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The catalytic dehydration of pentan-1-ol by alumina pillared Texas montmorillonites of differing pillar density

J.R. Jones and J.H. Purnell

Department of Chemistry, University of Swansea, Singleton Park,
Swansea SA2 8PP, Wales, UK

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Controlled calcination of Texas montmorillonite provides a family of materials differing only in cation exchange capacity (cec). Introduction of alumina pillar precursor ions, followed by calcination at 500°C, then provides a family of pillar densities ranging from near zero to the maximum attainable (ca. 0.16 pillars per unit cell) all, however, having cec below 10 mequiv. / 100 g dry clay and catalytically inactive. Cec and activity are regenerated by exposure to cyclohexylamine. All members of the regenerated family have cec of 36 ± 1 but the proton concentrations vary widely, with a maximum of about 45 mequiv. / 100 g. The reactivity with respect to pentan-1-ol dehydration to alkene or ether varies with pillar density in similar manner to the proton count and these parameters are essentially linearly related so that there is no correlation between reactivity and pillar density per se. The reactivity of the pillared variety is a maximum with that pre-calcined at ca. 200°C but is only about two-thirds that of the unpillared analogue. The pillared variety is highly selective towards alkene formation, whereas the unpillared analogue strongly favours ether formation. It is suggested that future emphasis be given to improving regeneration techniques, and that since unpillared montmorillonite predominantly catalyses addition of water to alkene to yield ethers, the pillared analogue may be more useful in alkanol production.

Keywords: alumina pillars; montmorillonite; catalytic activity; pillar density

1. Introduction

With only few exceptions, calcination of ion-exchanged montmorillonites leads to reduction in the cation exchange capacity (cec). It is thus readily possible, by controlled calcination, to produce a family of materials from a single source sample, differing only in cec. We have taken advantage of this situation [1] to synthesise a family of alumina pillared clays differing only in pillar density since the number of pillar precursor cations that can be introduced by ion exchange is determined by the cec of the host material. We describe here an investigation of the effect of varying alumina pillar density on the catalytic activity of Texas montmorillonite with respect to the proton catalysed dehydration of pentan-1-ol, a reaction we have established over a long period to be a reliable and quantitative indicator of such activity.

2. Experimental and results

2.1. SYNTHESIS AND CHARACTERISATION

A substantial sample of Texas montmorillonite (English China clays) was subjected to a series of sedimentations and centrifugations with substantial material rejection to provide eventually about 100 g of source material. This was divided into ten samples, each then calcined for 7 h at some temperature in the range 50–650°C. A small amount of each was then NH_4^+-exchanged to allow determination of the cec by the micro-Kjeldahl method. The results, which comprehensive study has indicated to be accurate to ± 1 mequiv./100 g dry material, are shown in fig. 1.

Each of the residual samples was then taken into suspension in water, heated to 80°C for 1 h, before addition to a solution of aluminium chlorhydrol (Reheis Co.) made up by adding 225 g of the 50% w/w solution to 2 dm^3 of deionized water and which had also been heated at 80°C for 1 h to induce polymerisation. The combined solutions were then stirred for 1 h at 80°C, allowed to cool overnight, and then carefully removed from the solid. Repeated washing with de-ionized water was carried out with solid recovery by centrifugation. The samples were then dried at room temperature prior to fixing of the pillars by calcination at 500°C for 20 h. At this point, all cec lay in the range 4–8 mequiv/100 g dry clay, and the materials were totally catalytically inactive towards pentan-1-ol.

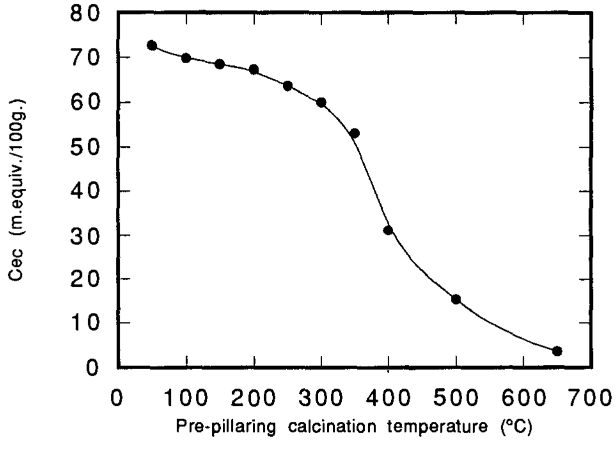

Fig. 1. Change of cec in 7 h calcinations of unpillared Texas montmorillonite at indicated temperatures. Cec of uncalcined material 74 mequiv./100 g dry clay.

As is well known, exposure of such materials to strong base leads to regeneration of cec by extraction of H^+ which have migrated into the sheets during calcination. Each sample was therefore dispersed in cyclohexylamine and refluxed for 2 h before repeated washing and centrifuging and subsequent drying at ca. 50°C. Each was then dispersed in a solution of Al^{3+} to produce a family of Al^{3+}-exchanged pillared Texas montmorillonites which had all been washed to neutrality. Cec determinations revealed that the values for all ten samples lay in the range 36 ± 1 mequiv./100 g dry clay.

The proton content of the samples was then determined by the method we have previously described [2], wherein, after exposure to cyclohexylamine, the material is subjected to TGA analysis. The peaks in the differential thermogram for cyclohexylamine·H^+ and dicyclohexylamine·H^+ (arising due to the deammoniation of cyclohexylamine during the heating process) are readily distinguished and knowing the relevant weight data the number of protons per unit weight of clay can be deduced. In distinct contrast to the cec results, the H^+-contents varied in an unexpected way, with a maximum corresponding to the clays pre-calcined at 200–250°C. The data, along with those for cec are shown in fig. 2.

Finally, the surface areas of the Al^{3+}-exchanged pillared samples were ascertained by use of nitrogen adsorption at 77 K using a Micromeritics Gemini 2360 surface area analyser. The data obtained are illustrated in fig. 3.

2.2. CATALYTIC STUDIES

Reactions were carried out for 1 h at 200°C in stainless steel batch reactors charged with 0.5 g clay with 5 cm^3 of pentan-1-ol. Reaction was quenched by rapid immersion of the reactor in an ice-bath. The reaction mixture was then transferred into a container fitted with a silicone rubber septum through which

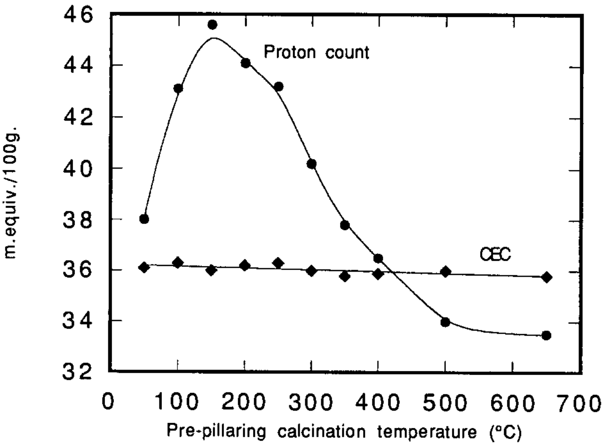

Fig. 2. Comparison of exchangeable ion count (cec) and proton count for alumina pillared materials.

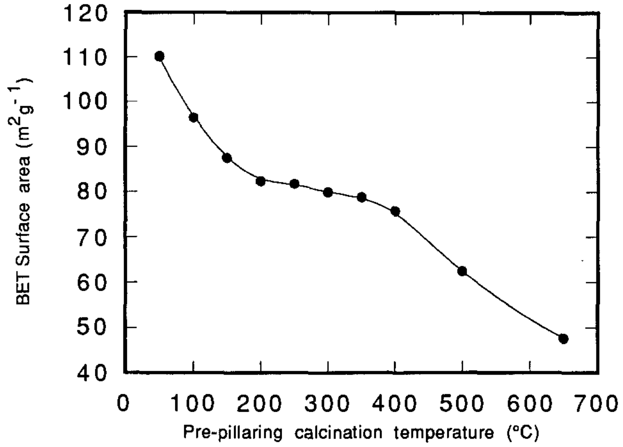

Fig. 3. BET surface areas of alumina pillared materials.

samples could be withdrawn for gas chromatographic analysis. The column employed was a 5 m stainless steel tube (6 mm o.d.) packed with Chromosorb-PAW coated with 10% by weight of Carbowax-20M and was operated at 150°C. This system provided complete resolution of the reactant and the anticipated organic products, pentenes, 1,1-dipentyl ether and 1,2-dipentyl ether: the system was absolutely calibrated for analysis of each component using authentic samples. The experimental data are listed in table 1 and illustrated in fig. 4. The quality of the data may be assessed from the fact that those for residual pentan-1-ol were not calculated from (100% – products) but directly from the calibration plots, yet the reactant + product totals, with only one exception, all exceed 99.9%.

Table 1

Reaction mixture composition (wt%) in 1 h/200°C reaction of pentan-1-ol with Al^{3+}-exchanged pre-calcined alumina pillared Texas montmorillonite

Precalcination temperature (°C)	Pillar density (pillars/unit cell)	Pentan-1-ol	Pentenes	1,1-dipentyl ether	1,2-dipentyl ether
50	0.174	91.4	7.66	0.69	0.09
100	0.169	89.4	9.75	0.68	0.08
150	0.163	88.9	10.3	0.65	0.08
200	0.156	88.3	11.0	0.63	0.08
250	0.146	88.0	11.3	0.65	0.08
300	0.137	91.0	8.19	0.64	0.08
350	0.119	91.3	7.92	0.61	0.09
400	0.077	92.3	6.95	0.60	0.09
500	0.033	93.7	5.51	0.57	0.09
650	0.010	94.8	4.58	0.45	0.07

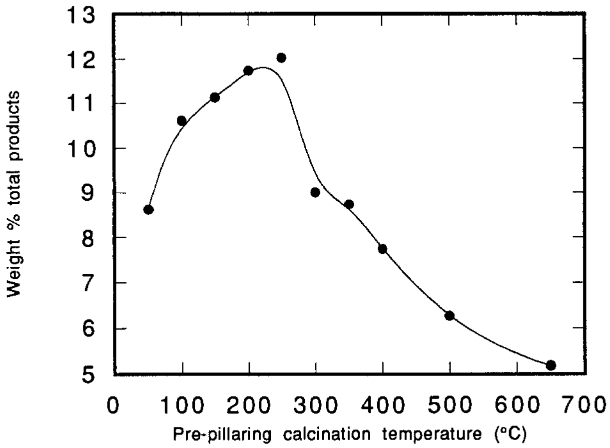

Fig. 4. Weight per cent of products of pentan-1-ol dehydration in reaction mixture after 1 h at 200°C in presence of alumina pillared materials.

3. Discussion

The form of fig. 4 is unexpected and if literally interpreted implies that to the left of the reactivity maximum, over which range reactivity doubles but pillar density hardly changes, there is no correlation, whereas to the right of the maximum there is a near-linear correlation of reactivity with increasing pillar density (see table 1). If there is any correlation it is clearly not a simple one. In contrast, the curve of fig. 4 may be closely superimposed on the H^+-plot of fig. 2 so that, not surprisingly, as fig. 5 shows, there is a very reasonably close to linear correlation of reactivity with proton content over the whole range of pillar densities. In the units of the figures this is represented to within experimental accuracy by the relationship

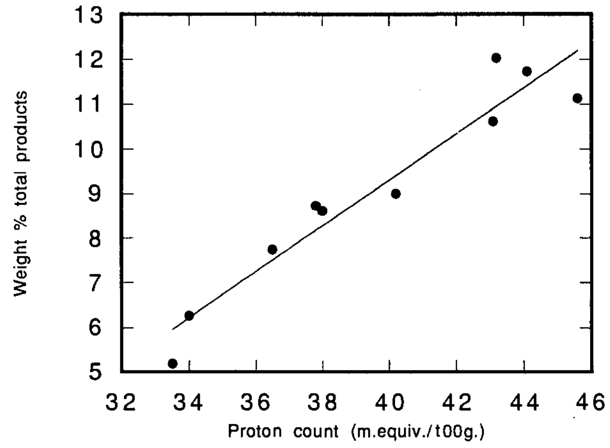

Fig. 5. Correlation of extent of reaction with proton count (cf. figs. 2 and 4).

$$(\%\text{wt products}) = 0.5[H^+] - 11$$

thus, reactivity reaches zero at $[H^+] = 22$ mequiv./100 g dry wt. This is entirely consistent with our findings [3] with the unpillared clay, where reactivity vanishes around $[H^+] = 20$.

What figs. 2 and 5 make clear is that, while a substantial number of protons are unexchangeable by NH_4^+ they are, nevertheless, available for catalytic action. It is tempting to identify these protons as being associated with the pillars. If we do this, the 9–10 mequiv./100 g of unexchangeable H^+ are associated with a pillar density of ca. 0.16 pillars per unit cell, in other words, close to one proton per two pillars. If we now suppose that the active exchangeable protons (36–22) are also pillar located, then we may calculate that, at the most, there is one proton per pillar. The foregoing is, of course, entirely speculative, in particular the second supposition since there must be some mobile protons emanating from the hydrolysis of Al^{3+}. However, the data put an upper limit to the involvement of pillar protons.

Finally, we may seek an explanation of the form of the H^+-content plot. Fig. 3 may well provide the explanation. We see that the surface area of samples pre-calcined at up to 150°C before pillaring fall off dramatically (ca. 33%) and then level out. It is clear that in the pre-calcination stage there is a very considerable reorganisation within the structure, which is manifested by a fall in cec and surface area and an increase in proton availability and which survives pillaring at 500°C. Numerous workers have observed, as we have ourselves, that pre-calcination of unpillared clays at ca. 150–200°C has a beneficial effect on catalytic activity.

The results presented here establish several useful practical points.

(a) For a material of low pillar density such as can be achieved with montmorillonites by alumina pillaring as described the maximum protonic activity is achieved at maximum pillar density.

(b) The active proton content at maximum pillar density is significantly enhanced by pre-calcination at ca. 150°C.

(c) Substantial regeneration of interlamellar proton content following pillaring at 500°C is possible, the value ca. 45 mequiv./100 g dry weight achieved here is, incidentally, the highest reported in the literature so far as we can ascertain.

Finally, we turn to a comparison of the catalytic activity of the pillared and unpillared analogues. Two things emerge. First, the 150°C pre-calcined unpillared clay is almost 50% more active for the pentan-1-ol reactions than the corresponding pillared variety. Second, the selectivity as between ethers and alkane is very different. As table 1 shows, the pillared species yields alkene : ethers in a weight ratio of about 16 : 1 whereas with the unpillared analogue the ratio is close to 1 : 3. We have hazarded the opinion previously [4] in our work on unpillared clays that these alternative reactions may proceed at different protonic sites. The present results are consistent with this view, which allows us some possible latitude in the search for modification of selectivity. For instance, we have shown that the predominant reaction of alkene with water with unpillared montmorillonite is ether rather than alkanol formation. The comparison offered here suggests that the converse would be the case with the pillared analogue, a possibility of some significance.

In conclusion, it is clear that, in the context of the kind of chemical reaction (soft conditions) studied here, a considerable increase in intrinsic catalytic activity of the pillared species is demanded if they are to compete with the unpillared varieties. This points to the need to emphasise more the study in greater depth of the regeneration process rather than further investigation of alumina pillared clay structure.

Acknowledgement

This work constitutes a contribution to the Concerted European Action on pillared, layered materials.

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