This view is confirmed by our finding of the value $Z = 3.15 \pm 0.10$. Such a value is not surprising given the complexity of the equilibria involved in the hydrolysis system. Alternatively, or perhaps in addition, the precursor ions may contain a range of values of Al. In any circumstances, it is clear that substantially more alumina is introduced into the layered host than a 7+ charged Al_{13} species would allow.

We note that the maximum natural pillar density (MNPD) attainable with this sample of montmorillonite is close to one pillar per six unit cells. The dimensions of the Keggin ion are sufficiently well known to allow the conclusion that, at this sort of density, the inter-pillar separation exceeds the d_{001} spacing of the sheets. Thus, pillaring at this level is most unlikely to introduce significant size/shape selectivity towards intercalation. To achieve this it will be necessary to use precursor ions of very low charge with a host of high CEC. Thus, for example, a host of (internal) CEC of, say, 140 used with a pillar precursor ion of unit charge should provide a pillar density close to unity. Controlled calcination of the host would then allow synthesis of pillared materials covering the whole practicable range of pillar density.

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