

Porous clay heterostructures with enhanced acidity obtained from acid-activated clays

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Porous clay heterostructures (PCHs) with enhanced acidity may be prepared from suitably acid-activated montmorillonite clays; the higher acidity arises from Brønsted acid sites generated by acid treatment of the clay prior to its use as a host for PCH formation.

Over the past decade, extensive research has been undertaken in the synthesis of porous inorganic materials, which may be used as heterogeneous catalysts, adsorbents or as hosts for composite materials. Examples are the synthesis of pillared clays and mesoporous molecular sieves.^{1–3} A recent class of clay based high surface area, porous materials are porous clay heterostructures (PCHs).⁴ In the synthesis of a PCH, the clay is firstly opened up by the introduction of an ionic surfactant (*via* a cation exchange reaction) thus allowing easier access to the interlayer region.⁴ Neutral amine co-surfactant molecules are then intercalated along with silica species, which leads to self-assembly of the silica into a porous network within the interlayer region. This gives an interlayer silica structure similar to that of MCM-41 molecular sieves.^{4,5} The synthesis of PCHs was first reported using a fluorohectorite clay with a high cation exchange capacity (CEC).^{4,6,7} A host clay with a high CEC was considered essential for the formation of PCHs.^{4,6,7} However, more recently PCHs have been successfully synthesised from saponites and montmorillonites.^{8,9} PCHs have been shown to act as solid acid catalysts;⁶ their acidity arises from the clay and also from protons which are released during the silica polymerisation reaction to balance the layer charge of the clay. The acidity of PCHs may be improved *via* post-synthesis grafting of Al⁹ or by using saponite clays with a high (tetrahedrally coordinated) Al content.⁸ Here we explore the possibility of enhancing the acidity of PCHs by using acid-activated clays as hosts for the formation of porous acid-activated clay heterostructures (PAACHs). Since most of the (Brønsted) acid sites on PCHs are associated with the layers of the clay, we have attempted to enhance the acidity of the host matrix by acid treatment prior to PCH formation.

It is known that the number of matrix protons (on clay sheets), not associated with the interlayer cation, may be increased by acid treatment.^{10,11} We have previously synthesised pillared acid-activated clays (PAACs) derived from an acid treated clay matrix and shown that due to the acidic nature of the host matrix, PAACs exhibit significantly different characteristics compared to conventional pillared clays and that they are superior (to conventional pillared clays) in terms of their acidity and catalytic activity for acid catalysed reactions.^{12,13} We show here that high surface area PCH materials with enhanced acidity may be prepared from suitably acid-activated clays. The lower CEC of the acid-activated clay does not seem to affect the formation of a porous clay heterostructure.

The starting raw clay used was a Peruvian montmorillonite with a CEC of 91 meq (100 g)⁻¹, a basal (001) spacing of 15.4 Å and an anhydrous structural (layer) formula: [Si_{7.86}Al_{0.14}]-[Al_{2.84}Fe_{0.30}Mg_{0.86}]O₂₀(OH)₄. The raw clay was acid treated as previously described^{11–13} to yield an acid-activated clay with a CEC of 71 meq (100 g)⁻¹ and a basal spacing of 15.5 Å. We

were careful to ensure that the level of acid treatment was such that the acid-activated clay retained a layered structure and a substantial CEC. PCHs were prepared as follows: the clay (raw or acid-activated) was suspended in water (100 cm³ per g clay) to which 0.5 M cetyltrimethylammonium bromide (CTAB) was added in a two fold excess of the clay CEC. The clay/CTAB suspension was stirred for 24 hours at 50 °C following which the clay was recovered by filtration and washed with deionised water to remove excess CTAB (*i.e.* until pH 7 was reached) and air dried overnight. The CTAB intercalated clay (Q⁺-clay) was then stirred in neutral primary amine (octylamine or decylamine) at room temperature for 20 minutes following which tetraethylorthosilicate (TEOS) was added and the resulting suspension stirred for a further 3 hours. The final synthesis gel mixture had the molar ratio: Q⁺-clay:amine:TEOS of 1:2:12. The precursor PCH was then recovered by filtration, air dried overnight and calcined at 650 °C for 5 hours. The final samples were designated PCH (from raw clay) or PAACH (from acid-activated clay) followed by C8 or C10 in parentheses to denote the use of octylamine or decylamine, *e.g.* PAACH(C8) is derived from acid activated clay using octylamine.

The CTAB solvated Q⁺-clays from both the raw and acid-activated clays had basal spacings of *ca.* 22 Å; an increase in interlayer spacing of 6.5 Å. On intercalation of TEOS the basal spacings increased further to between 35–40 Å and then decreased slightly on calcination. Fig. 1 shows a representative powder XRD pattern obtained for calcined PAACH(C8). It is clear that the interlayer space is greatly expanded and that the layered structure of the clay is retained as indicated by the presence of higher order peaks. It is worth noting that, in the present case, the basal peak for PAACH samples (see Fig. 1) was much more clearly defined compared to that of PCH samples. We however also note that, during calcination, the removal of the organic matter was far quicker for PAACHs samples than for PCH samples. The PCH samples required calcination for 16 hours (at 650 °C) to totally remove the organic matter and obtain an off-white sample while a heating time of 5 hours was sufficient for PAACHs. This may suggest that PAACHs are more reactive (acidic) and therefore more readily catalyse the decomposition and removal of organic

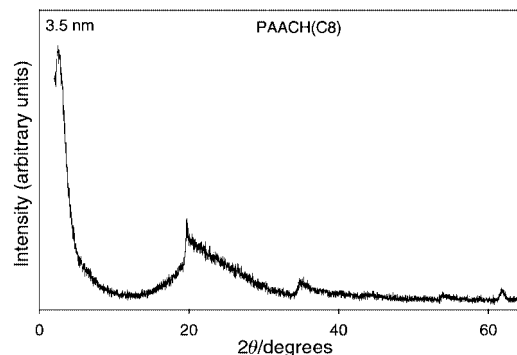


Fig. 1 A representative powder XRD pattern of a porous clay heterostructure (PAACH(C8)) derived from an acid-activated montmorillonite clay.

matter. Another possibility is that the more flexible acid-activated layers of the precursor PAACH allow easier removal (diffusion) of the organic matter; the assumption here is that acid activation disrupts the rigidity of the clay layers by removing some metal ions resulting in layers that are more structurally flexible. The manner and ease with which the organic matter is removed during calcination may therefore contribute to structural differences between PCH and PAACH that are reflected in the intensity of their basal peaks. We however note that calcining the precursor PAACH for 16 instead of 5 hours did not alter the properties of the final PAACH.

Table 1 shows the textural data obtained for PCHs and PAACHs. The PCH samples have surface area of *ca.* 800 m² g⁻¹ while the acid-activated clay derived samples have higher surface area of 915 m² g⁻¹ for PAACH(C8) and 951 m² g⁻¹ for PAACH(C10). All the samples however have comparable pore volumes. The surface areas of the present materials are generally higher than that of fluorohectorite-PCH⁶ but comparable to those of saponite and montmorillonite derived PCHs.^{8,9} The pore volumes observed here (0.71 to 0.82 cm³ g⁻¹) are similar to those of montmorillonite and saponite derived PCHs prepared by Ahenach *et al.*⁹ but higher than that of saponite-PCH reported by Polverejan *et al.*⁸ This is not unexpected since the synthesis method used here was similar to that of Ahenach *et al.*⁹ The chain length of the neutral amine used has no influence on the surface area. However, using a longer chain amine (decylamine, C10) results in a slightly higher pore volume. The N₂ sorption isotherms obtained here for the PCH and PAACH materials are shown in Fig. 2. The isotherms are similar to those previously reported for PCHs.^{8,9} A gradual increase in N₂ adsorption at low to medium partial pressures suggests that the materials possess supermicropores and small mesopores. The hysteresis loops are characteristic of cylindrical pores which are open at both ends, or of spaces between parallel plates, which is consistent with the structure of PCHs.⁴ It is worth noting that the isotherms in Fig. 2 are significantly different from those exhibited by so-called silica bonded montmorillonite, SBM.¹⁴

The textural properties discussed above clearly illustrate that PCHs can be obtained using acid-activated clays as hosts. The acid contents of the present PCHs and PAACHs are given in Table 1. The acid content was determined using thermally programmed desorption of cyclohexylamine (CHA) as previously described.^{15,16} Prior to thermogravimetric analysis, the base-containing samples were heated at 80 °C for 2 hours. The weight loss due to amine desorption from acid sites between 200 and 420 °C was used to quantify the acidity in mmol of CHA, assuming that each base molecule interacts with one Brønsted acid site. The total acid content (desorption between 200 and 420 °C) of PAACH is at least 30% higher than that of PCH. Furthermore the number of medium to strong acid sites (desorption between 300 and 420 °C) for PAACH is almost twice that of PCH. This suggests that the higher acidity in PAACHs is mainly due to an increase in the number of medium to strong acid sites. This is expected to have positive implications for the use of PAACHs as solid acid catalysts. We propose that the higher/stronger acid content of PAACHs is a consequence of the enhanced acidity on the clay sheets (after

Table 1 Textural properties and acidity of porous clay heterostructures derived from raw montmorillonite (PCH) and acid-activated montmorillonite (PAACH) clays

Sample	Surface area/m ² g ⁻¹	Pore volume/cm ³ g ⁻¹	Acidity ^a /mmol CHA g ⁻¹
PCH(C8)	795	0.75	0.54 (0.14)
PCH(C10)	782	0.82	0.56 (0.15)
PAACH(C8)	915	0.71	0.71 (0.25)
PAACH(C10)	951	0.78	0.74 (0.27)

^a Total acid content obtained from weight loss between 200 and 420 °C. Values in parentheses are the amounts of medium to strong acid sites obtained from weight loss between 300 and 420 °C.

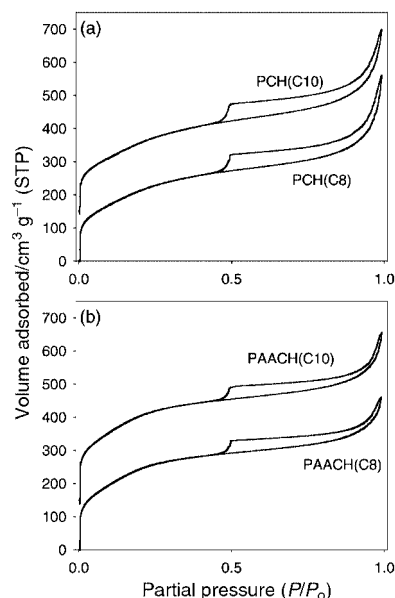


Fig. 2 Nitrogen sorption isotherms of porous clay heterostructures: (a) PCH, derived from a raw montmorillonite clay and (b) PAACH, derived from an acid-activated montmorillonite clay. C8 and C10 denote the use of octylamine or decylamine respectively as co-surfactant. For clarity, the isotherms of PCH(10) and PAACH(10) are offset (y axis) by 150.

acid treatment) used for PAACH formation. It is also possible that some loose Al, present in the host acid-activated clay, is incorporated into the interlayer silica network. We are currently investigating the effect of using aluminosilicate rather than silica sources for PCH formation and anticipate that even higher acidity can be obtained if acid-activated saponites are used as hosts or by combining an acid activated host matrix (saponite or montmorillonite) with an aluminosilicate interlayer structure. The findings reported here open new opportunities for the preparation of acidic PCHs where the acidity can be optimised by varying the nature of the host clay and/or the type of interlayer network.

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