Catalysis Letters 5 (1990) 203–210

CATALYSIS BY ION-EXCHANGED MONTMORILLONITES *

J.H. PURNELL

Department of Chemistry, University College of Swansea, Singleton Park,
Swansea SA2 8PP, Wales, U.K.

Received 29 January 1990; accepted 26 March 1990

Montmorillonite, swectite, Bronsted acid catalysts, intercalation

In this short review the special attributes that make modified layered clays such versatile and effective catalysts for the conversions of organic molecules are discussed and exemplified.

Clays have been used by man for a variety of purposes since pre-historic times. During this century that use has extended to the chemical industry, although until relatively recently, their role was essentially as absorptive supports for acid catalysts in which area there is a very large patent literature [1,2]. Comprehensive researches of the past fifty years or so have established, first, that the main mineral constituents of clays form an identifiable chemical group (the clay minerals) and, secondly, that to some extent on the basis of their chemical composition, but more generally, on the basis of structure and associated physical properties, these compounds may be grouped into families. The majority but, as shown later, by no means all, are micro-crystalline alumino-silicates, and irrespective of compositional detail, for the most part they share the property of having layered structures. The Smectite (sometimes called Montmorillonite) family occurs widely in Nature and since these materials also have useful properties they have come to be both the most widely used and studied. In this brief review, therefore, we concentrate on these materials.

The nominal parent in the Smectite family is Pyrophyllite, of composition $Si_8Al_4O_{20}(OH)_4$, which is structurally composed of a sheet of Al(O, OH) octahedra (O) sandwiched between two sheets of silica tetrahedra (T). The resulting three-layered (TOT) sheets are separated by an interlamellar space, sometimes called the gallery. In Nature, substitution of Si or Al (or other structural atoms) by atoms of lower valency in either or both T/O layers is almost universal. This confers negative charge on the sheet which is then balanced by cations held in the interlamellar space. Stability is gained by interlamellar intrusion (intercalation) of

---

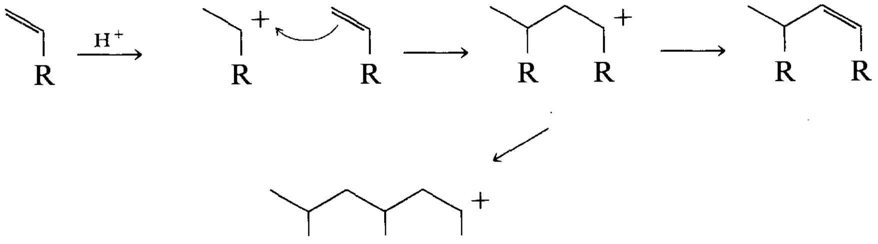
* Presented in part at the Royal Society-U.S.S.R. Workshop, Oxford, April 1989.

water and, as a result, the sheets, although unable to slide, may move apart (expand) to accommodate several water layers. This situation gives rise to two characterising properties of these clays, substantial liquid absorption capacity and ready cation-exchange; properties that are vital in determining soil behaviour, and as we now know, open the doors to catalytic use.

The more important members of the Smectite family are listed in table 1, wherein the structural, as opposed to the chemical, connecting link in categorisation is made plain. Each of these types of material can provide some or other degree of catalytic activity but much the most important is the montmorillonite species which itself provides a sub-group of the Smectites through variations of both the amount (x) and identity of the isomorphously substituted cation in the octahedral layer and/or some replacement of Si by Al in the tetrahedral layer.

It has long been known that almost any liquid can be intercalated within the interlamellar space, and that any cation may be exchanged. Indeed, it was the intense interest shown in the intercalation phenomenon, from about the early sixties, and which is reflected in a very substantial literature, that led to the recognition ten years or so later that the clay minerals presented catalytic opportunities in their own right rather than simply as acid supports. Research activity in the field has since become quite intense and a remarkable variety of reactions by now established to be strongly catalysed.

The intercalated cation in naturally occurring clays is Na^+ or Ca^{2+} and occasionally K^+, depending on geological origin. Such clays are very weakly catalytic, if at all. When, however, these ions are exchanged by the simple process of exposure to aqueous solutions of the relevant cation they become active to a greater or lesser extent. It is worth noting that an H^+-exchanged clay retains its activity when washed to neutrality. Its activity is thus associated with the intercalated proton rather than with any residual acid. Indeed, present evidence is that catalytic activity is associated with protons (irrespective of the identity of the exchanged ion) which are provided by the hydrolysis of the aquated ion. In essence, therefore, these clays are Bronsted acids, and can be expected to catalyse most if not all processes that are proton-catalysed. A typical example is the oligomerisation of alkenes [3], as illustrated below, wherein the carbocation initially formed is subject to nucleophilic attack by alkene to form a higher carbocation that may add further alkene or deprotonate.



Listed below are some examples illustrating the wide range of processes that respond with great facility to the clays [4–6].

$$R-CH_2-CH_2-OH \xrightarrow{-H_2O} R-CH_2-CH_2-O-CH_2CH_2R$$

$$R-CH_2-CH_2-NH_2 \xrightarrow{-NH_3} R-CH_2-CH_2-NH-CH_2-CH_2R$$

$$R-CH_2-CH_2-SH \xrightarrow{-H_2S} R-CH_2-CH_2-S-CH_2-CH_2R$$

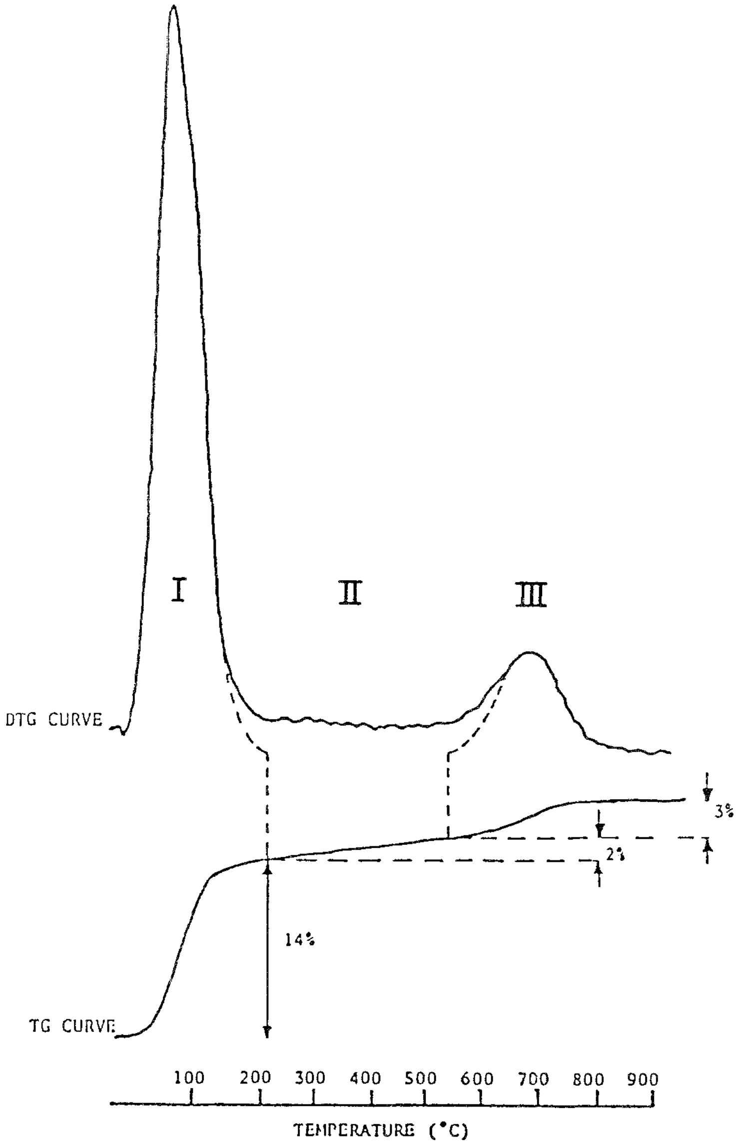


Fig. 1. Typical TGA (and DTG) of an ion (H^+)-exchanged montmorillonite (Bentonite) showing three discrete regions of water loss. The % weight loss in region I depends upon the relative humidity of the storage atmosphere. That in regions II and III is characteristic of the material.

Table 1

Classification of some montmorillonite clay minerals

Clay name	Octahedral occupancy	Origin of layer charge	Idealized structural formula
Montmorillonite	Dioctahedral	Octahedral	$[Si_8]^{Tet}\cdot[Al_{(4-x)}Mg_x]^{Oct}\cdot O_{20}\cdot(OH)_4\cdot xM^+$
Beidellite	Dioctahedral	Tetrahedral	$[Si_{(8-x)}\cdot Al_x]^{Tet}[Al_4]^{Oct}\cdot O_{20}\cdot(OH)_4\cdot xM^+$
Nontronite	Dioctahedral	Tetrahedral	$[Si_{(8-x)}\cdot Al_x]^{Tet}[Fe_4^{III}]^{Oct}\cdot O_{20}\cdot(OH)_4\cdot xM^+$
Hectorite	Trioctahedral	Octahedral	$[Si_8]^{Tet}\cdot[Mg_{(6-x)}Li_x]^{Oct}\cdot O_{20}\cdot(OH)_4\cdot xM^+$
Saponite	Trioctahedral	Tetrahedral	$[Si_{(8-x)}\cdot Al_x]^{Tet}[Mg_6]^{Oct}\cdot O_{20}\cdot(OH)_4\cdot xM^+$

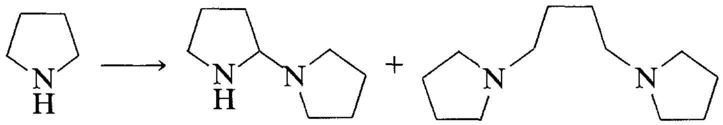
The alkanol also gives a small yield of $R\text{–}CH{=}CH_2$ but the absence of the alk-1-yl/alk-2-yl ether establishes that the carbocation, which would be alk-2-yl, is not involved, the active species is thus $R'CH_2OH_2^+$.

Diols also react readily, for example [4],

$$HO\text{—}CH_2\text{—}CH_2\text{—}OH \longrightarrow H\text{—}(\text{—}O\text{—}CH_2\text{—}CH_2\text{—})_n\text{—}OH$$

$$HO\text{—}CH_2\text{—}CH_2\text{—}O\text{—}CH_2\text{—}CH_2\text{—}OH \longrightarrow \text{1,4-dioxan}$$

but secondary alkanols provide virtually exclusively the alkene rather than the ether. Secondary amines also behave differently, a particularly interesting reaction is that of pyrrolidine [5], the first listed product below being primary,



the latter secondary. By careful control of conditions either of these can be made or predominate. Perhaps the most surprising reaction in this group, however, is that of benzyl alcohol which gives, not the ether, but poly(phenylenemethylene) $C_6H_5(\text{–}CH_2\text{–}C_6H_4\text{–}CH_2\text{–})_n\text{–}C_6H_4CH_2OH$. Except for the end group this is the product, also of the corresponding reaction of benzyl thiol [4,6].

Many addition reactions of a wide variety of types are also strongly catalysed [3–7], e.g.

$$C_3H_6 + H_2O \longrightarrow \text{di-isopropyl ether}$$

$$Me_2C{=}CH_2 + MeOH \longrightarrow Me_3C\text{—}OMe$$

$$R\text{—}CH{=}CH_2 + R'\text{—}SH \longrightarrow R\text{—}CH(SR')\text{—}CH_3$$

$$C_2H_4 + CH_3COOH \longrightarrow CH_3CO_2C_2H_5$$

$$CH_2{=}CH\text{—}CN + Me_3C\text{—}OH \longrightarrow CH_2{=}CH\text{—}CO\text{—}NH\text{—}CMe_3$$

$$C_6H_6 + C_3H_6 \longrightarrow C_6H_5CH(CH_3)_2$$

$$C_2H_4O + R\text{—}OH \longrightarrow HO\text{—}CH_2CH_2\text{—}OR$$

These represent a small propertion of the whole range of such reactions that have been established to be well catalysed.

The reactions exemplified above all proceed readily at temperatures below 200 ° C. Reactions requiring higher temperatures are less readily dealt with; and to understand this it is instructive to consider the thermogravimetric analysis (TGA) results [8] shown in fig. 1 which are typical of all Smectite clays.

We see first, a significant weight loss (I) starting at around 60 ° C and peaking at about 100 ° C. This corresponds to evolution of physically sorbed water (or other intercalate). From a little below 200 ° C we see a monotonous weight loss (II), which being essentially linear, shows no derivative peak. This loss corresponds to dehydration of the aquated cation (chemical water) which is complete at about 500 ° C. Shortly thereafter, a third weight loss (III), which is complete at about 800 ° C, is seen to start. This corresponds to dehydroxylation of the structure, which eventually collapses completely. The important further information we now need is that these weight losses are time dependent. That is, the extent of water loss in each region is greater at any temperature if the time of calcining is increased. This is of the greatest import with respect to region (II) since total weight loss in this region occurs at much lower temperatures than ca. 500 ° C in continuous operation. What is then crucial is that catalytic activity is closely associated with the amount of this "chemical" water as fig. 2 shows [9].

In the full line of the upper left diagram in fig. 2 we see the changes in cation exchange capacity (CEC) of a Cr^{3+}-exchanged bentonite (a montmorillonite mined in Benton, U.S.A.) as a function of temperature in 7 hr calcinations. In the lower left figure, the full line shows the change in "chemical" water content. There is quite substantial loss of CEC in the region of physical water loss while, from around 200 ° C, as the chemical water starts to reduce, there is a further rapid loss of CEC. Also included in these figures as open circles are corresponding data for a Cs^+-exchanged version of this clay which show no change. On the right we show results for dipent-1-yl ether production in 4 hr reactions of pentan-1-ol with the Cr^{3+}-exchanged clay. There is clearly little loss of activity at CEC down to ca. 45 mequiv./100 g clay, hence the CEC reduction associated with physical water removal is irrelevant. Thereafter, however, the fall-off in CEC, which mirrors that in chemical water, has catastrophic results. It is therefore clear that catalytic activity is directly associated with the chemical water content a fact that is highlighted by the total absence of any effect at all on calcining the Cs^+-exchanged material.

In simple terms, the explanation is as follows. An Al^{3+}-exchanged clay has, as the intercalated cation, hydrated species e.g. $Al^{3+} \cdot 6H_2O$, which can readily provide protons as, for example, via

$$Al^{3+}6H_2O \longrightarrow \left[Al^{2+}(OH) \cdot 5H_2O\right]H^+$$

and so on. At temperatures of 200 ° C and above, protons can migrate into the layer, so reducing the CEC, the surplus H_2O is released and can be driven off

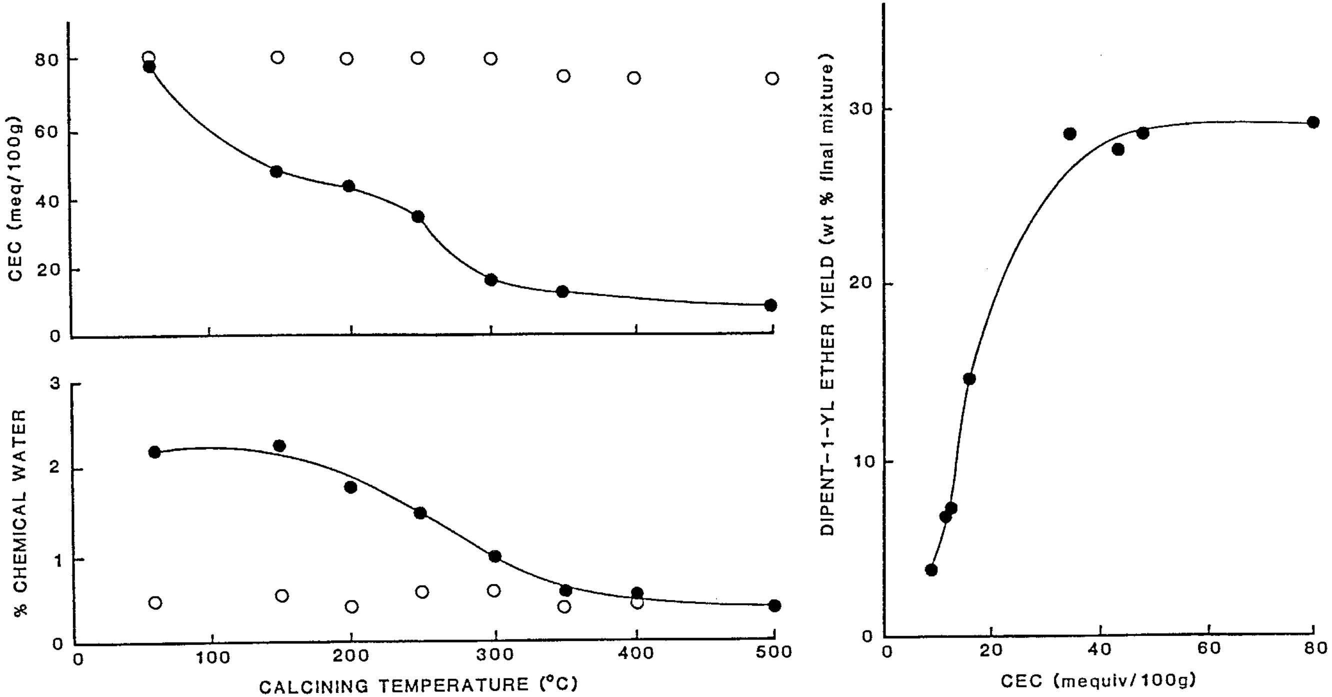


Fig. 2. Left: effect of calcination (7 hr) temperature on (upper) the CEC and (lower), “chemical” water content (see text). Full lines, Cr^{3+}-exchanged Bentonite; open-circles, Cs^{+}-exchanged Bentonite. Note almost total absence of effect on the Cs^{+} material, which also has negligible catalytic activity.

Eventually one could visualise the formation of $Al(OH)_3$, the loss of all protons to the layer and total expulsion of the three surplus water molecules. This is a highly simplified version of events but it gains credence from the fact that the CEC of such thermally charge reduced clays can be totally restored simply by exposure of the clay to a strong base such as cyclohexylamine at ca. 200 °C. Further, it can be shown by exchange that the clay then has $[Amine]H^+$ cations in the interlamellar space [10]. The only possible origin of these protons is the sheet layers and the process is clearly then the reverse of the events accompanying calcination.

As would be expected, the identity of the interlamellar cation is important in determining activity. Broadly, cations fall into one or other of four groups. High valency, highly hydrated cations are all more or less equally active and closely comparable in their catalytic influence with H^+. In a few instances of reaction, one or other has been found to be modestly superior, but in general, they can be taken as equivalent alternatives. Di-valent cations of transition metals form a second, very active group, again very similar in potency to one another, and very roughly, about one-half to two-thirds as active as the cations of the first group. Non-transition metal divalent ions confer a weak activity of little practical value, whilst the univalent ions only very exceptionally have discernible catalytic effects. Although we may expect a more detailed story to emerge as the body of research grows, it seems clear that the first group of cations is likely to dominate in industrial applications.

These materials are now well demonstrated to have enormous catalytic potential, at least in the area of low temperature synthesis. What are the drawbacks? There are two of significance. First, the materials "sand" readily (they are friable) in the presence of certain liquids, methanol for instance. Thus, the catalytic bed collapses and bed longevity is short. Second, at the high temperatures required for cracking, reforming, desulphurisation and other rather demanding reactions, the temperature instability of the structure leads to rapid loss of activity. These features have been recognised and research targetted on their removal since the mid-seventies. A successful approach to resolution of the problem is that of "pillaring" [11]. In this procedure, poly-oxymetal cations, such as the "Keggin ion", $[Al_{13}O_4(OH)_{24+x}(H_2O)_{12-x}]^{(7-x)+}$, are exchanged into the clay, which is then calcined. Polyoxyalumina pillars [12], linking the sheets, are formed and this confers thermal stability to as high as 700 °C, and eliminates solvent sanding. Such pillared clays are already in successful use in high temperature processes and research continues on the quest for alternative pillaring materials. One drawback to this otherwise encouraging situation is a substantial loss of activity with respect to the unpillared precursor. A real target now is the production of unpillared varieties having adequate thermal and solvent stability [11]. Work in this area is well advanced but, as is a feature of this whole area of study, our knowledge of progress is clouded by the confidentiality demanded in industrial development. But whatsoever the outcome of such deliberations may be, one thing is certain, modified clays will be significant industrial catalysts as we draw closer to the twenty first century.

References

[1] A. Weiss, Clays Clay Minerals 10 (1963) 191.

[2] J.M. Thomas, S.E. Morsi and J.P. Desvergne, Adv. Phys. Org. Chem. 15 (1977) 63, see also H. Heinemann, Catal Sci. Technol. 1 (1981) 1.

[3] J.M. Adams, J.A. Ballantine, S.H. Graham, R.J. Laub, J.H. Purnell, P.I. Reid, W.Y.M. Shaman and J.M. Thomas, J. Catal. 58 (1979) 238.

[4] J.A. Ballantine, M. Davies, I. Patel, J.H. Purnell, M. Rayanakorn, K.J. Williams and J.M. Thomas, J. Mol. Catal. 26 (1984) 37.

[5] J.A. Ballantine, J.H. Purnell, M. Rayanakorn, K.J. Williams and J.M. Thomas, J. Mol. Catal. 30 (1985) 373.

[6] J.A. Ballantine, R.P. Galvin, R.M. O'Neil, J.H. Purnell, M. Rayanakorn and J.M. Thomas, J. Chem. Soc. Chem. Commun. (1981) 695.

[7] J.A. Ballantine, M. Davies, R.M. O'Neil, I. Patel, J.H. Purnell, M. Rayanakorn, K.J. Williams and J.M. Thomas, J. Mol Catal. 26 (1984).

[8] A. Al-Owais, J.A. Ballantine, J.H. Purnell and J.M. Thomas, J. Mol. Catal. 35 (1986) 201.

[9] J.H. Purnell and J. Williams, in course of publication.

[10] J.A. Ballantine, P. Graham, I. Patel, J.H. Purnell and K. Williams, The Clay Minerals Soc. (1987) 311.

[11] J.H. Purnell, in : *Proc. E.C. Workshop on Pillared Layered Structures,* Brussels, December 1989, in press.

[12] D.T.B. Tennakoon, W. Jones and J.M. Thomas, J. Chem. Soc., Faraday Trans. I, 82 (1986) 545.