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REVIEW

CLAYS AS CATALYST AND REAGENT SUPPORTS

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Abstract: Applications of clay minerals as supports for platinum, palladium, ruthenium, rhodium, nickel and copper metallic catalysts are described. The expanding clays are usually the most effective supports for metallic catalysts and, in some cases, the lamellar structure of the support confers useful size and shape selectivity to these catalysts. The expanding clays are also highly suitable for supporting catalytically active metal complex ions, frequently offering activity advantages over other supports, and size and shape selectivity advantages over the homogeneous analogues. Clay minerals are also finding uses as supports for simple metal salt catalysts and reagents, in oxidation, alkylation, acylation and other reactions. The activities of some of these salts (e.g. $ZnCl_2$) are enhanced through deposition on clay-based supports. Although commercially available acid-treated clays have most often been employed as supports for this type of catalyst/reagent, the structural requirements for the support vary widely and maximum activity generally requires "tuning" of the support for individual adsorbed salts. Acid-treated clays have also been used as supports for microwave-activated organic reactions in the absence of solvent. The high reactivities achieved under these conditions are in part due to the stability of the clay supports towards intense microwave fields. Further enhanced reactivites may be possible with optimised acid-clay supports.

Key Words: clay(s), catalysis, catalyst support(s), acid-activated clay(s), acid-treated clay(s).

Introduction

The catalytic properties of clays have been exploited since the early days of synthetic organic chemistry. Most applications have been in acid catalysed reactions (Adams et al. 1983; Laszlo 1987; Ballantine 1992) but, as understanding of the intercalation properties of the swelling clays has developed, smectites in particular have been used as the bases for a large number of more varied catalysts.

The high surface areas of clays also makes them attractive as catalyst and reagent supports, and it is this role of clays which will be described here. Discussion will be largely confined to supported metal catalysts (mainly for hydrogenation) and supported inorganic salts, which are active towards a range of organic reactions. Although many clay-based catalysts in which metal complexes or other ions are incorporated by simple ion exchange may also be regarded as supported catalysts (Pinnavaia 1983), these materials will not be covered in depth in this review. Recent developments in the novel area of microwave-activated reactions will be mentioned, in which clays are proving to be effective supports for organic reactions carried out in the absence of solvent.

Clay-supported metal catalysts

Metal catalysts are frequently used in a supported form rather than pure. The role of the support is to maximise the surface area of the active phase by providing a large area over which it may be spread, to prevent coagulation and sintering of small metal particles under reaction conditions, and to allow the active phase to be cast into coarse particles suitable for use in reactor beds. Typical substances which find wide use as high area supports are γ-alumina, silica gel and activated carbon, all of which can be obtained with surface areas in the range 200 - 1000 $m^2.g^{-1}$. For clays to be effective supports they too must be capable of exhibiting surface areas of this magnitude. Only the swelling clays can approach these values and then only if the internal, interlayer surfaces are accessible in addition to the external crystallite surfaces.

The smectite clays do, however, offer some potentially attractive features as supports. In addition to their high surface area, the laminar structure may confer size or shape selectivity to the resultant catalyst. Another important feature is the negative charge on the silicate lattice, which may be able to polarise reactant molecules and hence facilitate interaction with the catalytic centre and enhance catalytic activity. Finally, the surface Brønsted acidity of clay minerals provides catalyst bifunctionality. This may be useful, for example in stabilising cationic hydride intermediates which would otherwise loose protons.

Platinum and palladium

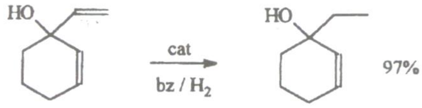
Metals can be introduced throughout a swelling clay from aqueous solution in ionic form, and then subsequently reduced. Harrison et al. (1988) have shown how $Pt(NH_3)_4{}^{2+}$ may be exchanged into a Wyoming bentonite from aqueous solution, dried and reduced with H_2 at 140 °C. Some migration of the platinum particles to the external surfaces is reported, although at low platinum loadings of 0.6 - 1.0 % a large proportion of metal particles are in the 3 nm range. At higher loadings there is a tendency towards metal clustering into films of undetermined thickness. It is interesting that the clay-supported metal catalysts retain some swelling capacity, suggesting that such catalysts might be useful in condensed phase hydrogenations.

Palladium can be introduced to montmorillonite supports via a similar ionic route, using $Pd(NH_3)_4{}^{2+}$ (Matsuda et al. 1987). However, better dispersions can be achieved if the metal ion is complexed with more electrophilic ligands to facilitate reduction. Crocker et al. (1993a, 1993b) have taken this approach in using the palladium(II) complex $[Pd(PPh_3)(NCMe)_3]^{2+}$ and subsequent reduction with H_2 in MeOH at 0 °C, to give palladium particles mainly in the size range 2 - 4 nm. The particles show platelet morphology, consistent with the constraints imposed on crystallite growth by the clay lamellar structure.

Despite the small metal particle size, however, the measured total surface area of supported palladium catalysts prepared in this way is only about 30 $m^2.g^{-1}$, suggesting that access to the clay interlayers is blocked, presumably by large metal crystallites on the outer edges of the clay platelets. These workers have adopted a modified procedure to reduce pore blocking. In this procedure the clay is first exchanged with $[Pd(PPh_3)\ (NCMe)_3]^{2+}$ as before, but only to a low palladium(II) loading of 0.1 $mmol.g^{-1}$. After drying, the ion exchanged clay is treated with a very bulky and less electrophilic second ligand, tri-o-tolylphosphine $[P(o\text{-}CH_3C_6H_4)_3]$. This replaces (NCMe) ligands, but only on accessible palladium(II) ions near the outside of the platelets. Under the mild reducing conditions employed, the palladium(II) near the platelet edges remains largely unreduced. The consequent absence of metal particles near the edges and the relatively low concentration of palladium throughout the clay means that access for reactants to palladium particles in the interlamellar spaces is improved. This modified process also results in smaller metal particles, with 73 % being smaller than 2 nm. As might be expected, this material also shows pronounced size selectivity, with hydrogenation rates for cyclic olefins in the order:

cyclopentene >cyclohexene >>cycloheptene (no activity).

Unreduced palladium(II) is also an effective hydrogenation catalyst when anchored in a clay matrix. Choudary et al. (1988, 1991, 1992) have used a number of palladium(II) complexes with large organic ligands to secure the ion in interlamellar exchange sites in montmorillonite. The large ligands prop the lattice layers apart, conferring shape and size selectivity on the resultant catalyst. For example, montmorillonite exchanged with diphenylphosphine palladium(II) chloride catalyses hydrogenation of cyclopentene very much more easily than cyclohexene and cyclooctene (Choudary et al. 1992). The catalyst is also very selective towards unhindered double bonds (reaction **1**).



(1)

A similar degree of selectivity has been achieved by Shimazu et al. (1989), who incorporated palladium(II) in a lithium hectorite by first aminating the hydroxyl groups on the hectorite and reacting palladium(II) ions with the resulting modified clay. Hydrogenation of olefins shows size and shape dependence, with reactivity in the following order:

1-pentene > 2-methyl-1-butene > cyclooctene.

Another application of montmorillonite-supported palladium has been in the subsidiary role of minimising coking. Matsuda et al. (1987) have shown that the presence of interlamellar palladium, combined with additional H_2 in the feedstock, significantly reduces coking in alumina pillared montmorillonite catalysts for use in high temperature gas phase hydrocarbon conversion. Added palladium was found to be much more effective in stabilising catalytic activity in the pillared montmorillonite catalyst than in H^+ zeolite-Y, with which it was compared.

Ruthenium

Giannelis et al. (1988) have produced a montmorillonite-supported ruthenium catalyst by exchanging $HRu_3(CO)_{12}{}^+$ into alumina pillared montmorillonite. Following intercalation of the carbonyl complex it was reduced in 1 atm H_2 at 400 °C, generating ruthenium clusters of less than 5 nm size embedded in the clay particles. The alumina pillars in this system are thought to mimic a bulk oxide surface by providing hydroxyl groups to immobilize the metal centres, ensuring a high dispersion of metal particles (Fig. 1), with resultant high activity towards Fischer-Tropsch synthesis.

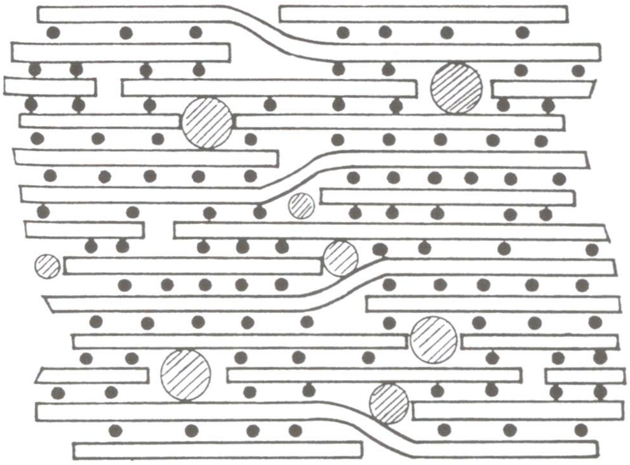


Fig. 1. Schematic illustration of suggested defect sites occupied by ruthenium in alumina pillared montmorillonite. Small circles represent pillaring alumina aggregates between the clay layers. Shaded circles represent ruthenium aggregates. Reprinted, with permission, from Giannelis et al. (1988). Copyright (1988) American Chemical Society.

The controlled gallery heights in this material, combined with the intrinsic acidity of the pillared clay, result in catalyst selectivity. Particularly impressive is the selectivity towards branched chain olefins, resulting from protonation of terminal olefins formed by Fischer-Tropsch chain propagation and subsequent rearrangement of the carbonium ions on the gallery surface (reaction **2**). Yields of branched chain hydrocarbons using this catalyst are comparable with the best yields achieved with zeolites.

$$\mathrm{CH_3\overset{+}{C}HCH_2CH_2R} \longrightarrow \mathrm{CH_3\underset{CH_3}{C}H\overset{+}{C}HR} \qquad (2)$$

Rhodium

There are several examples of hydrogenation catalysts based on clay-supported rhodium complexes (Pinnavaia et al. 1979; Pinnavaia 1987; Miyazaki et al. 1985). They are worthy of mention even though they are strictly modified clays prepared by ion exchange rather than supported catalysts. In one of the most successful applications of this type, the catalytically active complexes $\mathrm{RhL_n}^+$ (L = triphenylphosphine, n = 2.3) are exchanged into hectorite (Pinnavaia et al. 1979; Pinnavaia 1983, 1987). Unlike the same rhodium(I) complex ions in homogeneous solution, which catalyse both hydrogenation and isomerisation of olefins, the clay-supported complexes show high selectivity towards hydrogenation. The reason for this is related to the equilibrium existing between the dihydrogen and the hydride rhodium(I) complexes (reaction **3**).

$$\mathrm{RhH_2L_n}^+ \rightleftharpoons \mathrm{RhHL_n} + \mathrm{H}^+ \qquad (3)$$

The hydride complex catalyses both processes, whereas the dihydrogen complex preferentially catalyses hydrogenation. In a homogeneous system both complexes are present, but in the hectorite-supported catalyst the surface acidity of the clay ensures that the equilibrium is driven towards the dihydrogen complex, and hence the selectivity towards hydrogenation. This is an elegant example of the bifunctionality of clay-supported catalysts.

Further selectivity is observed with this hectorite-supported rhodium catalyst. The d_{001} spacing of the clay support is controlled by the intercalated rhodium triphenylphosphine complex. This imposes size and shape selectivity. For reaction to occur the olefin must align with the double bond perpendicular to the lattice layers (Fig. 2) and in general this is only possible if the double bond is either terminal or, at most, in the 2-position.

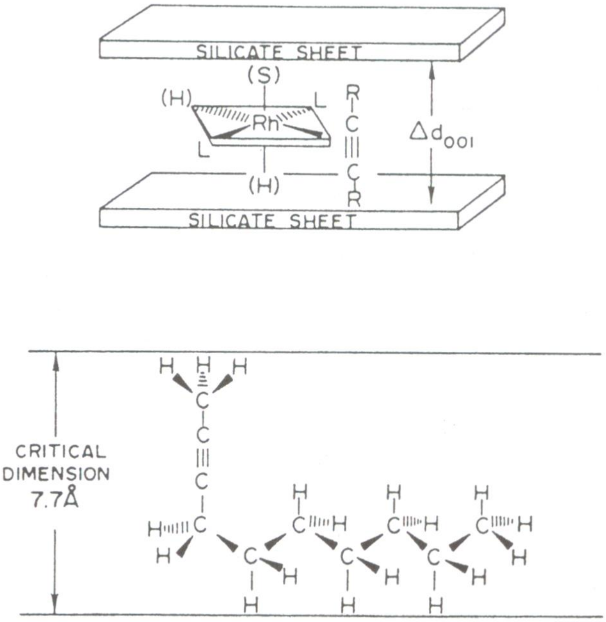


Fig. 2. Proposed orientation for the reactive $\mathrm{RhH_2(PPh_3)_2}^+$ -alkyne intermediate formed in the interlayers of hectorite. The critical dimension, illustrated for 2-decyne, is defined as the minimum distance spanned by the substrate to achieve a reactive configuration. Reprinted, with permission, from Pinnavaia et al. (1979). Copyright (1979) American Chemical Society.

Because the catalyst is prepared without calcination it retains swelling capacity in the active state. This means that the size selectivity mentioned above can be modified by choice of solvent. In, for example, the hydrogenation of 2-decyne this can be observed if the catalytic activity of the clay-supported rhodium triphenylphophine complex is compared with the activity of the homogeneous rhodium complex in different solvents. In benzene, which swells the hectorite to an interlamellar spacing of only 0.57 nm, the heterogeneous catalyst shows very low activity at only 2 % of the activity of the homogeneous catalyst. In $\mathrm{CH_2Cl_2}$, on the other hand, where swelling is more extensive and the interlamellar spacing is 1.0 nm, the heterogeneous catalyst shows much higher activity at 85 % of the value in a homogeneous system.

Nickel

Supported nickel catalysts are widely used in hydrogenation reactions. Most commonly silica gel and activated carbon supports are used, but a number of studies have shown layered minerals to be effective in maintaining high metal surface area under reaction conditions, and have sometimes conferred useful selectivity to the catalyst. Patel (1982a) has used scanning electron microscopy to demonstrate that H_2 reduction of intercalated Ni(II) ions in montmorillonite produces a high dispersion of metal particles of dimension 10 nm or less.

Deposition of nickel(II) by the incipient wetness technique (in which a nickel(II) salt solution of volume equal to the pore volume of the support is completely adsorbed and then dried), and by precipitation with urea, are also effective (Anderson et al. 1993a). Although the activity of the supported nickel catalyst formed on H_2 reduction is relatively insensitive to the impregnation technique used, it is sensitive to the conditions used for nickel reduction, and ultimate catalytic activity shows a dependence on the proportion of unreduced nickel (II) remaining in the catalyst.

Anderson et al. (1993b) compared bentonite with palygorskite as alternatives to silica and carbon supports for nickel catalysts in the hydrogenation of sunflower oil. Nickel was deposited by precipitation with urea, followed by H_2 reduction. High nickel loadings of 8 - 10 % w/w were used. Similar average metal particle diameters of about 10 nm were detected on both supports although IR measurements, made following CO adsorption, revealed a high proportion of bridging CO for the bentonite, suggesting the presence of other very small metal particles in this catalyst, probably located between the lamellae. The activity of the palygorskite supported catalyst was approximately 20 % higher than bentonite in the hydrogenation of sunflower oil to oleic acid, probably due to the greater accessibility of metal particles on the outside of the fibrous palygorskite particles than on bentonite, where accessibility for particles between lamellae is much lower.

Conclusions were also drawn about the role of surface acid sites in hydrogenations of this type. Although acid sites can play a role in coordinating olefinic double bonds on adsorbed triglycerides prior to reduction, the observation that bentonite exhibits the lower activity despite its very much higher surface acidity, suggests that the presence of surface acid sites may be relatively unimportant.

Differences in selectivity were observed between the two catalysts. Where palygorskite supported nickel showed 95 % selectivity towards oleic acid formation from the reduction of linoleic acid, the bentonite supported catalyst showed only 66 %, with a large proportion being further reduced to the less desirable stearic acid. This tendency for bentonite to promote further reduction than palygorskite is thought to be due to reactant entering slit-shaped pores between lamellae, from which diffusion of products is slow, allowing the reaction to proceed through to stearic acid.

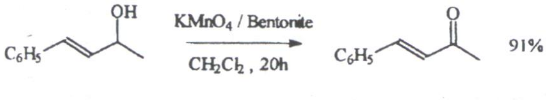
Copper

Patel (1982b) has studied the formation of 10 nm copper particles on H_2 reduction of Cu(II) exchanged montmorillonite. An alternative technique has been reported by Malla et al. (1991, 1992), in which copper acetate hydroxide is deposited by precipitation on a Na^+ montmorillonite support, through controlled addition of NaOH solution to a suspension of clay in copper(II) hydroxyacetate [$Cu(OH)(O_2CMe).H_2O$] solution. The resultant clay is dried and reduced by the "polyol" process with ethylene glycol. Very small metal particles of 0.4 - 0.5 nm diameter are reported which do not migrate from the interlamellar regions, even on heating, unlike the larger copper particles which form on H_2 reduction. These very small copper clusters are reported stable to 500 °C. They appear to prop the silicate layers apart in a regular way and interesting molecular sieving and catalytic properties are anticipated.

Supported metal salt catalysts and reagents

Potassium permanganate/montmorillonite

Potassium permanganate supported on montmorillonite has been used for oxidation of secondary alcohols to ketones (Lee & Noureldin 1981). The reagent is prepared by grinding potassium permanganate with an equal weight of dry montmorillonite. Reactions are performed by gentle warming with the reactant in dichloromethane. Primary alcohols are generally less readily oxidised with this reagent. However, these reagents show high selectivity in the oxidation of allylic secondary alcohols to the corresponding ketones, with minimal oxidation of the olefinic bond (reaction **4**).



(4)

The use of supported potassium permanganate in these reactions offers practical advantages over more usual oxidants such as activated manganese dioxide, in terms of ease of preparation, and separation of products.

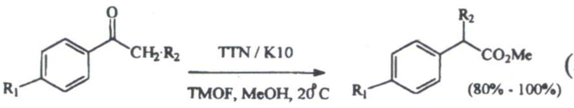
Acid-activated montmorillonite supports

A large proportion of the successful applications of clays as supports for inorganic salt catalysts have involved the acid-activated montmorillonite K10, supplied by Sud-Chemie. This material is based on the Bavarian montmorillonite Tonsil-13. Details of the acid activation process are not available. However, even though the alumina content of K10 is relatively high at 14 % (Fluka Chemie 1990), the radically increased surface area (typically 300 - 350 $m^2.g^{-1}$) compared to a natural montmorillonite, and the reduced exchange capacity of 50 - 60 $mequiv.100g^{-1}$ (Rhodes & Brown 1990), suggest that acid treatment has been quite severe, possibly in hot concentrated acid. Another indication of the extent of acid treatment is the X-ray diffraction pattern of K10, in which the intensities of montmorillonite lines are reduced to 25 - 50 % of untreated clay values, leading several workers to describe K10 as having "25 - 50 % clay character".

The properties that make K10 an attractive support are its large surface area and its surface acidity, which arises largely from its remaining exchange capacity. Most catalytic applications involve non-swelling reaction media so the increased accessible surface of the clay exposed by acid activation more than compensates for the loss in cation exchange capacity that accompanies acid leaching.

Thallium(III) nitrate/K10

Thallium(III) nitrate (TTN) forms a convenient and useful oxidising agent when supported on K10 (McKillop & Taylor 1976; McKillop & Clissold 1987; Chiang et al. 1976). The reagent is prepared by stirring K10 with TTN in a mixture of methanol and trimethyl orthoformate, followed by evaporation to dryness. It is used in an inert solvent. Examples of the utility of the catalyst include the oxidation of aryl alkyl ketones, with rearrangement, to the corresponding methyl aryl acetates in excellent yield at room temperature (Chiang et al. 1976) (reaction **5**).



(5)

Montmorillonite K10 has been shown to be a more effective support than bentonite for TTN although, in general, supports with a lamellar structure, particularly acidic ones such as K10, are more effective than nonacidic spongelike supports (Chiang et al. 1976). The physical nature of TTN/K10 is unclear. However, it is likely that trimethyl orthoformate removes some of the water of hydration from the salt, and the reagent consists of partially hydrated thallium(III) nitrate and methanol adsorbed on the surface of the acidic clay. A disadvantage of the reagent is that the TTN can be easily removed in polar solvents.

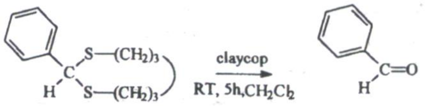
Copper(II) nitrate/K10 and iron(III) nitrate/K10

The acid clay K10 montmorillonite has also been used as a support for copper(II) and iron(III) nitrates, producing the oxidising agents for which the familiar names "claycop" and "clayfen" have been adopted (Cornelis & Laszlo 1980, 1986; Laszlo & Cornelis 1988). The basis of these reagents is the very powerful oxidising potential of the covalent anhydrous nitrates (Addison 1966). Although the anhydrous nitrates can be explosive when pure, deposition on a support like K10 renders them safe to handle. Preparation of the reagents is straightforward. Clayfen, for example, is prepared by deposition of the acetone solvate of iron(III) nitrate on K10 montmorillonite by evaporation. Clayfen is the more active of the two, but is more difficult to store in an active condition than claycop.

Claycop and clayfen are commonly used for oxidising alcohols to aldehydes or ketones, thiols to disulfides and benzoins to benzils. In the last of these, yields using clayfen generally compare very favourably with those from Kagan's procedure using the much more expensive reagent ytterbium(III) nitrate (Cornelis & Laszlo 1985; McKillop & Clissold 1987) (reaction **6**).

(6)

Claycop is inactive towards carbonyl groups so is useful for the removal of thioacetal groups (reaction **7**).



(7)

Both claycop and clayfen are sources of the nitrsononium ion NO^+, and oxidation reactions occur through the formation of an intermediate nitrous ester, $R_1R_2CH\text{-}N{=}O$. The overall mechanism is thought involve both nitrate ions and acid sites on the clay (reaction **8**).

$$R_1R_2CHOH + 2H^+ + 2NO_3^- \xrightarrow{\text{clayfen}} R_1R_2C{=}O + 2NO + 4H_2O \qquad (8)$$

However, Bekassy and coworkers (1991, 1993a) report yields of oxidation products by claycop and clayfen greater than stoichiometric, even in the absence of atmospheric oxygen, suggesting that a catalytic mechanism may also be involved.

A different facet of claycop reactivity is its power as a nitrating agent in the presence of acetic anhydride (Menke conditions) (Cornelis et al. 1988). It is moderately effective even with deactivated halobenzenes. High regioselectivities are observed in some cases. For example, nitration of fluorobenzene using claycop in n-hexane yields a para/ortho ratio of 25.0, compared to 6.6 for nitration with HNO_3/H_2SO_4. It is worth mentioning, however, that higher yields, together with similar para selectivity, can be achieved using iron(III)-exchanged K10 montmorillonite *catalyst* (not reagent) in the presence of nitric acid-acetic anhydride as nitrating agent (Choudary et al. 1994).

Characterisation of K10-supported nitrates

Bekassy and coworkers have studied claycop, clayfen and other nitrates adsorbed on montmorillonite K10, using thermal analytical techniques and X-ray diffraction (Bekassy et al. 1993b). They conclude that the metallic nitrates are held on the clay support not as the acetone solvates but as the normal hydrated salts. However, they observe major differences between the thermoanalytical profiles (due to water loss and nitrate decomposition) for adsorbed nitrates and for the bulk salts, suggesting that there are structural differences between the salts in the adsorbed and the bulk states. Significantly, although these differences are observed for nitrates which produce effective oxidants when adsorbed on K10, that is iron(III), copper(II) and chromium(III) nitrates, others, such as zinc(II) nitrate, which show almost no oxidising activity when adsorbed on K10, fail to exhibit the different thermal behaviour characteristic of adsorbed active nitrate.

Although zinc(II) nitrate is a very poor oxidising agent when adsorbed on K10, it is very effective when adsorbed on silica gel (Nishiguchi et al. 1989). This illustrates that the requirements for an effective support can be highly dependent on the type of active salt adsorbed.

Iron(III) chloride/K10

By analogy to clayfen as an aromatic nitrating agent, K10 supported iron(III) chloride (known as "clayfec") has been used successfully as an aromatic chlorinating agent, particularly in conjunction with the oxidiser m-chloroperbenzoic acid. High yields are reported for the chlorination of adamantane (Chalais et al. 1985), and toluene and anisole (Delaude & Laszlo 1990). Supported $FeCl_3$ is very much more active than the bulk salt, and K10 has been shown to be a more effective support than typical zeolites, silicas and neutral aluminas (Chalais et al. 1985).

Advantages of clayfec are ease of work-up, relative lack of side reactions and ease of product isolation. However, reactivity is sensitive to the technique used for reagent preparation; deposition of $FeCl_3$ from methanolic solution appears to produce the most active reagent.

K10-supported alkylation catalysts

Probably the most promising application of clays as catalyst supports centres on the catalytic activity of $ZnCl_2$/K10 montmorillonite ("clayzic") towards Friedel-Crafts alkylation reactions (e.g. reaction **9**). Adsorbed $ZnCl_2$ exhibits very much higher catalytic activity than the bulk salt in this type of reaction (Clark et al. 1989, Clark 1993).

(9)

Enhancements in activity are also seen for $CuCl_2$, $NiCl_2$ and several other metal halides when adsorbed on montmorillonite K10 (Clark et al. 1989). Earlier, Chalais et al. (1985) had also observed that $FeCl_3$ supported on K10, in addition to promoting chlorination reactions, shows very high activity as a Friedel-Crafts catalyst in the arylation of adamantane. A number of metal fluorides supported on K10 have also been shown to exhibit activity as alkylation catalysts (Asseid et al. 1990, 1992).

Clayzic has been the basis of the commercial development of a range of solid acid catalysts of this type, known as "Envirocats", by Contract Chemicals, Merseyside, UK. The impetus behind this development is largely the environmental pressure to replace the traditional homogeneous acid catalysts such as $AlCl_3$, HF and H_2SO_4 with solid, heterogeneous catalysts which can be handled and disposed of more easily.

The preparation of K10-supported $ZnCl_2$ (clayzic) is straightforward. The salt is deposited by evaporation of $ZnCl_2$ solution. Although eventual catalytic activity depends little on the solvent used, some workers appear to have standardised on acetonitrile for this purpose (Cornelis et al. 1990). The catalyst must be activated before use. Barlow et al. (1994) report that maximum activity is achieved with an activation temperature of 275 °C but in other work only 150 °C has been used (Rhodes et al. 1991). Following activation the catalyst is extremely hygroscopic and exposure of activated catalyst to moisture must be carefully avoided.

Clayzic is active towards alkylations involving nonpolar reactants. Barlow et al. (1991) report high activity in aromatic alkylations using a number of ring substituted benzyl chlorides, alkyl halides and also paraformaldehyde, to form diphenylmethanes and alkylbenzenes (Barlow et al. 1991), and in this type of reaction the catalyst is a viable alternative to homogeneous $AlCl_3$. The related catalysts $CuCl_2$/K10 and $MgCl_2$/K10, while exhibiting similar enhancements of activity over the bulk salts, remain an order of magnitude less active than clayzic in these reactions. Recently another group (Clark et al. 1994) has demonstrated the usefulness of clayzic and, to a lesser extent, $FeCl_3$/K10 in the benzylation of thiophene. They report high activities for the catalysts and impressive regioselectivity towards 2-substitution when the reaction is carried out

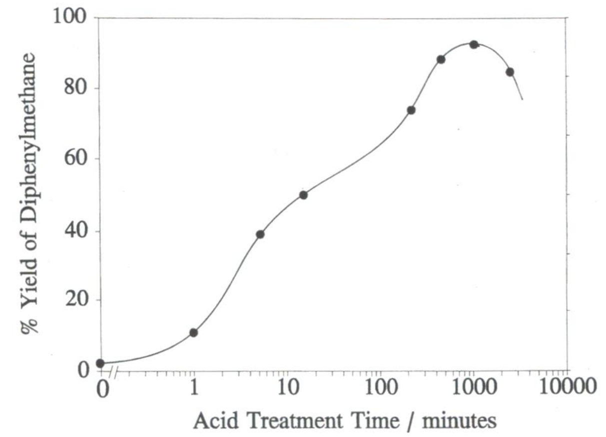


Fig. 3. The dependence of catalytic activity of $ZnCl_2$ (2 mmol.g^{-1}) alkylation catalyst supported on acid-treated montmorillonite Carmargo White, on acid treatment time of support in boiling 30 % H_2SO_4 (Rhodes & Brown 1992).

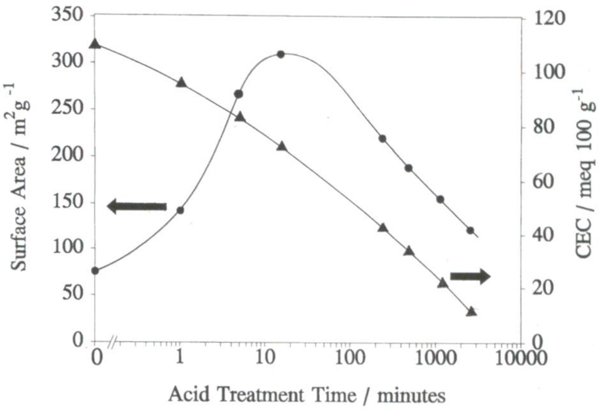


Fig. 4. The dependence of the cation exchange capacity (▲) and the N_2 BET surface area (●) of montmorillonite Carmargo White, on acid treatment time in boiling 30 % H_2SO_4 (Rhodes & Brown 1992).

in nitrobenzene. Lower reaction rates and less specificity are generally observed in other solvents.

Characterisation of supported zinc(II) chloride catalysts

Typical salt loadings of active catalyst on K10 support are 1-2 mmol.g^{-1}. This corresponds to many times the exchange capacity of K10, and it is clear that the activity is not due simply to zinc(II) ions in exchange sites. Indeed, K10 which has been ion exchanged with zinc(II) shows only limited activity in Friedel-Crafts alkylation reactions (Laszlo & Mathy 1987). The major active catalyst in clayzic is adsorbed $ZnCl_2$.

Several structural studies have been performed on clayzic to characterise the Lewis acid centre. Laszlo (1990) has compared the ^{27}Al and ^{29}Si MASNMR spectra of K10 before and after deposition of $ZnCl_2$. Although no change is seen in the aluminium signal on deposition of $ZnCl_2$, the silicon spectrum shows significant changes. The spectrum of K10 shows a signal due to ^{3}Q silicon at about -95 ppm, associated with regions of laminar clay structure, and a second signal of about twice the intensity at -107 to -108 ppm due to ^{4}Q silicon, characteristic of "amorphous" silica. On adsorption of $ZnCl_2$ the ^{3}Q Si signal is unchanged but the ^{4}Q Si signal shifts to -110 ppm, suggesting that (**1**) there is some direct interaction between adsorbed salt and silicate surface, and (**2**) this interaction is with the "amorphous", rather than the laminar, regions of the structure.

In another study, a calcium montmorillonite (Carmargo White, supplied by American Colloids), has been progressively acid-treated and tested for its effectiveness as a support for $ZnCl_2$ alkylation catalyst (Rhodes et al. 1991). Maximum activity is achieved with clay subject to 20 h treatment in boiling 30 % H_2SO_4 (Fig. 3). Almost no "clay character" is observed after this treatment. The exchange capacity is very low. The material is amorphous to X-rays and elemental analysis suggests a composition close to silica (Rhodes & Brown 1992). Catalysts prepared using this support are almost twice as active as those based on K10. This illustrates the importance and potential benefit of "tuning" clay-based supports for particular catalysts.

The surface area of the most effective acid-treated clay support is also low at about 100 m^2.g^{-1}, and there is no direct relationship between surface area and effectiveness as a support (Fig. 4). There is, however, some correlation between the porosity of the support and its effectiveness. The average pore size increases steadily throughout acid treatment and a requirement for an effective support appears to be a significant volume in pores of diameter 10 - 14 nm (Rhodes & Brown 1993). Active $ZnCl_2$ is that which is adsorbed in pores in this size range. Supports tend to have a well defined capacity for active $ZnCl_2$, and if this is exceeded the catalyst is almost inactive. The capacity of acid-treated montmorillonite Carmargo White for active catalyst correlates reasonably well with the pore volume in the critical range.

The importance of porosity has been confirmed through an additional study of a range of porous silica supports with large pore volumes and well defined pore size distributions (Rhodes & Brown 1993). The correlation between the catalytic activity of supported $ZnCl_2$ and the average pore size of the support is shown in Fig. 5 for a series of progressively acid-treated montmorillonite and some microporous and mesoporous silica supports.

The question of how adsorption in mesopores enhances the activity of $ZnCl_2$ is largely unanswered. Attempts to measure the Lewis acid strength of adsorbed zinc(II) centres by studying the 1440-1450 cm^{-1} IR band of adsorbed pyridine (Rhodes & Brown 1993) indicate that there is no significant difference in acid strength between adsorbed and bulk salt. It has been suggested that enhanced activity may arise through increased accessibility of acid centres to reactant molecules as a result of a modified crystal structure adopted by the adsorbed salt. Alternatively, since catalyst activation involves the dehydration of $ZnCl_2$, enhanced activity may be related to the ease and completeness with

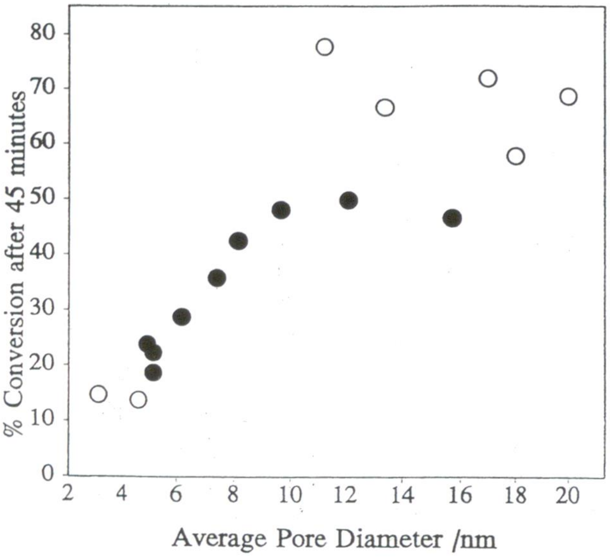


Fig. 5. Dependence of the catalytic activity of supported $ZnCl_2$ alkylation catalyst on the average pore diameter of the support. Open circles represent silica gel supports. Filled circles represent a series of progresively acid-treated montmorillonite (Carmargo White) supports, the last point (at 16 nm pore diameter) corresponding to 20h treatment in boiling 30 % H_2SO_4 (Rhodes & Brown 1993).

which adsorbed salt can be dehydrated or, possibly, its resistance to rehydration in the presence of trace amounts of water (Rhodes & Brown 1993).

Catalytic selectivity with clayzic

Some interesting observations of unusual relative reactivities towards clayzic have been made which may be useful in characterising the catalytic centres in this catalyst. For example, in benzylation reactions using benzyl chloride, the order of reactivities of methyl substituted benzenes is not as expected, but as follows:

toluene > benzene > p-xylene > mesitylene (Cornelis et al. 1991).

It seems likely that steric constraints in the vicinity of the active site depress the rate of benzylation with the more substituted benzenes. In another study it has been shown that, while clayzic is a powerful alkylation catalyst using benzyl chloride, it is far less active using benzyl alcohol. Despite this, if alkylation is attempted using a mixture of the alcohol and the chloride, the alcohol always reacts first, almost quantitatively, before reaction with the chloride begins (Davister & Laszlo 1993). Evidently, the alcohol, although not very reactive, strongly coordinates the Lewis acid sites on the catalyst, effectively poisoning them for reaction with the more reactive halide. The halide is therefore denied access to the active site until the alcohol has reacted and the products desorbed. Selectivity such as this, based on competitive adsorption of alcohols over halides, is not unusual and is also observed on a variety of other catalysts (Yadav et al. 1993).

Further evidence for the ability of polar molecules to deactivate the catalyst through acid-base interaction is provided by Barlow et al. (1993) who have shown how benzyl chloride reacts with benzene faster than with anisole ($C_6H_5OCH_3$) over clayzic, contrary to expectation. It is suggested that anisole, or the benzylated product, coordinate strongly with Lewis acid sites, either preventing reaction or retarding product desorption. The observation that at high temperatures the order of reactivities reverts to that expected is explained by dissociation of the Lewis acid-anisole complex at these temperatures.

In recent work Barlow et al. (1994) have observed that the relative rates of benzylation (with benzyl chloride) of halobenzenes compared to benzene are much higher using clayzic than in homogeneous systems. The explanation for the high activity of clayzic towards halobenzene benzylation is in terms of the rate determining step, which is the attack of the aromatic substrate on the benzyl chloride-catalyst complex (the electrophile). This occurs at zinc(II) centres located in mesopores on the support. These mesopores are very polar, and it is for this reason that selectivity is observed towards the more polar substrates, in this case halobenzenes, which enter the pores more readily than non-polar substrates like benzene.

The polarity of the mesopores depends on the activation of the catalyst. Minimal or no activation leaves the zinc(II) centres hydrated and very polar so, although these activation conditions result in low overall yields, there is significant selectivity towards the polar halobenzenes. High activation temperatures dehydrate the zinc(II) centres and generate a more active catalyst, but polarity in the mesopores is now reduced and selectivity towards polar substrates is less pronounced (Tab. 1).

Table 1: Effect of different activation methods on the rates at 40 °C of the benzylation of benzene and halobenzenes with benzyl chloride, using clayzic (Barlow et al. 1994).

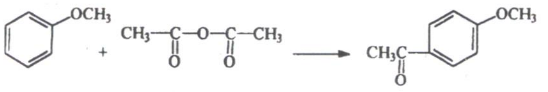
Activation method	Substrate	$k(\pm sd)/h^{-1}$
No activation		
	Benzene	0.065 ± 0.004
	Fluorobenzene	0.064 ± 0.001
	Chlorobenzene	0.081 ± 0.002
	Bromobenzene	0.227 ± 0.018
	Iodobenzene	0.154 ± 0.003
Thermal activation at 275 °C		
	Benzene	2.010 ± 0.250
	Fluorobenzene	0.603 ± 0.085
	Chlorobenzene	1.320 ± 0.200
	Bromobenzene	1.730 ± 0.280
	Iodobenzene	2.750 ± 0.240

Clay-supported acylation catalysts

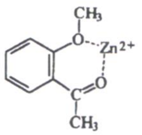
The relatively low activity of clayzic in the presence of polar molecules results in disappointing activity for clayzic in industrially important Friedel-Crafts acylation reactions (Cornelis et al. 1990, 1993a). Successful applications have generally been only with relatively facile acylations such as the reaction between benzoyl chloride and anisole to produce p-methoxybenzophenone (Cornelis et al. 1990). In one of the few cases where other clays have been examined, Georgia Kaolin (KGa-1) and an unspecified Japanese acidic clay were compared with K10 as supports for $ZnCl_2$ in this acylation study, but product yields for both were generally less than for K10-supported catalyst.

Most striking, however, is the observation that the activity of clayzic is matched or exceeded by iron(III)-exchanged K10 montmorillonite in acylation reactions (Cornelis et al. 1990), in stark contrast to most alkylation reactions where clayzic is very much more active than the ion exchanged clays. This suggests that the active site may be quite different in the two reactions, and the structural requirements for an optimised support may also differ.

Despite the disappointing overall activity of clayzic in acylation reactions, there are again examples where useful selectivity is displayed. Cornelis et al. (1993) have shown how, in the acetylation of anisole with acetic anhydride, p-acetylanisole is the major product (reaction **10**). This is attributed to the slow desorption of the other major product, o-acetylanisole, which is an excellent chelator for the catalytically active zinc(II) centres (**11**).



(10)



(11)

Clay-supported $AlCl_3$

An alternative heterogeneous acid catalyst to clayzic which would be expected to exhibit high activity is clay-supported $AlCl_3$. Deposition of $AlCl_3$ has to be carried out quite differently to $ZnCl_2$ since the salt can readily hydrolyse and lose all Lewis acidity irreversibly. Drago & Getty (1988) have successfully adsorbed $AlCl_3$ on silica by refluxing support and catalyst in CCl_4, and the same technique can be used to adsorb $AlCl_3$ on acid-treated clays (Rhodes & Brown 1992). However, the requirements for an effective support for $AlCl_3$ are rather different to those for $ZnCl_2$. Montmorillonite treated for 20 h in boiling concentrated acid forms an alkylation catalyst with $AlCl_3$ which is significantly more active than supported $ZnCl_2$, but when less thoroughly acid-treated clays are used, including montmorillonite K10 and untreated montmorillonite, supported $AlCl_3$ shows very low activity.

Despite the potential for higher activity associated with supported $AlCl_3$ catalysts, the storage difficulties (they must be kept scrupulously dry at all times) and the relatively complex method required for their preparation, may render them less attractive solid acid catalysts than the more robust clayzic family.

Clays as supports for microwave-activated reactions

Several inorganic oxides have recently been used as hosts for microwave-activated reactions in which the reactants are adsorbed on the host and no solvent is present. These "dry reactions" eliminate the flammability risks associated with using bulk organic solvents with microwave sources. Furthermore, because these inorganic hosts are generally transparent to the microwave frequencies used, activation of the adsorbed organic reactants can be extremely efficient. There are many examples where microwave activation results in very much higher reactivity than thermal activation (Bram et al. 1992).

The acid montmorillonite K10 (see above) and the related KSF have been used in acid-catalysed dry reactions of this type (Bram et al. 1992, and references therein). Phthalodinitrile impregnated on K10 exchanged with metallic cations [Cu(II), Co(II), Mn(II), Fe(II)] gives metal complexes of phthalocyanines on the clay support. These can be extracted with concentrated H_2SO_4. Benzaldehyde and pyrrole yield coloured porphyrins on the same supports under microwave activation. This reaction is a possible model of prebiotic synthesis of metalloporphyrins.

Pinacol is easily rearranged to pinacolone on KSF acid montmorillonite (Alloum et al. 1989). Activity is lost if the KSF is exchanged with Na(I) or Ca(II), clearly demonstrating the essential role of surface Brønsted acid sites in this reaction.

Tetronic acid and aromatic aldehydes adsorbed on KSF or K10 yield 3-(arylmethylene) derivatives under microwave activation. This type of structure is known in many biologically active compounds, some of which show anti-tumour activity (Villemin & Labiad 1990).

Clay-supported oxidation reagents have also been used in microwave-activated dry reactions. Alverez et al. (1991) have reported the efficient oxidation of several 4-aryl-1,4-dihydropyridines to pyridine compounds using MnO_2 supported on a Mexican bentonite under microwave activation and in the absence of solvent.

Conclusion

Clays have been used with some success as supports for metal catalysts. They are, however, unlikely to replace the traditional silica, alumina and activated carbon supports which, in general, provide higher surface areas and finer metal dispersions. Nevertheless, in certain applications where the lamellar nature of the support can provide molecular sieving or selectivity advantages, there may be justification for using a swelling clay or a pillared smectite as a catalyst support. Similarly, in cases where there are advantages in having some of the metal in cationic form, clays again have clear application. Although they do not fit the definition of supported catalyst adopted in this review, those clay-based catalysts where the active centres are not metal particles but intercalated ionic metal complexes often elegantly exploit the potential of clay supports, to provide activity and selectivity in a wide range of reactions.

Clays are finding an increasing number of roles as supports for simple metal salt catalysts. Perhaps the most important are supported metal halides for use in Friedel-Crafts alkylations and acylations. In general acid-treated clays are used. In addition to providing bases for stable, easy to handle catalysts, these supports confer remarkable enhancements in activity to the supported salts. However, relatively little effort has been devoted to systematically optimising the properties of the acid-treated clay supports for particular catalysts, and there is no doubt that the full potential of this class of clay-supported catalyst is still to be exploited. Acid clays in particular are proving very useful as supports in "dry reactions" under microwave activation. Again, systematic study of the precise role of the clays in these reactions may well yield further improvements in activity.

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