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Contribution of different mechanisms and different active sites to the clay-catalyzed Diels–Alder reactions

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Abstract

Cation-exchanged K10 montmorillonites display a high Lewis/Brønsted acidity ratio, and efficiently promote the reaction of (–)-menthyl acrylate with cyclopentadiene. The clays silylated with trimethylchlorosilane are worse catalysts, due to the decrease in the number of acid sites. This effect is particularly important when the silylation is carried out under argon atmosphere. On the other hand, rehydration of the silylated clay gives rise to the appearance of Brønsted acid sites, able to promote the reaction. The elimination of Lewis acidity by silylation shows the role of the hydroxyl groups of the clay. The use of anisole as a solvent improves the catalytic activity of the silylated clays, but the endo/exo and the diastereofacial selectivities are lower, which is due to a radical cation mechanism. Given that the Zn(II)-exchanged clay also shows this effect, the structural Fe(III) of the clay must contribute to this radical cation mechanism. The results obtained show how different treatments modify the properties of the clays.

Keywords: Diels–Alder; Clays; Montmorillonites; Acid sites

1. Introduction

Clay minerals are the solids most frequently used to promote Diels–Alder reactions and, as a consequence, several mechanisms have been proposed to account for their catalytic activity.

The increase in rate and endo/exo selectivity of some Diels–Alder reactions carried out in aqueous media has been invoked to propose that internal water of the clays is responsible for a part of their catalytic activity [1]. However, the

elimination of water by calcination improves the catalytic activity of the cation-exchanged K10 montmorillonite, which indicates that the role of water is not very important [2].

Reducible species in the catalyst are able to accept one electron and promote Diels–Alder reactions through a radical cation mechanism, and this mechanism has been proposed to act in the dimerizations of 1,3-dienes promoted by Fe(III)- [3] and Cr(III)-exchanged clays [4] and in the reaction of 2,3-dimethylbutadiene with acrolein promoted by Fe(III)-exchanged K10 montmorillonite in the presence of 4-*tert*-

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butylphenol [5]. The formation of radical cations has been shown by EPR with Fe(III)-, Cu(II)- and Ce(IV)-exchanged K10 montmorillonites and it is favoured by the use of anisole as a solvent [6]. Whereas the formation of radical cations favours the dimerization of 1,3-dienes [3,4], it is not so clear that it favours Diels–Alder reactions with activated dienophiles because its effect has been always studied in solids with acid properties. The formation of radical cations promotes the polymerization of the diene and, as a consequence, may be negative in Diels–Alder reactions of normal type [7].

Acid properties seem to be the main responsible for the catalytic activity of clays in Diels–Alder reactions with activated dienophiles, in fact the catalytic activity is proportional to the number of acid sites [8]. Although clays with higher Lewis/Brønsted acidity ratios are better catalysts [2,6,7], the catalytic role of Brønsted acid sites could not be discarded. However, in a recent paper [9] it has been suggested that d orbitals of the exchanged transition metal cations are responsible for the catalytic activity of cation-exchanged clay minerals and the role of Brønsted acid sites has been discarded.

In view of this, it seems that the following three mechanisms: Brønsted acidity, Lewis acidity and radical cations, or some of them, are the responsible for the catalytic activity of cation-exchanged clays in Diels–Alder reactions. However, the relative importance of these mechanisms and their influence on the different selectivities is not clear. With the aim of clarify this point we have modified several cation-exchanged K10 montmorillonites in order to favour

one or another mechanism, and these clays have been used in the reaction of cyclopentadiene (**1**) with (*1R, 2S, 5R*)-menthyl acrylate (**2**) (Scheme 1). The use of this reaction as a model is justified because it is not very fast in solution in the absence of a catalyst, and therefore the conversion characterizes the catalytic activity of the solid. Furthermore, the asymmetric induction may be very sensitive to changes of the reaction mechanism.

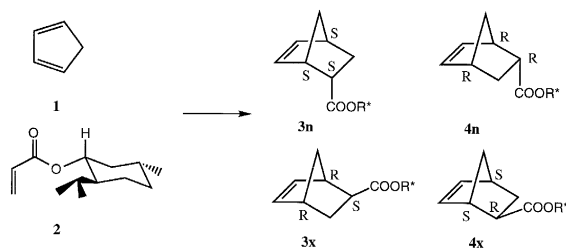
2. Experimental

K10 montmorillonite and tris(4-bromophenyl)ammoniumyl hexachloroantimonate were purchased from Aldrich. Cation exchange and calcination were carried out as previously described [7]. Surface areas were calculated from BET isotherms determined at 77 K. In all cases the values obtained fall within the range of 220–240 m² g⁻¹. X-ray diffraction patterns were recorded using Cu–K_{α1} radiation and they do not change upon silylation.

Acidic properties were determined by adsorption of pyridine as a probe molecule on self-supported wafers. The wafers were compressed under 5 tons cm⁻² pressure to obtain thin disks 18 mm in diameter with a weight of ca. 10 mg g⁻¹. The resulting wafers were placed in cells (equipped with KBr windows and connected with stopcocks to a vacuum line) where the treatment of the catalysts was carried out. Infrared spectra were recorded using a Nicolet 320 FT-IR spectrophotometer, after desorption of pyridine at different temperatures.

2.1. Silylation procedure

1 g of the calcined clay was suspended in a solution of trimethyl chlorosilane (0.4 ml) in 40 ml of dry toluene and the mixture was refluxed overnight. The clay was separated by filtration, washed with dichloromethane (3 × 50 ml) and heated at 140°C overnight before use. Alternatively, the treatment was carried out under ar-



Scheme 1.

gon atmosphere, the solvent and the excess of trimethyl chlorosilane were eliminated at reduced pressure under argon flow, and the catalyst was used immediately.

2.2. Reaction between cyclopentadiene (1) and (–)-menthyl acrylate (2) catalyzed by clays

Under argon, to a suspension of the corresponding clay-catalyst (0.5 g) in dry dichloromethane or anisole (8 ml), (*1R*, *2S*, *5R*)-menthyl acrylate (2) (0.210 g, 1 mmol) and freshly distilled cyclopentadiene (1) (amounts described in Table 1) were added with a syringe. The reactions were monitored by gas chromatography (FID from Hewlett-Packard 5890 II, cross-linked methyl silicone column 25 m × 0.2 mm × 0.33 μm, helium as carrier gas 19 psi, injector temperature 230°C, detector temperature 250°C, oven temperature program 190°C (1 min)–2°C/min–180°C (0 min)–

1°C/min–170°C (5 min), retention times: (*1R*, *2S*, *5R*)-menthyl acrylate (2) 3.9 min, (5) 4.2 min, (6) 4.6 min, (3x + 4x) 18.9 min, (3n) 19.6 min, (4n) 20.0 min). Absolute configurations were assigned by comparison with the gas chromatograms obtained in Lewis acid-catalyzed reactions previously described [10]. To eliminate the possibility of adsorption of reagents and/or products, clays were filtered, thoroughly washed, and the solutions analyzed again by gas chromatography.

2.3. Reaction between cyclopentadiene (1) and (–)-menthyl acrylate (2) catalyzed by (BrC₆H₄)₃NSbCl₆

Under argon, to a solution of (BrC₆H₄)₃NSbCl₆ (0.082 g, 0.1 mmol) in dry dichloromethane or anisole (8 ml), (*1R*, *2S*, *5R*)-menthyl acrylate (2) (0.210 g, 1 mmol) and freshly distilled cyclopentadiene (1) (amounts

Table 1

Results obtained in the Diels–Alder reaction of cyclopentadiene (1) with (–)-menthyl acrylate (2), in CH₂Cl₂, promoted by K10 clays calcined at 550°C, with and without end-capping (EC) carried out in normal or argon (Ar) atmosphere, together with their Lewis/Brønsted acidity ratios

Clay	Solvent	1 h				24 h				
		2:1	% conv. ^a	endo/exo ^a	% de ^{a,b}	2:1	% conv. ^a	endo/exo ^a	% de ^{a,b}	L/B ^c
Zn(II)	CH ₂ Cl ₂	3	46	92:8	41	5	99	92:8	41	16.3
Zn(II)-EC	CH ₂ Cl ₂	3	17	92:8	46	5	48	89:11	37	1.0
Zn(II)-EC-Ar ^d	CH ₂ Cl ₂	3	8	93:7	46	5	22	90:10	41	—
Zn(II)-EC-Ar	anisole	3	9	84:16	30	5	22	84:16	25	—
K10-EC-Ar	CH ₂ Cl ₂	3	10	93:7	46	5	24	89:11	40	—
K10-EC-Ar	anisole	3	11	85:15	29	5	28	83:17	26	—
Ti(IV)	CH ₂ Cl ₂	3	52	91:9	38	3	86	91:9	38	5.6
Ti(IV)-EC	CH ₂ Cl ₂	3	14	92:8	41	3	27	88:12	38	2.2
Cu(II)	CH ₂ Cl ₂	3	11	92:8	44	5	46	92:8	43	7.1
Cu(II)-EC	CH ₂ Cl ₂	3	12	94:6	46	5	47	91:9	45	1.2
Cu(II)-EC-Ar	CH ₂ Cl ₂	3	4	94:6	46	5	9	91:9	42	—
Cu(II)-EC-Ar	anisole	3	8	87:13	31	5	44	85:15	27	—
Fe(III)	CH ₂ Cl ₂	3	16	92:8	45	5	54	90:10	39	4.4
Fe(III)-EC	CH ₂ Cl ₂	3	10	92:8	47	5	28	86:14	31	0.9
Fe(III)-EC-Ar	CH ₂ Cl ₂	3	9	93:7	47	5	24	90:10	40	—
Fe(III)-EC-Ar	anisole	3	11	86:14	29	5	29	84:16	26	—
—	anisole	3	9 ^e	76:24	10	—	—	—	—	—
(BrC ₆ H ₄) ₃ NSbCl ₆	anisole	3	4	85:15	31	9	78	78:22	12	—
(BrC ₆ H ₄) ₃ NSbCl ₆	CH ₂ Cl ₂	3	0	—	—	9	23	81:19	14	—

^a Determined by gas chromatography. ^b 4n is the major cycloadduct. ^c Determined using the ratio between the extinction coefficients found in zeolites: $\epsilon_B = 5.8 \epsilon_L$ [11]. ^d Ar means that the modification of the clays and the Diels–Alder reactions are carried out under argon atmosphere. ^e Result obtained after 2.5 h.

described in Table 1) were added with a syringe. The reactions were monitored by gas chromatography.

3. Results and discussion

It has been described that calcined clays have a high Lewis/Brønsted acidity ratio, which makes them efficient catalysts in Diels–Alder reactions of the normal type. A further modification of this acidity can be achieved by elimination of the hydroxyl groups of the clay by silanization. Thus, several calcined clays were treated with trimethylchlorosilane (TMCS), and then used as catalysts in the above-mentioned Diels–Alder reaction.

The results obtained with the non-silylated and silylated calcined clays (Table 1) show that, in general, end-capping reduces the catalytic activity of these clays, but some residual activity remains. This is shown by the *endo/exo* and the diastereofacial selectivities that reach values typical of catalyzed reactions, and are much higher than those obtained in solution of CH_2Cl_2 (*endo/exo* = 78.7:21.3, %de = 6%). In the case of the Cu(II)-exchanged clay both the end-capped and non-end-capped solids lead to almost the same results, which is due to the low conversions reached with the non-silylated clay. It has been shown [7] that K10 montmorillonites exchanged with very easily reducible cations, such as Cu(II) or Ce(IV), promote the radical cation polymerization of cyclopentadiene even in CH_2Cl_2 , which gives rise to an important decrease in the conversion of the dienophile.

In order to explain these results the acidity of these clays was studied by infrared spectroscopy of adsorbed pyridine [11], and the relative proportion of Lewis and Brønsted acid sites was determined using the extinction coefficients previously found in zeolites ($\epsilon_{\text{B}} = 5.8 \epsilon_{\text{L}}$). As expected, the intensity of the peaks corresponding to pyridine adsorbed onto acid sites is reduced with regard to the structural peak of the montmorillonite ($1920\text{--}1827 \text{ cm}^{-1}$). However, the

most surprising result is that the relative proportion of Brønsted acid sites increases in all cases (Table 1).

These results show that Lewis acidity is almost completely eliminated upon silylation, which may be due to two different reasons. Firstly, the silylation hinders the access of the reagents and of pyridine to these sites. Secondly, some Lewis acidity is linked to the hydroxyl groups of the clay. In fact, the hydroxyl groups on the surface of silica gel also act as Lewis acid sites, and are able to promote the reaction studied in this work [12]. Moreover, the same behaviour is observed for the reaction carried out in solution of a fluorinated alcohol in the absence of a catalyst [13]. The conversion and selectivities obtained with the clays are otherwise better than those obtained with silica gel or fluorinated alcohols, which is not due to the presence of a greater amount of acid sites, but to the different strength of these sites. In fact, a silicoaluminate is more acidic than silica gel, and furthermore the coordination of the hydroxyl groups to the exchanged cation must increase their acidity.

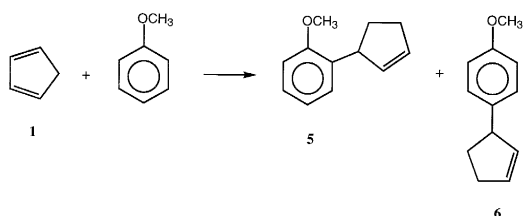
Given that the calcination almost completely eliminates the Brønsted acidity [2], the above-mentioned increase in the proportion of Brønsted acid sites must be related to the silanization process, and it may be due to the rehydration of the clay when handled under atmospheric conditions. Both silylated and non-silylated clays lead to similar selectivities. However, the reactions with the end-capped clays are, in general, more *endo* and diastereofacial selective at low conversions, but both selectivities decrease at higher conversions. This may be due to a greater contribution of the less selective non-catalyzed reaction, which is greater on the less active catalysts.

If the appearance of this acidity is due to atmospheric rehydration, it could be even more reduced if the silanization of the clay was completely carried out under argon atmosphere. In fact, the solids obtained in this way are less efficient than those end-capped in air. In spite

of the low conversions observed, both selectivities remain high during the reaction, so that the results obtained do correspond to catalytic reactions (Table 1). It is important to note that this reduction of catalytic activity is achieved by avoiding the rehydration of the clay, which indicates the catalytic role of Brønsted acid sites.

The other way to promote Diels–Alder reactivity is through a radical cation mechanism, where a species able to act as a one electron acceptor (a metal cation in this case) is needed. The addition of an organic compound able to easily reduce this cation, an electron rich aromatic compound, for instance, favours this mechanism. Therefore the catalytic activity of the silylated clays was tested in the presence of anisole. The use of this solvent gives rise to several effects, first of all it reduces both endo/exo and diastereofacial selectivities, however these values are higher than those obtained in solution of anisole and in the absence of a catalyst, so that the clay plays some role. The selectivities obtained are similar to those obtained using $(\text{BrC}_6\text{H}_4)_3\text{NSbCl}_6$, a promotor of radical cation mechanism [14]. Surprisingly, the clay exchanged with Zn(II) (a non-easily reducible cation) shows the same behaviour, which indicates that the Fe(III) present in K10 montmorillonite can also promote this kind of mechanism. In fact, the effect of the anisole on the selectivities was also observed when the commercial K10 clay was end-capped under argon and tested as a catalyst in CH_2Cl_2 and anisole (Table 1).

The use of anisole as a solvent increases the conversion obtained with silylated clays, which is particularly noticeable in the case of Cu(II)-



Scheme 2.

Table 2

Friedel–Crafts alkylation of anisole using silylated clays under argon

Catalyst	2:1	(3+4)/(5+6) ^a	6/5 ^a
$(\text{BrC}_6\text{H}_4)_3\text{NSbCl}_6$	3	0.9	4.8
	9	9.6	4.2
Zn(II)-EC-Ar	3	1.9	5.4
	5	1.4	5.7
K10-EC-Ar	3	1.1	5.0
	5	1.0	5.3
Fe(III)-EC-Ar	3	0.7	4.9
	5	1.0	5.2
Cu(II)-EC-Ar	3	1.5	4.9
	5	2.0	5.0

^a Determined by gas chromatography. The products were identified by GC-MS and ¹H-NMR.

exchanged clay. This positive effect of the anisole is not so clear with $(\text{BrC}_6\text{H}_4)_3\text{NSbCl}_6$. In this case the cyclopentadiene disappears very quickly and with a further amount of this reagent the reaction takes place in a non-catalyzed way. However the results are even worse in CH_2Cl_2 , so the anisole also shows the above mentioned favourable effect.

To sum up, although the results in endo/exo and diastereofacial selectivities indicate that all the reactions carried out in anisole take place mainly through a radical cation mechanism, the comparison of the percentage of conversion shows the differences related to the use of different reducible species to promote this mechanism.

The low percentages of conversion of the reactions carried out in anisole are not only due to the oligomerization of the diene, but also to the Friedel–Crafts reaction of the cyclopentadiene with anisole (Scheme 2). The Friedel–Crafts alkylation of aromatic compounds is promoted by acid catalysts, but also takes place through a radical cation mechanism, and the corresponding *ortho*- and *para*-alkylated products are obtained in the presence of $(\text{BrC}_6\text{H}_4)_3\text{NSbCl}_6$ (Table 2). In agreement with this observation, the same products are obtained in the reactions carried out in anisole, in the presence of clays silylated under argon. The ratio between Friedel–Crafts and Diels–Alder adducts, as well

as the *para/ortho* selectivity, hardly change from one catalyst to another.

4. Conclusion

The results described in this work show that clays can promote Diels–Alder reactions in three different ways. The most efficient and most selective reactions are due to the Lewis acid sites. Brønsted acid sites also catalyze the reaction, leading to similar selectivities. Finally, the reaction can take place through a radical cation mechanism, which is favoured by the addition of a promoter, such as anisole. In this case the endo/exo and diastereofacial selectivities are noticeably reduced. Another interesting result is that by means of calcination of the exchanged clay, the Lewis/Brønsted acidity ratio is increased, but this ratio is greatly reduced by silylation and rehydration of the calcined clay, so that the combination of these treatments allows to modify the properties of the clay.

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