Clays as Selective Catalysts in Organic Synthesis*

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Abstract. Suitably modified smectite clays can be very selective catalysts for a wide range of organic reactions. While it has long been known that such materials can act as Bronsted and Lewis acids, it has been shown recently that they are also effective Diels-Alder catalysts. A selection of illustrative reactions is given which emphasises their wide range of use, their selectivity, and the ease of work-up after reaction. In each case, mechanistic information is presented, e.g., on the site of reaction (whether interlayer or surface), rate determining steps, etc. The regiochemical consequences of the restricted reaction space are stressed.

Key words: Clay, montmorillonite, bentonite, catalyst, catalysis, organic synthesis, organic reactions.

1. Introduction

Organic synthesis has much to gain from the introduction of suitable heterogeneous catalysts [1]. In the last few years numerous examples in this field have shown great selectivity with reduction in the severity of reaction conditions and with great ease of work-up (see, e.g. [2]). One family of catalysts that has received much attention is based on clay minerals. A glance at any of the standard works dealing with these materials (see, e.g. [3]) shows that much is already known about the interaction of a variety of organic materials with these solids. Moreover, many spectroscopic and other studies have been carried out on sorption complexes (see, e.g. [4, 5]). Much less, however, and that of a relatively recent nature, is known about reactions which have been carried out on a preparative scale.

Smectite clays and their derivatives [6] show catalytic activity in a variety of reactions. Here we will concentrate mainly on reactions of the sub-groups of smectites known as montmorillonites. These materials have a layered structure (Figure 1) with each layer having a small net negative charge due to isomorphous substitution of ions in the framework [6]. This charge is compensated by interlayer cations which are surrounded in nature by a co-ordination shell of water.

Catalysts based on these clays have been used over the last few decades in such industrial processes as the dimerization of fatty acids [7]. They have also begun to be used in laboratory syntheses of, e.g., acetals [8, 9].
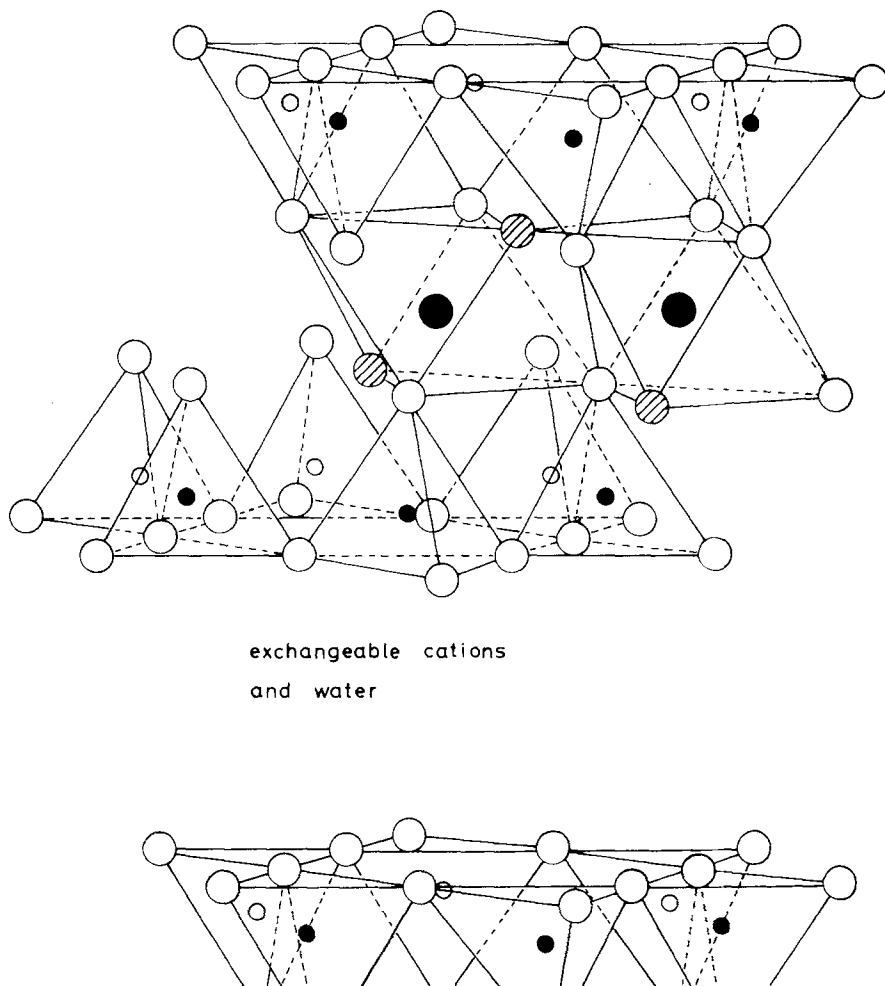
exchangeable cations

and water

Fig. 1.   Structure of smectite clays.

Most of the reactions catalyzed by montmorillonites make use of their acidic nature. Both Bronsted and Lewis activity have been noted, the latter deriving from iron and aluminium ions at the edges of crystallites [3].

The Bronsted activity, however, results from the dissociation of the interlayer water molecules coordinated to polarizing exchangeable cations. This acidity has been shown [10, 11] to increase at low water content and is maximized when the sodium and calcium ions, often present in natural clays, have been replaced with more highly polarizing species such as Cr^{3+}. The equilibrium $[Cr(OH_2)_n]^{3+} \rightleftharpoons$ $[Cr(OH_2)_{n-1}OH]^{2+} + H^+$, provides the 'free' protons for reaction with organic molecules.

Although clay catalysts have often been used merely as convenient solid acids, they are more versatile than is often imagined. It is, for example, possible (by use of clays from different sources, with different degrees of substitution) to select particular distances between the interlayer cations. On occasion this has been shown to affect

the size of product molecules formed [12]. The distance between the clay layers – the other variable in the design of 'reaction space' – can also be independently varied, often by suitable choice of solvent [13]. The nature of the interlayer cation can be crucial in reaction design and performance [14] while substitution of the related minerals hectorite* and beidellite* can completely alter the product yield and distribution [15, 16].

It is apparent, then, that clay-based catalysts have a wide potential degree of utility in acid-catalyzed and other reactions. Shape selectivity and product distribution ratio engineering are also possible.

2. Catalyst Preparation

While not essential in most preparations, if the highest activities are required, the montmorillonite component of the natural bentonite ore should be separated from mineral impurities using well-documented sedimentation procedures [17]. Methods of cation exchange of the clay and the subsequent washing steps to remove excess salt are also well known [13]. It should be noted in this context, however, that while some cationic species are stable in solution over a wide concentration and pH range, others are not. The most obvious example of the latter situation is with solutions containing aluminium. For this element, many polyoxo cationic species are known to be stable, each in a limited pH (and therefore concentration) range [18]. Consequently it can be difficult to ensure a reproducible Al^{3+}-clay.

Heating of cation-exchanged clays leads to loss of interlayer water. Especially for clays exchanged with small monovalent cations, heating much above 100 °C leads to a decrease in the interlayer spacing ('collapse of the clay layers'), after which re-expansion is difficult. For multivalent-cation-exchanged clays the greater stability of the primary co-ordination sphere of the interlayer cation means that the layers do not collapse completely even at 300 °C. As a general rule it is preferable to dry clay at as low a temperature as possible (usually 40–50 °C). Recent work by Breen and Deane [9] has shown how excessive heating of Al^{3+}-, Cr^{3+}- and Fe^{3+}-clays leads to a reduction in acidity.

Since the Bronsted activity of smectite clays depends so critically on water content [10, 11] it is advisable to ensure a known interlayer water content by equilibration of the clay at a known relative humidity (RH) before reaction [20].

While solvents in clay catalyzed reactions are often chosen for their reflux temperatures or for solubility reasons, it is known that even allowing for these factors, use of different solvents can cause large variations in yield (see, e.g. [21, 22]). Not enough is yet known concerning the relationship between interlayer reactant and product concentrations, the rates of diffusion of these species and how these are related to the interlayer spacing of the clay as a function of solvent type.

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* Hectorite and beidellite have similar structures to montmorillonite; they also have layer charges which are comparable to that mineral. The chief differences between these silicates is in the elemental composition in the octahedral and tetrahedral sites in the clay layers. Typical natural formulae are:

	octahedral	tetrahedral	interlayer
Montmorillonite	$(Al_{3.5}Mg_{0.5})$	Si_8	$O_{20}(OH)_4 \cdot Na_{0.5}(H_2O)_n$
hectorite	$(Mg_{5.5}Li_{0.5})$	Si_8	$O_{20}(OH)_4 \cdot Li_{0.5}(H_2O)_m$
beidellite	Al_4	$(Si_{7.3}Al_{0.7})$	$O_{20}(OH)_4 \cdot Ca_{0.35}(H_2O)_p$

3. Reactivity

3.1. BRONSTED ACID CATALYSIS

These reactions involve a nucleophilic attack on a protonated species. It follows that if this cationic moiety can rearrange in some way (e.g. protonated alkenes undergo hydride shifts and other rearrangements), then a variety of possible products may result, whereas if a stable ion such as Me_3C^+ is formed, essentially one product may be given in high yield.

Ballantine *et al.* [23] have pointed out that montmorillonite based clays act as a reactive source of a limited number of protons. In many reactions, for example between alkenes and alcohols, products are formed after nucleophilic attack on the less electronegative species [13]. This implies that reactions might be limited by protonation of the alkene and subsequent nucleophilic attack, rather than by diffusion through the interlayer region.

After surveying the Bronsted acid activity of cation-exchanged clays, Adams *et al.* [24] produced a set of 'rules' which are given below:

1. (a) Cr^{3+} and Fe^{3+} are the most active interlayer cations.
   (b) Although Al^{3+} is also active, the exact procedures used for the ion-exchange and washing steps are critical for giving catalysts of reproducible activity.
2. (a) Below 100 °C, the reactions proceed provided they involve tertiary or allylic carbocation intermediates.
   (b) At 150–180 °C reactions involving primary and secondary carbocations are possible.
3. (a) Reactions of carbocations with unsaturated hydrocarbons take place overwhelmingly in the interlayer region of the clay, where the hydrocarbon double bond can be polarized.
   (b) Reactions of carbocations with polar, oxygenated, species can take place on the surface of the clay particles as well as in the interlayer space.
4. (a) When acid-catalyzed reactions are performed in the liquid phase and involve tertiary carbocations, the most suitable solvents are those that provide miscibility; 1,4-dioxan is especially good.
   (b) When more acid conditions are required for the formation of primary and secondary carbocations, a non polar solvent is more efficacious.

Laszlo [25] has pointed out that the involvement of primary carbocations (rules 2(b) and 4(b)) is unlikely. Moreover, in rule 2(a) benzyl carbocations should also be included.

3.2. LEWIS ACID CATALYSIS

Potential Lewis acid centres exist in smectite clays. Al^{3+} and Fe^{3+} ions are normally associated with the octahedral sheets of the montmorillonite, but the co-ordination sphere of these ions is likely to be made up of water molecules or OH groups when they are exposed at crystal edges. Moreover, it is only as a result of magic angle spinning nuclear magnetic resonance (MASNMR) studies (see, e.g. [26]) that it was discovered that 5–10% of the aluminium in montmorillonites is in tetrahedral sites.

When reactions are carried out at low temperatures in solvents which could

coordinate to the potential Lewis centres, it appears unlikely that Lewis acid processes could be occurring. However, in many cases reactions are carried out above 100 °C after dehydration of the clay by vacuum or heat treatment or both. In these circumstances, the possibility of Lewis rather than Bronsted acid activity exists.

3.3. DIELS-ALDER REACTIONS

Until very recently, montmorillonites were not recognized as Diels-Alder catalysts, except in the special case of oleic acid dimerization [7], and here it can be argued that the function of the clay is to effect necessary preliminary processes before the Diels-Alder step, while this cycloaddition itself could well be thermal, since the reactions are carried out at ~230 °C.

Laszlo and Lucchetti [27–29] and Adams *et al.* [30, 31] have, however, shown that montmorillonites exchanged with transition metal ions (or Fe^{3+}-exchanged acid treated montmorillonite) are effective for a variety of Diels-Alder reactions, while clays exchanged with non-transition metals are often poor catalysts. It appears possible that in many cases the clays act not as Lewis acid Diels-Alder catalysts [32], but rather a one-electron transfer to the transition metal ion is involved, leading to a radical cation catalyzed process [33].
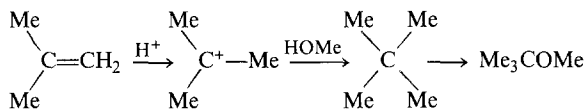
3.4. POLYMERIZATIONS

Studies on polymerization of a variety of monomers over clays led Solomon and his co-workers (see, e.g. [34]) to suggest the involvement of one electron transfer processes taking placing at aluminium ions and, more likely in our view, transition metal ions of the clay framework exposed at edge sites. A body of work on polymerization of aromatic species over Fe^{3+}- and Cu^{2+}-exchanged montmorillonites (see [35] and references therein) has also confirmed the formation of radical cations (by electron transfer from the aromatic ring to the metal cation) as intermediates in the production of high molecular weight species.

4. Examples of Preparative Reactions

The examples we have set out below were chosen because they illustrate some features of interest in the behaviour of this class of catalysts, i.e. the effect of clay water content, control of reactivity by choice of inter-layer cation, the effect of solvent on yield and stereochemistry and the effect of variation in layer charge of the smectite. In all cases the reactions are carried out at low temperatures, they are very selective and the work-up is simple.
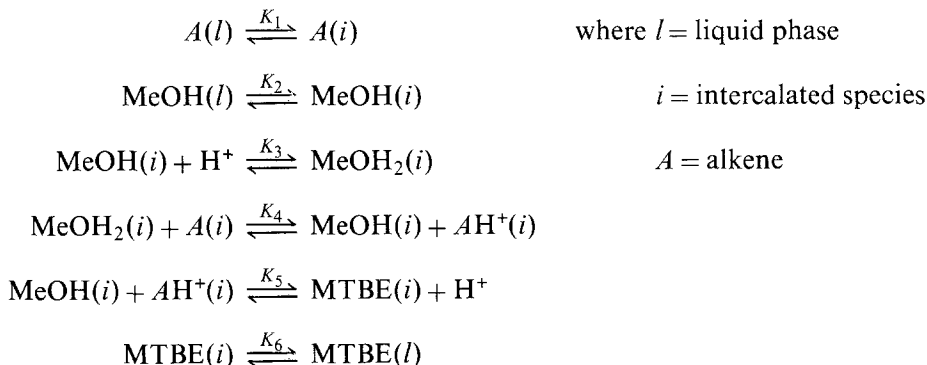
4.1. ETHER PRODUCTION FROM ALCOHOLS AND ALKENES

Alcohols can add on to alkenes in the presence of montmorillonite catalysts to give ethers [13, 36]. The reaction with alk-1-enes is slow and gives mixtures of alk-2-yl and alk-3-yl ethers [36] due to rearrangement of the intermediate carbocation formed on protonation of the alkene. In contrast, the reaction of alcohols with isobutene gives high yields of the tertiary ether at low temperatures [21, 22] .

$$\underset{Me}{\overset{Me}{}}\hspace{-0.5em}C{=}CH_2 \xrightarrow{\ H^+\ } \underset{Me}{\overset{Me}{}}\hspace{-0.5em}C^+{-}Me \xrightarrow{\ HOMe\ } \underset{Me}{\overset{Me}{}}\hspace{-0.5em}C\hspace{-0.5em}\underset{Me}{\overset{Me}{}} \longrightarrow Me_3COMe$$

<div align="center">Scheme 1.</div>

Montmorillonites of suitably high acidity (Cr^{3+}, Fe^{3+} and Al^{3+}-exchanged clays equilibrated at low humidity (12% RH)) give yields of ~60% after 50 min at 60 °C [21], an activity around 60% of that of the ion-exchange resins used industrially for this process [37]. Only small amounts of various by-products are formed: *t*-butanol and 'isobutene dimers' from attack of water and alkene on the intermediate carbocation, and dimethyl ether from dehydration of methanol [21]. When using divalent interlayer cations such as Cu^{2+}, Co^{2+} and Ni^{2+}, the reaction yields are much lower, certainly not giving more than ~10% of the activity of clays containing M^{3+} ions [21]. Monovalent cation-exchanged clays are essentially inactive. This critical dependence on interlayer cation suggests strongly that the reaction is catalysed by the Bronsted acidity associated with interlamellar hexaquo-M^{3+} ions, and this can be confirmed either by using catalysts in which the interlayer cation has been replaced by diprotonated DABCO⋆ molecules [21] or those in which heat treatment has effectively collapsed the silicate layers, making ingress of reactant species difficult [13]. In both cases the catalysts lack activity.

Following the procedure adopted by Purnell and Ballantine [38] we can construct a reaction scheme as shown below:

$$A(l) \underset{\rightleftharpoons}{\overset{K_1}{}} A(i)$$

$$MeOH(l) \underset{\rightleftharpoons}{\overset{K_2}{}} MeOH(i)$$

$$MeOH(i) + H^+ \underset{\rightleftharpoons}{\overset{K_3}{}} MeOH_2(i)$$

$$MeOH_2(i) + A(i) \underset{\rightleftharpoons}{\overset{K_4}{}} MeOH(i) + AH^+(i)$$

$$MeOH(i) + AH^+(i) \underset{\rightleftharpoons}{\overset{K_5}{}} MTBE(i) + H^+$$

$$MTBE(i) \underset{\rightleftharpoons}{\overset{K_6}{}} MTBE(l)$$

where l = liquid phase

i = intercalated species

A = alkene

As was found previously in resin catalyzed reactions when using stoichiometric amounts, or an excess of methanol [39], the rate of reaction was found to be proportional to the isobutene concentration [22], with the rate determining step appearing to be the protonation of the alkene (step 4 above). This result adds weight to the view that diffusion limitations are often not apparent in clay catalyzed reactions [46]; however, such a view is open to dispute, since little work on the application of Fick's Laws to diffusion in clays had been published.

Solvent effects in this reaction can be very great, with use of 1,4-dioxane increasing the rate six-fold over reactions without solvent, while carbon tetrachloride, toluene, 1,2-dimethoxyethane, diethylene glycol diethyl ether, *n*-pentane, tetrahydropyran, *N*-methylmorpholine and tetrahydrofuran are all at least ten times worse than
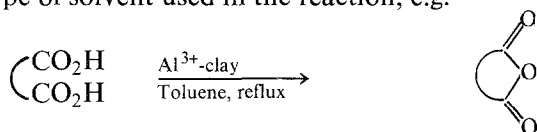

⋆ 1,4-Diazabicyclo [2.2.2]octane. *CA* Registry No. 280-57-9.

dioxane [21, 22]. The reason for this is not clear. Certainly dioxane promotes miscibility of all reagents and products and can also give high concentrations of interlayer isobutene, but other solvents in this list, such as tetrahydropyran and tetrahydrofuran should not be very much poorer in these regards [21].

In conclusion then, provided a high acidity clay is used with a suitable solvent, tertiary ethers can be produced in good yields at low temperatures. At the end of the reaction, the catalyst can be removed simply by filtration.

4.2. CYCLIC ANHYDRIDE FORMATION

α, ω-Dicarboxylic acids generally require quite severe conditions to convert them to cyclic anhydrides – i.e. high temperatures with strong acids [40], yet clays are known to be excellent dehydration catalysts (see, e.g. [41]). Studies made using Al^{3+}-exchanged clays with a range of acids have shown that the efficiency of the reaction is highly dependent on the size of the anhydride ring formed, and also on the type of solvent used in the reaction, e.g.

Toluene was found to be an excellent solvent for formation of 5-ring anhydrides with essentially complete conversion being achieved in 2 h under reflux. However, with this solvent, formation of 5-, 7- and 9-ring anhydrides was poor (Table I). The facility of 5-ring formation is due to the low ring strain of these planar (or near planar) anhydrides together with the favourable entropy factors in bringing the two ends of the molecules together; for larger rings these factors are less favourable. A variety of solvents with a range of boiling points were used for similar large-ring-forming reactions, but gave essentially no product unless the solvent gave both a suitably high reaction temperature and a relatively great distance between the clay layers (Table II). These facts confirm that the reaction is truly interlamellar and that the Bronsted acidity of the hexaquo aluminium ions is probably responsible for the catalytic effects. When these conditions were achieved, there was a marked improvement, especially for 6-ring anhydrides, with glutaric acid giving almost complete conversion when heated under reflux in 1,1,2,2-tetrachloroethane.
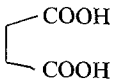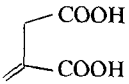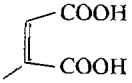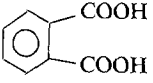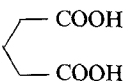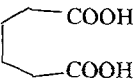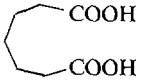
One of the special features of this reaction is that the position of carbon-carbon double bonds in the diacid reagent remains unchanged, i.e. no isomerization occurs, whereas comparable reactions carried out with zeolites* cause double bond migration [42]. As the diacid molecules are too bulky to enter the zeolite pores the catalytic sites in this instance are probably defects on the surface.

4.3. DIELS-ALDER REACTIONS

Laszlo and Lucchetti [27–29] showed that a commercial acid-treated montmorillonite (K10, Sud-Chemie) exchanged with Fe^{3+}-cations was a very effective catalyst in a

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* We have recently noted that $3A$, $4A$ and $5A$ molecular sieves, but not $13X$ or $13Y$ sieves, are able to catalyse the formation of 5- ring anhydrides together with double bond migration. However, the rate of reaction rapidly decreases as the zeolite pore size increases: $3A$ ca 2 h, $4A$ ca 4 h and $5A > 6$ h under similar conditions.

Table I. Yields of cyclic anhydrides from α, ω-diacids in Al^{3+}-clay catalyzed reactions using toluene solvent

Acid		Type of product	Time	% yield
Succinic	COOH / COOH	5-ring	$2\frac{1}{2}$ h	98
Itaconic	COOH / COOH	5-ring	$2\frac{1}{2}$ h	95
Citraconic	COOH / COOH	5-ring	$2\frac{1}{2}$ h	100
Phthalic	COOH / COOH	5-ring	$2\frac{1}{2}$ h	100
Glutaric	COOH / COOH	6-ring	3 days	<5
Adipic	COOH / COOH	7-ring	3 days	0
*Suberic	COOH / COOH	9-ring	3 days	0

* A small yield of this 9-ring anhydride was obtained after 2 days under reflux in 1,1,2,2-tetrachloroethane with Al^{3+}-clay.

Table II. Influence of solvent boiling point and clay interlayer spacing on reaction yield

Solvent	Δ_d*	b.pt/°C	% conversion	
			itaconic acid to 5-ring anhydride	glutaric acid to 6-ring anhydride
1,1,1-trichloroethane	14.0	75	0	0
2,2,4-trimethylpentane	4.1	99	100%, 18 h	0
1,4-dioxan	5.0	101	100%, 18 h	0
toluene	5.5	111	100%, $2\frac{1}{2}$ h	<5%, 3 days
n-octane	2.9	126	25%, 24 h	0
ethyl benzene	4.3	136	100%, 4 h	trace
o-xylene**	4.3	146	–	88%, $2\frac{1}{2}$ h
1,1,2,2-tetrachloroethane**	5.5	147	100%, $3\frac{1}{2}$ h	100%, 7 h

* Δ_d is the interlayer space free for reaction. It is defined as the basal spacing of the clay minus the spacing obtained if the layers are collapsed, i.e. Δ_d = basal spacing − 9.6 Å.
** At these high reflux temperatures the catalyst began to coke up after ~3 h.

range of Diels-Alder processes. The efficiency of the catalyst was high, and it could be removed from the reaction mixture merely by filtration. Somewhat earlier, Downing *et al.* [43] had shown that Cu^+-exchanged montmorillonite could be used successfully at ~ 100 °C to cyclodimerize 1,3-butadiene.

This type of study has now been extended to examine the efficiency of various metal exchanged (non-acid-treated) montmorillonites. Adams and Clapp [44] showed that all of the clays they examined, which had been exchanged with transition metal ions, were effective for the dimerization of butadiene and isoprene, with this activity starting at very low temperatures, below 50 °C. It was apparent that although the percentage conversion of the diene increased dramatically in the series $M^+ < M^{2+} < M^{3+}$ for interlayer ions, this mainly resulted from competitive, nonconcerted (i.e. acid catalyzed) processes. The yield of cyclodimer was comparable in all cases. While Diels-Alder reactions with polar dienophiles are often catalyzed by Lewis acids [32], with conjugated hydrocarbon dienophiles the most likely mechanism involves transfer of one electron from the dienophile [33] to the interlayer cation or to Fe^{3+}-ions in the clay layer possibly via the interlayer cation. Certainly it was noted that Al^{3+}-exchanged clays proved ineffective as catalysts.

The reaction of cyclopentadiene with methyl vinyl ketone in dichloromethane was studied as a direct comparison with the work of Laszlo and Lucchetti [28]. Their work was also extended to the dimerization of cyclopentadiene and by comparing the Fe^{3+}-K10 catalyst with various cation exchanged montmorillonites. Fe^{3+}- and

Table III. Comparison of the activity of various catalysts for the reactions (a) of cyclopentadiene and methyl vinyl ketone and (b) of cyclopentadiene dimerization

Catalyst	(a) Reaction of cyclopentadiene and methyl vinyl ketone[1]		(b) Reaction to give cyclopentadiene dimers[2]
	Yield after 20 min (%)	*Endo:exo* ratio[3] in product	Yield after 15 min (%)
Fe^{3+}-K10	97	9:1	53
Fe^{3+}-montmorillonite	93	7:1	39
Cr^{3+}-montmorillonite	91	9:1	30
Al^{3+}-montmorillonite	20	8:1	–
No catalyst (control)	17	~13:1	0

Note: (1) Reactions carried out at 22 °C with dichloromethane solvent. The solvent and dienophile were equilibrated with the clay before addition of the diene. No diene dimers were seen.

(2) *Endo:exo* ratios for the cyclopentadiene dimerization could not be obtained from the proton NMR data measured.

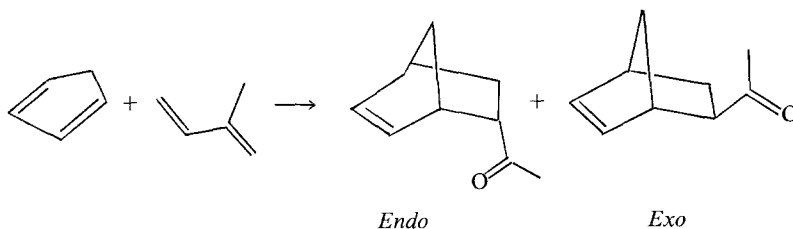(3) The reaction of cyclopentadiene with methyl vinyl ketone is:

Endo   *Exo*

Table IV. Effect of the variation of the dienophile on the reaction rate[1]

Dienophile	Yield after 5 min (%)	*Endo*:*exo* ratio in product
Methyl methacrylate	0	–
Methyl acrylate[2]	60 (22 h)	2:1
Methyl vinyl ketone	~60	9:1
Cyclopentadiene	10–15	–
Allyl chloride	0[3]	–

Note: (1) Reactions were between cyclopentadiene and the dienophile specified. They were carried out with Cr^{3+}-montmorillonite catalysts at 22 °C in dichloromethane solvent.

(2) If a normal clay was used, severe coking up occurred and reaction stopped. De-ferration of the Cr^{3+}-clay catalyst [45] enabled the yield quoted above to be achieved.

(3) With allyl chloride, only cyclopentadiene dimers were detected.

Cr^{3+}-clays were found to have activities comparable to that of Fe^{3+}-K10 (Table III) and it was noteworthy that Cr^{3+}-clays gave a much cleaner reaction (with no coking) than Fe^{3+}-clays. Since Fe^{3+}-K10 has a much larger nitrogen surface area than the ion-exchanged clays (250 *vs* 50 $m^2 g^{-1}$), it is apparent that reactions were not catalyzed solely at the surface, but must have involved the M^{3+} species in the interlayer region of the nonacid treated clays (note that the cation exchange capacity of the materials are similar). This involvement of interlayer ions implies that diffusion in the interlayer space is not limiting. The fact that transition metal cations are active, while Al^{3+} is not, again suggests a radical cation catalyzed Diels-Alder reaction [33]. Most of the solvents tested were of about equal efficiency in the reaction (benzene, carbon tetrachloride, dichloromethane, chlorobenzene and 1,1,2,2-tetrachloroethane); only chloroform gave a significantly different (and lower) yield, probably because of the notable catalyst coagulation that took place.

The rates of reaction of cyclopentadiene with various dienophiles were also compared (Table IV). The order of reactivity did not, however, follow that predicted by consideration of the degree of activation of the double bond. Methyl methacrylate and methyl acrylate were much less active than expected. Similar inhibition of free radical polymerization of clays was suggested by Solomon [34] to be due to bidentate coordination of the ester to aluminium ions at the edges of the clay platelets.

We also considered the interesting question of *endo*:*exo* ratios in these reactions. Although the transition state is the same for both products, the *endo* and *exo* forms have different degrees of bulkiness. If the reactions are taking place between the clay layers, it was considered that the less bulky product would be preferred if the layers were held more tightly together. We carried out reactions using three related Cr^{3+}-exchanged clay mineral catalysts and were able to alter the *endo*:*exo* ratio by a factor of 4 [Table V] .

We have shown then that, as Laszlo and Lucchetti [27] first pointed out for Fe^{3+}-K10, it is not necessary to use inconvenient aqueous solution or suspension to promote rapid regioselective Diels-Alder reactions, they can also be carried out in the presence of clay catalysts. By choice of a suitable clay it is possible to select suitable *endo*:*exo*

Table V. Summary of catalytic performance of Cr^{3+}-exchanged clay catalysts for the reaction of cyclopentadiene with methyl vinyl ketone at 22 °C in dichloromethane (20 min reaction)

Clay catalyst	Layer charge*	Δ_d/Å	Yield %	Endo/exo ratio
Cr^{3+}-montmorillonite[1]	0.37	6.8	91	9 : 1
Cr^{3+}-montmorillonite[2]	0.60	3.2	80	6 : 1
Cr^{3+}-vermiculite[3]	0.65	3.1	43	3 : 1

[1] Tonsil-13 clay supplied by Sud-Chemie AG, Munich.
[2] Clay RLO1987 supplied by English China Clays International, St. Austell.
[3] Vermiculite from Palabora, South Africa.
* Layer charge quoted is per $(Si, Al)_4O_{10}(OH)_2$ unit.

ratios. Moreover, we can stress again that for organic synthesis there is a greater ease of reaction work-up, the catalysts being easily removed by filtration. However, the degree of reactivity of a diene/dienophile pair cannot always be predicted accurately in advance.

5. Conclusions

As we hope we have illustrated satisfactorily, ion exchanged clay minerals have a wide variety of uses as Bronsted acid and radical catalysts. The cleanliness of the reactions and the ability to control the inter-layer distance and the interlamellar solvent environment has led to the development of highly regioselective and enthalpy selective processes. Such selectivity engineering could prove to be invaluable in both industrial processes and to the synthetic organic chemist.

Acknowledgements

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