Pillared Acid-activated Clay Catalysts

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Pillared acid-activated clays are shown to be effective solid acid catalysts for Brønsted catalysed processes with activities significantly greater than conventional pillared clays.

Cation-exchanged montmorillonite clays act as efficient catalysts for a variety of organic reactions.[1,2] Their applicability is, however, restricted by a lack of thermal stability and subsequent loss of activity at moderate to high temperatures.[2] This restriction has, to some extent, been circumvented by the strategy of introducing oligomeric hydroxymetal cations into the interlayer region to generate, on calcination, so called pillared clays which are expanded cross-linked materials with metal oxides acting as props (pillars) which bridge the clay layers.[3–5] Chromia, zirconia and in particular alumina pillared clays have attracted interest as solid acid catalysts for petroleum cracking[6–8] and other acid-catalysed reactions.[9–13] The catalytic properties of these pillared clays are believed to be associated with the high surface area generated by pillaring and the acidity introduced by the pillars.[14] Despite their considerable thermal stability, however, pillared clays are less efficient catalysts compared to cation (*e.g.* Al^{3+}) exchanged clays.[2] Post modification of pillared clays (*e.g.* by cation exchange with various cations) has been shown to influence their catalytic properties.[15] However, there is no report to date on the effect of varying the acidity of the clay lattice before pillaring on catalytic activity.

The acidity of a clay matrix can be improved by acid-activation. The acid-activation process increases the number of Brønsted acid sites on the clay due, partly, to the introduction of lattice protons.[16] We have recently reported the preparation of pillared materials derived from an acid-activated clay matrix.[17] These materials combine the high acidity of their non-pillared analogues and enhanced thermal stability, properties which are necessary for medium to high temperature catalysis. We report here the preparation of a pillared acid-activated clay catalyst and preliminary catalytic activity data. Comparisons with other clay materials are made.

A Peruvian montmorillonite (M) supplied by Laporte plc was used as starting material. The anhydrous structural formula of the clay, calculated from elemental analysis, was $Ca_{0.24}[Si_{3.93}Al_{0.07}][Al_{1.42}Fe_{0.15}Mg_{0.43}]O_{10}(OH)_2$. The clay was treated with sulfuric acid to yield an acid-activated montmorillonite (AM); the raw clay M was first slurried with a minimum amount of water, a known amount of sulfuric acid (98%) was added to the slurry and then water so as to give a 20% clay (m/m) mixture. This mixture was maintained at 95 °C for 16 h with constant stirring. At the end of the activation time, a large amount of cold water was added to the mixture to stop the reaction. The solids were recovered by filtration, washed with hot water, air-dried and subsequently ground so as to pass through a 150 μm sieve. The level of activation was such that 23.5% of octahedral ions (Al, Fe, Mg) were leached out.

Clays M and AM were exchanged at 80 °C with the pillaring species (0.06 mol dm^{-3} aluminium chlorhydrate)[17] to obtain the precursor pillared clays PM and PAM respectively. Calcination at 500 °C for 4 h yielded the pillared materials CPM and CPAM respectively. AM was similarly calcined to yield clay CAM. Some of the properties of the calcined materials are given in Table 1.

Despite incorporating less alumina CPAM had higher surface area, pore volume and surface acidity compared to CPM. The cyclohexylamine method used to determine surface acidity is a good indication of the number of available protons capable of interacting with the base. It appears that calcination renders some acid sites in CAM inaccessible (possibly due to the collapse of the clay—see basal spacing, Table 1); pillaring introduces thermal stability thereby ensuring that the sites remain exposed even after calcination at 500 °C.

Two test reactions were performed: The alkylation of benzene by dodec-1-ene and the dehydration of pentan-1-ol. The reactions were carried out in small stainless steel pressure vessels (*ca.* 20 cm^3 capacity); a typical charge for the alkylation reaction was 0.15 g of catalyst and 10 ml of reactant (containing benzene and dodec-1-ene at a molar ratio of 10 : 1)

Table 1 Amount of alumina incorporated, surface area, pore volume and surface acidity of variously treated clays

Clay	Alumina incorporated/ mmol g^{-1}	Surface area/ $m^2\,g^{-1}$	Pore volume/ $cm^3\,g^{-1}$	Surface acidity[a]/ mmol $H^+\,g^{-1}$[b]
CPM	1.50 (18.8)[c]	341	0.20	0.43
CPAM	1.28 (19.3)	364	0.38	0.64
CAM	— (9.8)	249	0.47	0.36

[a] Surface acidity determined using the cyclohexylamine method of Breen.[18] [b] Mmol H^+ per gram of clay at 240 °C. [c] Figures in parentheses are the basal spacing (Å) of the calcined materials.

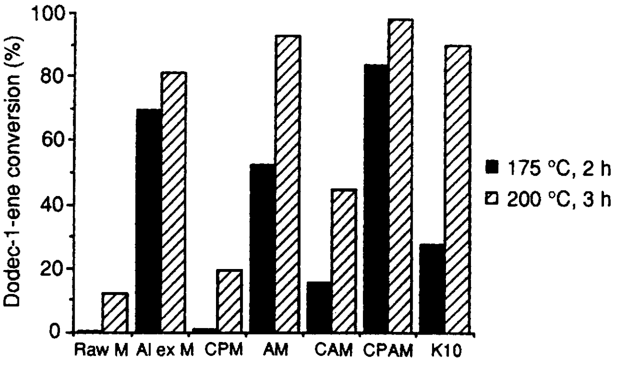

Fig. 1 Activity of clay catalysts for dodec-1-ene alkylation of benzene

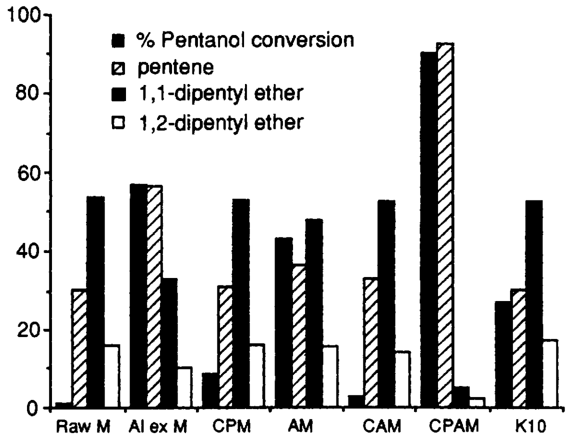

Fig. 2 Activity and selectivity of clay catalysts for pentan-1-ol dehydration

while for the pentan-1-ol dehydration reaction (4 h at 200 °C) the charge was 0.3 g of catalyst and 3.0 ml of reactant. The pressure vessels were heated in an oven and at the end of the reaction time immersed in ice. The products were analysed using gas chromatography. The catalysts were used without prior activation except that the non-calcined catalysts were oven-dried overnight at 60 °C.

The results of the benzene alkylation reaction are summarised in Fig. 1. The main products are mono-alkylated benzenes (*i.e.* a mixture of 2–6-phenyldodecane); no dialkylated products were detected. For the three calcined catalysts the order of activity is CPAM > CAM > CPM. The results indicate that both acid-activation (compare raw M with AM and CAM) and pillaring (compare raw M and CPM) have beneficial effects; when combined, however, the resulting pillared acid-activated material (CPAM) is an excellent catalyst with higher activity than a range of other clay materials *e.g.* Al^{3+} exchanged M and K10 (a commercially available acid-activated montmorillonite).

The results of the pentan-1-ol dehydration reaction are shown in Fig. 2. The general trends in catalytic activity are similar to those observed for the benzene alkylation reaction. For the calcined clays the order is CPAM > CPM > CAM. The main products are the alkene, produced by proton catalysed dehydration, and a mixture of 1,1- and 1,2-dipentyl ether with the 1,1-dipentyl ether in larger amounts. The selectivity of the products is very dependent on the activity of the catalyst. Higher activity is accompanied with higher selectivity to the alkene.

Fig. 3 shows the powder XRD patterns (Cu-Kα radiation) obtained for M, AM and the pillared derivatives after calcination at various temperatures. The basal spacing of AM is 15.1 Å compared to 15.8 Å for M as a result of the exchange of H^+ for Ca^{2+} in the interlayer region of the activated clay AM.[19] However, the XRD pattern of AM (including the presence of higher order *hk* reflections at 2-θ values of 19.8, 34.8 and 53.6 not shown in Fig. 3) indicates that the montmorillonitic structure of the parent clay is preserved despite the acid treatment. The patterns of the pillared clays clearly indicate that there is an expansion of the basal spacing. Furthermore the spacing obtained for the precursor pillared acid-activated clay, PAM (*ca.* 19.6 Å) is similar to that obtained for the precursor pillared clay (PM) indicating that the pillaring species, in both cases, are similar. The intensity of the basal reflection suggests that both the pillared materials are fairly well ordered and possess comparable thermal stability.

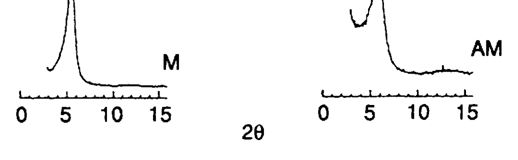

Fig. 3 Powder XRD patterns for clay catalysts before and after pillaring

The chemistry of pillared clays and their properties are complex. However, what is apparent from the results given here is that it is possible to improve the activity of a pillared clay in acid catalysed reactions by varying the acidity of the host matrix prior to pillaring. To date we have no evidence that the activity of a conventional pillared clay cannot be improved by prior acid activation. However, the extent of acid treatment plays a critical role in the properties of the final pillared material. Such activation conditions therefore need to be optimised for each clay matrix.

We are grateful to Laporte plc for financial assistance and to Dr C. Breen for the acidity measurements. Discussions with Dr M. E. Davies and Dr E. Fowles as well as the supply of samples are appreciated.

Received, 25th November 1993; Com. 3/07029H

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