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# Catalytic activity of acid-treated montmorillonite in polar and non-polar reaction media

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The catalytic activity of acid-treated montmorillonite clay towards Brønsted acid catalysed reactions is shown to be highly dependent on the degree of acid treatment received by the clay. Using two contrasting model reactions, one involving highly polar reactants and the other a non-polar reactant, the optimum treatment conditions for an acid-treated clay catalyst are also shown to depend upon the type of reaction being catalysed. In addition, the role of exchangeable $Al^{3+}$ ions in generating catalytically active acid sites in the two reactions is investigated.

**Keywords:** Montmorillonite catalyst; acid catalysis; acid-treated clays; acid-activated clays

## 1. Introduction

Acid-treated clays have been used as solid acid catalysts for many years and their activity has been demonstrated in a wide variety of reactions [1–5]. Pressure to replace many traditional homogeneous acid catalysts with environmentally preferable heterogeneous catalysts has recently generated added interest in these materials. Up to now however, the full potential of acid-treated clay catalysts has not always been exploited. Commercially available acid-treated clays, for instance, are rarely optimised for particular catalytic applications and, in general, the often dramatic dependence of catalytic activity on the acid treatment conditions applied to a clay is not widely recognised.

The most frequently used clay in acid catalysis is montmorillonite, a member of the smectite, or swelling, group of clays. Acid treatment of a typical montmorillonite clay results in the leaching of soluble metal ions such as $Al^{3+}$ from the clay lattice and the gradual delamination of the clay structure [6,7]. As acid treatment proceeds, changes in the surface area and the porosity of the clay, and changes in the type and concentration of ions in exchange sites, are all expected to affect catalytic activity. The acid treatment conditions corresponding to maximum

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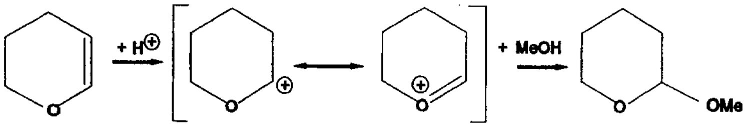
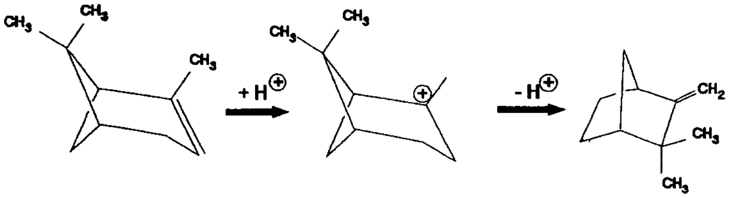
catalytic activity are also expected to depend upon the precise reaction being catalysed; the size and shape of reactant molecules, their basicities and their polarities are all likely to influence the requirements for optimum activity. In the reported study we have used two contrasting Brønsted acid catalysed reactions, one involving highly polar reactants and one involving a non-polar reactant, to illustrate the importance of "tuning" the clay acid treatment conditions for a particular reaction.

There are many examples of clays catalysing reactions between alcohols and alkenes to produce ethers [8,9], and the first test reaction, involving polar reactants, is the acid catalysed addition of 3,4-dihydropyran to methanol. The dihydropyran molecule is protonated to give a stabilised carbocation which reacts with methanol to form tetrahydropyranyl ether as the only product:



The reaction is catalysed under very mild conditions. An important feature of this reaction is that it does not generate water, avoiding the potential reduction in surface acidity which additional water could produce [10].

The second reaction, involving a non-polar, hydrophobic reactant, is the acid catalysed rearrangement of α-pinene to camphene:



In this reaction protonation of the less substituted end of the double bond of α-pinene leads to a delocalised cation in which the cyclobutane ring strain is relieved by the migration of one of the ring bonds to the positive carbon.

The site of surface Brønsted acidity in acid-treated clays is usually thought to be highly polarising hydrated $Al^{3+}$ and similar ions which have been dissolved from the lattice and relocated in cation exchange sites [11,12]. (The alternative, direct exchange of protons or hydronium ions from mineral acid into exchange sites is thought to result in an unstable material, in which protons rapidly become bound to the lattice with the release of soluble lattice ions into exchange sites [2]). To examine the role of exchangeable $Al^{3+}$ ions in surface acidity we have additionally tested the catalytic activities of the series of acid-treated clays after ion exchange with aqueous $Al^{3+}$ solution.

## 2. Experimental

The parent clay used in this study was a Texas montmorillonite supplied by Laporte Industries. The nominal $<2$ μm fraction was collected and acid-treated with 30% $H_2SO_4$ solution at 95°C for times ranging from 5 min to 40 h. The acid-treated clays were washed thoroughly with deionised water until the pH of the washings was 7. The samples were dried in a vacuum oven at 25°C.

For the reaction between methanol and dihydropyran, 50 mg catalyst was activated under $N_2$ at 150°C for 1 h. The catalyst was cooled and added to a mixture of 0.01 mol dihydropyran and 0.3 mol methanol at 0°C. Catalytic activities were determined by measuring the conversion of dihydropyran after 30 min at 0°C with GLC.

For the rearrangement of α-pinene to camphene, 50 mg catalyst was activated in the same way and added to 0.06 mol α-pinene at 80°C. No additional solvent was used. The percentage conversion of α-pinene after 2 h was measured using GLC.

Surface areas of the acid-treated clays were measured by $N_2$ adsorption at 77 K, using a Micromeretics ASAP 2400 porosimeter and application of the BET equation. Cation exchange capacities were determined by monitoring the adsorption of $Co^{2+}$ ions from aqueous $CoSO_4$ solution [13]. Clays were exchanged with $Al^{3+}$ by stirring 1% suspensions of the clays in 1.0 mol $dm^{-3}$ $Al(NO_3)_3$ solution overnight. The ion exchanged clays were filtered, thoroughly washed and dried.

## 3. Results

The effect of acid-treatment on the catalytic activity of the clay towards the reaction between dihydropyran and methanol is shown in fig. 1. The increase in catalytic activity after quite short acid treatment times is dramatic (note the logarithmic time scale). The maximum activity occurs after 15 min treatment, and longer treatments reduce activity. Ion exchange with $Al^{3+}$ can be seen to enhance the activities of clays subject to short acid treatments. Maximum activity amongst $Al^{3+}$ exchanged clays is seen for the parent, untreated montmorillonite. Acid treatment reduces activity and, at treatment times beyond an hour or so, activities differ little from those of the unexchanged clays.

Fig. 2 shows the effect of progressive acid treatment on the catalytic activity of the clay in the rearrangement of α-pinene to camphene. Maximum activity is achieved after 4 h, much longer than the optimum treatment time of the polar reactants. Activity falls with more severe acid treatment. Acid-treated clays subsequently exchanged with $Al^{3+}$ ions show slightly higher activities than the unexchanged clays up to 2 h treatment but beyond this the activity is not significantly altered by $Al^{3+}$ exchange.

The BET surface areas of the clays, determined by $N_2$ adsorption, are shown in

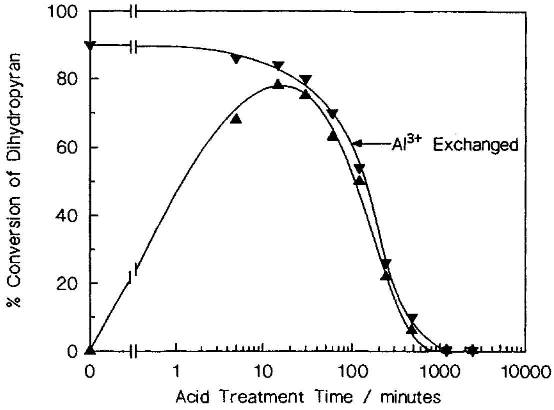


Fig. 1. Effect of acid treatment time on the catalytic activity of acid-treated Texas montmorillonite clay towards the reaction between dihydropyran and methanol. Data is shown for the acid-treated clay as prepared (▲) and following $Al^{3+}$ exchange (▼).

fig. 3. Maximum surface area is reached after 4 h acid treatment. The cation exchange capacities are also shown in fig. 3. As expected, these fall steadily as acid treatment proceeds.

## 4. Discussion

The surface area of the parent montmorillonite measured by $N_2$ adsorption is less than 60 $m^2$ $g^{-1}$. It is important to note that this represents only the external sur-

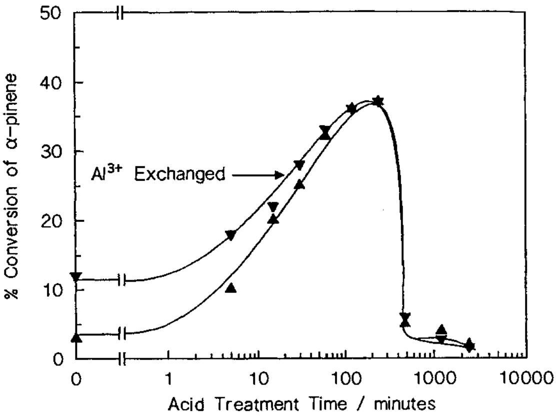


Fig. 2. Effect of acid treatment time on the catalytic activity of acid-treated Texas montmorillonite clay towards the rearrangement of α-pinene to camphene. Data is shown for the acid-treated clay as prepared (▲) and following $Al^{3+}$ ion exchange (▼).

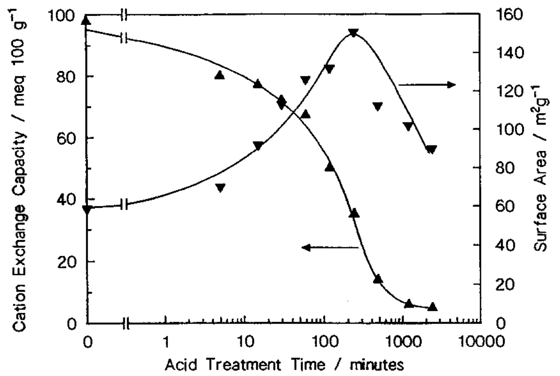


Fig. 3. Effect of acid treatment time on the surface area by $N_2$ adsorption (▼) and the cation exchange capacity (▲) of Texas montmorillonite.

face of the clay platelets since $N_2$, a non-polar adsorbate, does not access the interlaminar regions of the clay. Acid treatment, as indicated above, disrupts the laminar structure of the clay and progressively exposes parts of the interlayer surface to $N_2$ and other non-swelling adsorbates. Thus the surface area accessible to these molecules increases. Eventually, on prolonged acid treatment, the fragile silica structure remaining after dissolution of soluble lattice metal ions gradually collapses, and the surface area falls.

In contrast, the surface area of a montmorillonite clay accessible to a swelling solvent such as water is typically over ten times the external surface area measured by $N_2$ [14]. The surface area accessible to swelling, polar molecules is expected to fall as acid treatment proceeds. Ultimately, at long acid treatment times, when the capacity of the acid-treated clays to swell in polar solvents is lost, the surface areas accessible to polar and non-polar molecules might be expected to converge.

This is borne out by the catalytic profiles in figs. 1 and 2. The activity in the non-polar medium of α-pinene (fig. 2) shows a maximum at 4 h acid treatment, coincident with the maximum surface area by $N_2$ adsorption, whereas maximum activity in methanol/dihydropyran (fig. 1) is shown by the untreated montmorillonite ($Al^{3+}$ exchanged) which provides the largest accessible surface area in the polar, swelling medium.

We conclude that there are three major factors which control the catalytic activity of acid-treated clays. The first is the accessible surface area of the catalyst to the reactant. Our results indicate that, for polar reactants, this is maximum in the untreated montmorillonite, but for non-polar reactant systems the maximum is reached after quite extensive acid treatment.

The second is the number of surface acid sites. Since Brønsted acidity arises from ions in exchange sites, this is expected to fall as acid treatment progresses, in line with the trend in cation exchange capacity seen in fig. 3. For polar reactants, where most or all acid sites are accessible, maximum activity coincides with the maximum abundance of acid sites and falls with the cation exchange capacity. In the non-polar system, only those acid sites on external, accessible surfaces contribute to catalytic activity. Since the fraction of the total exchange sites on these external surfaces depends on the external surface area (measured by $N_2$ adsorption), catalytic activity is controlled, in the early stages of acid treatment, by the competing factors of falling overall exchange capacity and increasing $N_2$ surface area.

The third factor is the strength of the acid sites. Although many structural and other features of the catalyst affect the strength of these sites, it is clear from these results that $Al^{3+}$ ions in exchange sites are necessary for high acidity. Comparing the catalytic activities of $Al^{3+}$ exchanged acid-treated clays with the unexchanged acid-treated clays in figs. 1 and 2, for treatment times of 2 h or more there is little difference in activity between the two, but on shorter treatments the $Al^{3+}$ exchanged clays are significantly more active. The convergence of the catalytic activities of $Al^{3+}$ exchanged and unexchanged clays at acid treatment times beyond 2 h suggests that only after acid treatment of this severity are all exchange sites in the clay occupied by $Al^{3+}$ ions leached from the lattice. In the earlier stages of acid treatment exchange sites may be occupied by the original $Ca^{2+}$ ions, or possibly $H^+$ ions from the $H_2SO_4$. These ions, or combinations of them with some $Al^{3+}$, are clearly less acidic and less catalytically active than complete occupancy of exchange sites by $Al^{3+}$ ions.

In summary, through the use of two test reactions, we have shown that the catalytic activity of acid-treated clays can be carefully optimised for specific reactions. Changes in the surface area, the cation exchange capacity and the nature of the exchangeable cation influence activity in different ways, depending on the reactant system. If optimum activity is to be achieved for clay-based catalysts the balance between these properties must be considered.

## Acknowledgement

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