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THE INFLUENCE OF EXCHANGEABLE ALUMINIUM ION CONCENTRATION AND OF LAYER CHARGE ON THE CATALYTIC ACTIVITY OF MONTMORILLONITE CLAYS

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The catalytic activities, in two proton-catalysed reactions, of two series of montmorillonite clays prepared from a common starting material have been determined. Both series covered a range of interlamellar Al^{3+} concentrations $[Al^{3+}]$ but one had a constant and the other covered a range of layer charge. In each case two thresholds were observed: an upper value of $[Al^{3+}]$ beyond which no further enchancement in activity is observed; a lower value at ca. 20 meq/100 g dried clay, at which activity ceases. The upper threshold is considerably higher for the clays of constant layer charge than for those encompassing a range of charge. The latter are, however, more active. In the region of its fall-off the activity for the clays of constant layer charge is closely proportional to the change in $[Al^{3+}]$ whereas for the other series it is much more pronounced.

Naturally occurring montmorillonites are characterised by a residual negative charge in the central octahedral layer resulting from isomorphous replacement of Al^{3+} by a divalent ion, normally Mg^{2+}. The idealised formula based upon that of pyrophyllite, is

$$\left[(\mathrm{Si}_8)^{\mathrm{tet}}(\mathrm{Al}_{4-x}\mathrm{Mg}_x)^{\mathrm{oct}}\mathrm{O}_{20}(\mathrm{OH})_4\right]^{x^-} \text{ with } 0.5 < x < 1.2.$$

The layer charge is balanced by exchangeable cations in the interlamellar region which are normally hydrated. However, a variety of solvating molecules may be intercalated along with, or in place of, water. Since cation-exchange-capacities (CEC) often exceed analytically deduced layer charges on the basis of chemical analysis it appears probable that a minor fraction of the exchangeable cations reside at defects at layer edges.

Appropriately ion-exchanged montmorillonites have in recent years been shown to be highly catalytically active, in a wide range of organic reactions [1–7]. Little of a quantitative nature, however, is known of the influence on catalytic activity of the concentration of the active exchangeable cation $[x^{n+}]_{\text{exch}}$ of the active cation, or of the layer charge. Such data as are available reveal no clear-cut correlation of activity with $[x^{n+}]_{\text{exch}}$, although one is expected. One explanation for this is that any correlation that exists is obscured by the extreme variability of natural materials in terms of impurity levels, by interstratification, by isomorphous replacement or variations of the inhomogeneity in layer charge. But one recognises that the operation of such factors could equally lead to a situation where a correlation was indicated where none existed.

It is desirable, therefore, to study the catalytic performance of clays in which $[x^{n+}]_{\text{exch}}$ are deliberately varied using a common clay. Two of the possible routes to this end are to produce: (a) a series of constant layer charge but varying $[x^{n+}]_{\text{exch}}$ by incorporating a second, catalytically inactive cation, to make up the CEC; and (b) a series covering a range of layer charge and hence of $[x^{n+}]_{\text{exch}}$. It is now well documented that whereas Al^{3+}-exchanged montmorillonites are potent Bronsted-acid catalysts [1–5], their Na^{+}-exchanged analogues are inactive. Thus, series (a) can be generated by co-ion exchange between Al^{3+} and Na^{+}-exchanged forms mixed in suspension in different ratios, Na^{+} being the so-called co-ion. Series (b) can be generated by taking advantage of the well-known fact that when Li^{+}-exchanged dioctahedral clays (such as montmorillonite) are heated at 200 ° C or more, the small Li^{+} ions migrate into non-exchangeable positions in the octahedral layer thereby reducing the layer charge. Starting with a co-ionic clay of known Li^{+}/Na^{+} ratio, calcination leads to controlled CEC reduction, which can then be followed by replacement of residual, interlamellar Na^{+} by Al^{3+}.

Using, as starting material, a sample of Gelwhite L (English China Clays Lovering Pochin & Co. Ltd.) of CEC 101 meq/100 g dried clay, two such series of clays of $[Al^{3+}]_{\text{exch}}$ ranging down to CEC of about 20 were prepared. Their individual catalytic activities were then compared by study of their effect in two distinct reactions, both proton-catalysed: (i) the esterification of ethanoic acid by hex-1-ene to hex-2-yl and hex-3-yl acetates, which is accompanied by hexene isomerisation; and (ii) the dehydration of pentan-1-ol which yields dipent-2-yl ether, pent-2-yl pent-3-yl ether and pent-2-ene. These reactions have been studied in considerable detail [1] and their main mechanistic features unequivocally established. Reactions were carried out in 20 ml stainless steel reactors, 0.3 g of catalyst being added to 3 ml of reactant which, in the esterification, was an equimolar mixture. Reaction time was 4 h in each case, with reaction temperature being 160 ° C for the esterification and 200 ° C for the dehydration.

Figure 1 illustrates the results in the form of a plot of total product yield expressed as mol percent of final mixture against $[Al^{3+}]_{\text{exch}}$, expressed in meq/100 g dried clay.

A correlation of catalytic activity with $[Al^{3+}]_{\text{exch}}$, is apparent. For the co-ionic series of clays, the influence of $[Al^{3+}]_{\text{exch}}$ on activity is similar for both reactions. Activity is also similar for the two reactions with the charge-reduced clays.

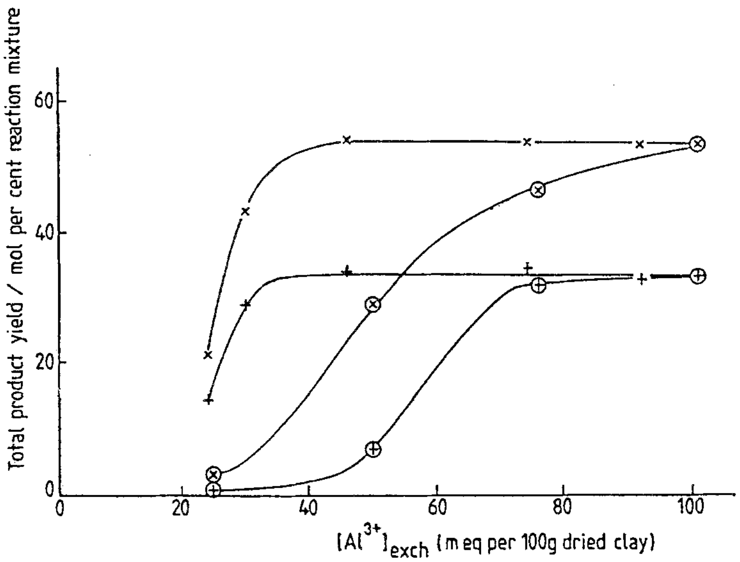

Fig. 1. Plot of total product yield (mol percent final reaction mixture) against [Al^{3+}]$_{exch}$ (meq/100 g dried clay) for: co-ionic clays, ⊕ hex-1-ene + ethanoic acid; ⊗ dehydration of pentan-1-ol; charge-reduced clays, + hex-1-ene + ethanoic acid, × dehydration of pentan-1-ol.

Further, while there are quantitative differences from one clay series to the other, the form of the correlation is the same. In each case, reduction of [Al^{3+}]$_{exch}$ has no effect on activity down to some threshold value. Thereafter, activity falls off progressively for the co-ionic material but dramatically for the charge-reduced varieties. Below [Al^{3+}]$_{exch}$ of ca 20 meq/100 g dried clay, the activity falls to zero for each series of clays.

Since the reactions studied here are indubitably proton catalysed, the form of correlation observed reflects changes of active proton concentration as a function of [Al^{3+}]$_{exch}$. It is well established [1–5] that Al^{3+}-exchanged montmorillonites behave quantitatively as do H$^+$-exchanged analogues in many catalytic processes, a fact which is attributable to cation hydrolysis of Al^{3+} (6H$_2$O), the nominal hydrated form of Al^{3+}. The results indicate that, above the threshold values of [Al^{3+}]$_{exch}$, further Al^{3+} present is incapable of providing an increase in active H$^+$. This observation is consistent with our unpublished data which indicate that exchanged, natural montmorillonites of different origin and CEC (ranging from 70–135) have comparable catalytic activity for these same reactions.

In the region where activity falls off, we note that, for the co-ionic clays, the rates of the reactions diminish, as might have been expected, in almost direct proportion to the change in [Al^{3+}]$_{exch}$. For the charge-reduced series, however, the fall-off is much more dramatic. There is no simple explanation for this, but it is noteworthy that charge-reduced clays in the relevant CEC range expand in water only with difficulty, if at all (although they still swell in certain organic liquids).

Finally, we note the loss of activity for $[Al^{3+}]_{exch}$ at values of CEC less than ca 20. One plausible interpretation is that, at this level, a CEC of 20 reflects the exchangeable-ion concentration outside the interlamellar region. Two things militate against this view, however. Two things militate against this view, however. First, at $[Al^{3+}]_{exch}$ of 25, there is $[Na^+]_{exch}$ of 75 present in the interlamellar region of co-ionic clay. It is hardly likely that the external sites are exclusively taken up by Al^{3+}. Second, it is possible to produce an Al^{3+}-exchanged clay of CEC as low as 9 following Li^+-exchange and calcination. (This is, incidentally, a more reasonable estimate [8] of the external CEC.) We must conclude, therefore, that, at CEC around 20, there are echangeable Al^{3+} located within the interlamellar region that are not hydrated. Given the swelling characteristics of such clays at very low CEC it may therefore be that there is no interlamellar water available to provide protons. However, we note much the same lower threshold for the co-ionic clays the swelling ability of which would not be expected to be affected since they all have the same, original, total CEC.

Since all the clays in the co-ionic series have the same total CEC, and ability to take up water, we would expect, as observed, a regular diminution of proton activity as $[Al^{3+}]_{exch}$ diminishes below the threshold value. It is not obvious, however, why the charge-reduced series exhibits so much lower a threshold followed by such an abrupt activity fall-off. It appears likely that this is connected with the change in ability to swell. A more thorough explanation demands more detailed information. However, a correlation of activity with layer charge is established, and the unexpected nature of the results presented here reveals that more comprehensive studies of this type should shed new light on events in the catalytically active region of ion-exchanged montmorillonites.

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