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# Effect of Clay Calcination on Clay-Catalysed Diels-Alder Reactions of Cyclopentadiene with Methyl and (-)-Menthyl Acrylates

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**Abstract:** Zn(II) and Fe(III)-exchanged K10-montmorillonites, activated by several methods, are used as catalysts in the reaction between methyl acrylate and cyclopentadiene. Calcined clays are better catalysts than dried clays. Zn(II) clays, dried and calcined, are compared as catalysts of the asymmetric Diels-Alder reaction between (-)-menthyl acrylate and cyclopentadiene. Calcined clay again shows a higher catalytic activity and leads to better percentages of diastereomeric excess. Furthermore, calcined clays are easily recovered with no loss of catalytic properties.

## INTRODUCTION

The Diels-Alder adducts of acrylic acid derivatives constitute an important class of compounds as key intermediates for the total synthesis of a variety of natural products[1].

Excellent diastereofacial selectivities have been achieved in asymmetric Diels-Alder reactions between prochiral 1,3-dienes and chiral acrylates.[2] However, these good results are only obtained when a Lewis acid is used as a catalyst. This methodology suffers drawbacks such as use of large quantities of catalyst and the disposal of environmentally hazardous residues. Therefore, the development of new catalytic systems able to overcome these problems constitutes an interesting task.

It has been reported that several inorganic solids, such as silica gel,[3,4] magnesium silicate,[4] alumina,[4,5] zeolites[6] and clays[7] are efficient catalysts in Diels-Alder reactions. Recently, we have studied several factors influencing the K10 montmorillonite catalysed Diels-Alder reaction between methyl acrylate and cyclopentadiene[8] and have shown that the solvent used plays a decisive role.[9]

The heterogeneous catalysis of the benchmark asymmetric Diels-Alder reaction between (-)-menthyl acrylate and cyclopentadiene has also been studied. The results obtained in this reaction, catalysed by γ-alumina[10] and Fe(III) and Zn(II) doped K10 montmorillonites,[11] have been published. The latter catalysts afford good endo/exo and diastereofacial selectivities, but (-)-menthyl acrylate is a worse dienophile than methyl acrylate. Consequently, oligomerization of cyclopentadiene takes place to a great extent and the oligomers formed deactivate the catalyst. Given the interest of asymmetric Diels-Alder reactions in the field of organic synthesis, it is important to search for solids with better catalytic properties for reactions of carbonyl-containing dienophiles.

To the best of our knowledge there are no references to the use of calcined clays as catalysts in Diels-Alder reactions. As the water contained in the structure of the clay is eliminated in the calcination process, these solids display only Lewis acidity and, given that Lewis acids are the best catalysts for Diels-Alder reactions of carbonyl-containing dienophiles, they are interesting candidates.

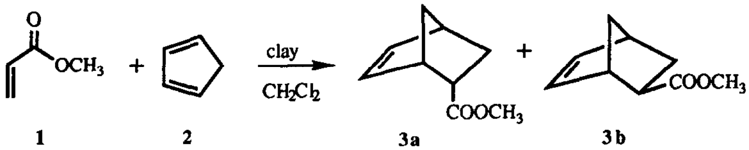
In this paper we present the results obtained when calcined Fe(III) and Zn(II) K10 montmorillonites are used as catalysts in Diels-Alder reactions. First of all, the calcination process is optimised by studying the Diels-Alder reaction of methyl acrylate with cyclopentadiene, the catalysts obtained under the best conditions of calcination are then used in the reaction between (-)-menthyl acrylate and cyclopentadiene. Finally, the regeneration of the catalyst is studied.

## RESULTS AND DISCUSSION

In order to choose the initial calcination program, thermogravimetric analysis of the Fe(III) and Zn(II) doped K10 montmorillonites was carried out. In both cases a constant weight was reached after 3 h at 500°C (Fe(III) loss of weight = 4.39%; Zn(II) loss of weight = 4.69%). Therefore, in the initial calcination procedure the clays were kept at this temperature for 5 h. The clays were calcined in dry air (25-30 ml/min) by the following methods.

Method 1: 24°C, 8°C/min, 120°C, 1°C/min, 500°C (5h), -1°C/min, 40°C (1h).
Method 2: this method is the repetition for three times of method 1.
Method 3: 24°C, 8°C/min, 120°C, 1°C/min, 550°C (10h), -1°C/min, 40°C (1h).
Method 4: 24°C, 8°C/min, 120°C, 1°C/min, 650°C (10h), -1°C/min, 40°C (1h).

The catalytic activity of these clays was tested in the reaction of methyl acrylate (**1**) with cyclopentadiene (**2**) carried out under standard conditions, which were chosen taking into account previous work[8] with Fe(III) and Zn(II) doped K10 montmorillonites.



Figures 1 and 2 show the evolution of the percentage of conversion with time, as a function of the previous treatment of the clay. As can be seen, calcination improves the catalytic activity of Zn(II) K10 montmorillonite and total conversion can be achieved using clays calcined under several conditions. Nevertheless, the calcination conditions have a greater influence on the catalytic activity of Fe(III) K10 montmorillonite. So, whereas the clay calcined by method 1 is worse than the solid dried at 120°C, the catalytic activity of clay is improved when calcined by any other of the previously mentioned methods.

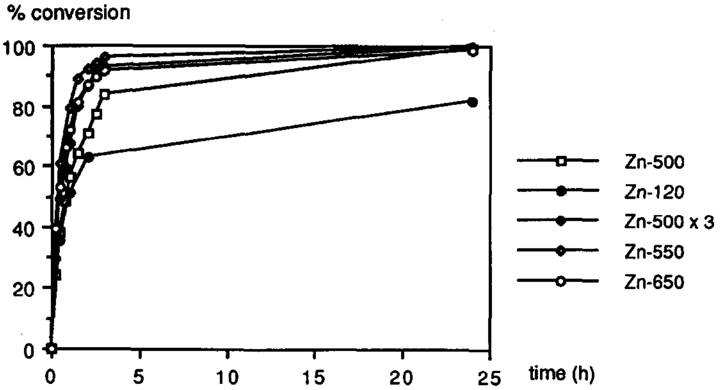


Figure 1

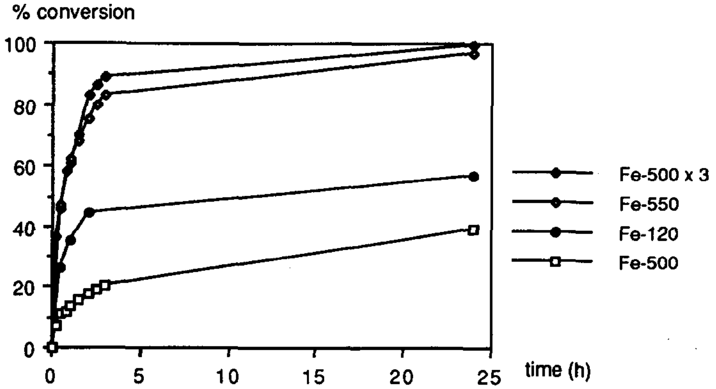


Figure 2

Table 1 summarizes these results together with endo/exo selectivity. It is shown that endo/exo selectivity is also improved when calcined clays are used as catalysts. There are no differences of behaviour between the clays calcined by methods 2, 3 and 4, so, the fastest one, method 3, can be chosen as the standard calcination procedure.

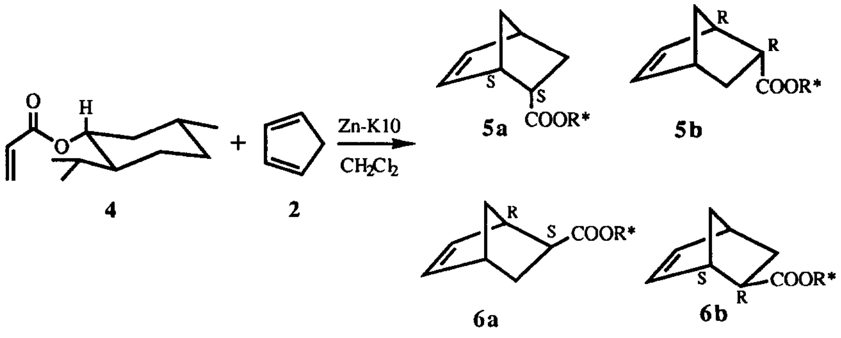
**Table 1.** Results of the Reaction between Methyl Acrylate (**1**) and Cyclopentadiene (**2**) Catalysed by K10 Montmorillonites in $CH_2Cl_2$ at 20°C.

| Exchanged cation | Method of calcination | % conversion after 24 h[a] | endo/exo (**3a**:**3b**)[a] |
|---|---|---|---|
| Zn (II) | 120°C[b] | 82 | 9.7 |
| Zn (II) | 1 | 99 | 11.5 |
| Zn (II) | 2 | 100 | 14.1 |
| Zn (II) | 3 | 100 | 14.7 |
| Zn (II) | 4 | 100 | 14.7 |
| Fe (III) | 120°C[b] | 57 | 9.8 |
| Fe (III) | 1 | 39 | 7.3 |
| Fe (III) | 2 | 100 | 14.9 |
| Fe (III) | 3 | 97 | 14.5 |

[a]Determined by gas chromatography. [b]Clay dried at 120°C overnight.

To sum up, the calcination of clay improves the reaction rate and the endo/exo selectivity of the Diels-Alder reaction between methyl acrylate and cyclopentadiene catalysed by Fe(III) and Zn(II) K10 montmorillonites.

In view of these results, Zn(II) K10 montmorillonite, calcined by method 3, was chosen as a catalyst for the asymmetric Diels-Alder reaction between (-)-menthyl acrylate (**4**) and cyclopentadiene (**2**)



The reaction was monitored by gas chromatography, **5a** and **5b** were assigned by comparison of the gas chromatograms, obtained in the clay-catalysed reactions, with those obtained in several reactions of cyclopentadiene and (-)-menthyl acrylate using Lewis acids as catalysts. The results of diastereoselectivities and absolute configurations of these reactions are described in papers previously published by Oppolzer and coworkers.[12]

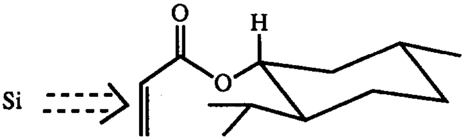
Table 2 gathers the results obtained in the above-mentioned asymmetric Diels-Alder reaction. Better conversions and diastereofacial selectivities are obtained when the calcined clay is used as a catalyst, whereas endo/exo selectivities are almost the same. As expected, both, endo/exo and diastereofacial selectivities, increase when the reaction temperature is lowered. At -20°C, when the calcined clay is used, high conversion can be achieved with diastereofacial selectivity that is the same or even better than that obtained when classical Lewis acids are used as homogeneous catalysts.

**Table 2.** Results of the Reaction between (-)-Menthyl Acrylate (**4**) and Cyclopentadiene (**2**) Catalysed by Zn(II) K10 Montmorillonites in $CH_2Cl_2$.

| Method of calcination | Temp (°C) | **2**:**4** | time (h) | % conversion[a] | endo/exo (**5**:**6**)[a] | % d.e.[a,b] |
|---|---|---|---|---|---|---|
| 120°C[c] | 20 | 6:1 | 2 | 34 | 9.7 | 29 |
| | | | 6 | 47 | 9.5 | 30 |
| | | | 24[d] | 53 | 9.2 | 31 |
| 3 | 20 | 3:1 | 2 | 66 | 11.0 | 38 |
| | | | 6 | 72 | 11.0 | 38 |
| 3 | 20 | 6:1 | 2 | 54 | 10.5 | 37 |
| | | | 6 | 72 | 10.3 | 36 |
| | | | 17 | 90 | 9.8 | 36 |
| 3 | 20 | 3:1 | 2[e] | 67 | 11.0 | 41 |
| | | 5:1 | 3.5 | 88 | 11.0 | 41 |
| | | | 24 | 99 | 11.0 | 41 |
| 120°C[c] | -20 | 3:1 | 3.5[f] | 14 | 23.0 | 45 |
| | | 4.5:1 | 9[f] | 33 | 23.0 | 45 |
| | | 6:1 | 24[f] | 61 | 20.1 | 43 |
| | | 7.5:1 | 33[d] | 75 | 20.0 | 43 |
| 3 | -20 | 3:1 | 2[e] | 30 | 19.4 | 55 |
| | | 5:1 | 23[e] | 75 | 19.3 | 54 |
| | | 7:1 | 46 | 85 | 19.6 | 54 |

[a]Determined by gas chromatography. [b]**5b** is preferably obtained. [c]Clay dried at 120°C overnight. [d]From this time further progress of the reaction does not take place even when additional amounts of diene are added. [e]At this time 2 eq. of diene are added. [f]At this time 1.5 eq. of diene are added.

The direction of the asymmetric induction can be explained by the model used in the Lewis acid-catalysed reactions of chiral acrylates.[2] In this model the dienophile displays an anti-enoate conformation where the isopropyl group of the (-)-menthol shields the re-face of the dienophile and the attack of the diene preferentially takes place on the si-face



During the Diels-Alder reaction a competitive oligomerization of the cyclopentadiene takes place, and the oligomers formed poison the catalyst. So, we tested the possibility of recovering and reusing the catalyst. After the Diels-Alder reaction the clays were filtered, washed with methylene chloride and two different methods to recover the catalyst were tested. In the case of Zn(II) exchanged K10 montmorillonite dried at 120°C, the clays were extracted with toluene and methylene chloride in a Soxhlet apparatus for 2 months. The solids obtained did not show any catalytic activity after drying at 120°C in an oven overnight.

In the case of Zn(II)-exchanged K10 montmorillonite calcined by method 3, the solid was re-activated by the same calcination procedure. The solid obtained was used as a catalyst in the Diels-Alder reaction between cyclopentadiene (**2**) and (-)-menthyl acrylate (**4**), and recovered again by the same method. The results obtained (Table 3) show that the catalyst is recovered without loss of catalytic activity and the reaction takes place with the same endo/exo and diastereofacial selectivities. As expected, the oligomers of cyclopentadiene are eliminated during the calcination.

**Table 3.** Results of the Reaction between (-)-Menthyl Acrylate (**4**) and Cyclopentadiene (**2**) in $CH_2Cl_2$ at 20°C, Catalysed by Recovered Zn(II) K10 Montmorillonites

| Number of recovering[a] | 2:4 | time (h) | % conversion[b] | endo/exo (5:6)[b] | % d.e.[b,c] |
|---|---|---|---|---|---|
| 0 | 3:1 | 2[d] | 67 | 11.0 | 41 |
| | 5:1 | 3.5 | 88 | 11.0 | 41 |
| | | 24 | 99 | 11.0 | 41 |
| 1 | 3:1 | 2[d] | 65 | 10.9 | 41 |
| | 5:1 | 3.5 | 86 | 11.2 | 40 |
| | | 24 | 99 | 11.0 | 41 |
| 2 | 3:1 | 2[d] | 57 | 10.8 | 40 |
| | 5:1 | 3.5 | 82 | 11.2 | 39 |
| | | 24 | 95 | 11.1 | 39 |

[a] Clay is recovered by re-calcination using method 3. [b] Determined by gas chromatography. [c] **5b** is preferably obtained. [d] At this time 2 eq. of cyclopentadiene are added.

The X-ray diffraction spectrum shows that the original K10 contains mainly silica impurities in the form of quartz and cristobalite which are commonly associated with natural clays. The presence of these silicious impurities is also evidenced by the presence of a relatively weak signal at -110 ppm in the $^{29}$Si-MAS-NMR spectrum.[13] These minerals, which amount has been estimated to 10-15 %, give sharp diffraction lines, then they are in the form of big crystals of low surface area (<1-2 $m^2/g$) which simply dilute the active phase since the surface area of these clays, determined by nitrogen adsorption, fall in the range of 220-240 $m^2/g$. The original K10, the exchanged Fe(III) and Zn(II) K10 montmorillonites and the calcined by method 3 Fe(III) and Zn(II) K10 clays show the same X-ray diffraction spectrum, then the same crystallinity (estimated to more than 80 %) and the same impurities. These results show that the different behaviour of these clays cannot be explained on the basis of structural changes in the K10 montmorillonite. Furthermore, the initial K10 montmorillonite as well as the exchanged and calcined clays have mesopores (2-4 nm) and the diffusion of the reagents into the clay and the products out of the clay are not swelling-dependent.

Therefore, two main reasons may account for the better catalytic activity of calcined clays as compared with dried exchanged clays. First of all, the calcination eliminates the Brønsted acidity of the clay. Figure 3 shows the IR spectra of pyridine adsorbed in wafers of Zn(II)-K10 clays and desorbed at 120°C. As can be seen the IR band corresponding to Brønsted acidity (1548 $cm^{-1}$) disappears after calcination. The Fe(III)-K10 clays display a similar behaviour. Secondly, the EPR spectra of the clays dried at 120°C show a weak signal at $g = 2.004 \pm 0.002$[8] not present in calcined clays. This signal could be characteristic of free radicals and could be due to traces of organic material present in the dried clays. Taking into account that organic radicals promote diene dimerization via a cation-radical intermediate[7a], the absence of free radicals may reduce diene polimerization leading to higher percentages of conversion. Possibly the absence of Brønsted acidity has a similar effect.

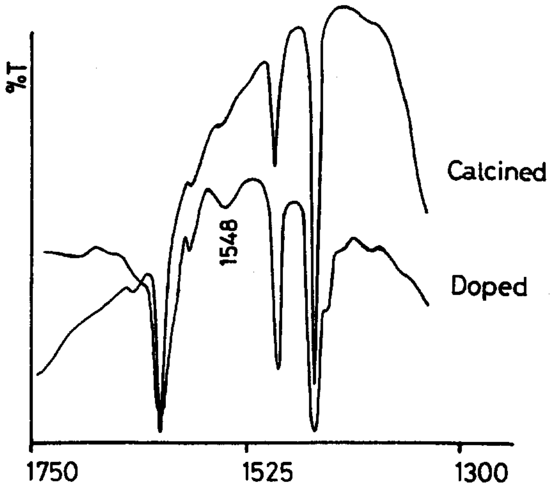


Figure 3

To sum up, calcined clays are better catalysts than doped clays in Diels-Alder reactions. In particular, they allow us to obtain high percentages of conversion, with good endo/exo and diastereofacial selectivities, in the asymmetric Diels-Alder reaction between (-)-menthyl acrylate (**4**) and cyclopentadiene (**2**). Furthermore, calcined clays have the additional advantage of the easy recovery of the catalyst without loss of catalytic activity.

## EXPERIMENTAL

### *Preparation and characterisation of the catalysts.*

K10 montmorillonite was purchased from Aldrich. Cation exchange was performed by gradually adding K10 montmorillonite (10 g) to stirred ferric or zinc chloride solutions (125 ml, 1 M) at room temperature.[7d] The suspensions were stirred for 24 h, filtered and washed chloride-free with deionised water. The resulting solids were dried overnight on a thin bed at 120°C in an oven, and ground in a mortar. The catalysts were equilibrated over saturated salt solutions in order to give reproducible water contents.

Clay calcination was effected in dry air (25-30 ml/min) by one of the following methods:

Method 1: 24°C, 8°C/min, 120°C, 1°C/min, 500°C (5h), -1°C/min, 40°C (1h).
Method 2: this method is the repetition for three times of method 1.
Method 3: 24°C, 8°C/min, 120°C, 1°C/min, 550°C (10h), -1°C/min, 40°C (1h).
Method 4: 24°C, 8°C/min, 120°C, 1°C/min, 650°C (10h), -1°C/min, 40°C (1h).

Surface areas were calculated from BET nitrogen isotherms determined at 77 K. In all cases the values obtained fall within the range of 220-240 $m^2/g$. Water contents were analyzed by thermogravimetry in a Perkin-Elmer TGS-2 apparatus equipped with a System 4 microprocessor controller. Acidic properties were determined by adsorption of pyridine as 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 ~10 $mg.cm^{-2}$. The resulting wafers were placed in cells (equipped with KBr windows and connected via stopcocks to a vacuum line) where the treatment of the catalysts was performed. Infrared spectra were recorded using a Nicolet 320 FT-IR spectrometer after desorption of pyridine at different temperatures. X-ray diffraction patterns were recorded on a Phillips computer-driven X-ray diffractometer using $CuK\alpha_1$ radiation. The cation-exchanged and calcined montmorillonites retain the structure of the initial K10. MAS-NMR spectra were recorded on a Brucker AM 300 apparatus.

### *Reaction procedures.*

Methyl acrylate and acryloyl chloride were purchased from Merck and used without further purification. (-)-Menthol was purchased from Aldrich.

**1.- Reaction between methyl acrylate and cyclopentadiene.** Pre-weighed cation-exchanged montmorillonite was dried at 120°C overnight or calcined by one of the above-described methods. The flask was charged with the catalyst and methylene chloride (15 ml) under Ar atmosphere at 20°C. Methyl acrylate (0.645 g, 7.5 mmol) and freshly distiled cyclopentadiene (1.485 g, 22.5 mmol) were added via syringe. The reaction flask was shaken for 24 h and the reaction monitored by gas chromatography (FID from Hewlett-Packard 5890 II, cross-linked methyl silicone column 25 m x 0.2 mm x 0.33 µm, helium as carrier gas 16 psi, injector temperature 230°C, detector temperature 250°C, oven temperature program 50°C (3 min) - 25°C/min - 100°C (9 min), retention times: methyl acrylate 2.7 min, exo cycloadduct 12.7 min, endo cycloadduct 12.9 min).

**2.- Reaction between (-)-menthyl acrylate and cyclopentadiene.** (-)-Menthyl acrylate was prepared according a procedure described in the literature.[14] Pre-weighed Zn(II)-exchanged montmorillonite (1.5 g) was dried at 120°C overnight or calcined following method 3. The flask was charged with the catalyst and methylene chloride (15 ml) under Ar atmosphere at the working temperature. (-)-Menthyl acrylate (0.630 g, 3 mmol) and freshly distiled cyclopentadiene (amounts described in Table 2) were added via syringe. The reaction was monitored by gas chromatography (FID from Hewlett-Packard 5890 II, cross-linked methyl silicone column 25 m x 0.2 mm x 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: (-)-menthyl acrylate 3.9 min, **6a+6b** 18.9 min, **5a** 19.6 min, **5b** 20.0 min). Absolute configurations were assigned by comparison of the gas chromatograms obtained in clay-catalysed reactions with those obtained in Lewis acid-catalysed reactions previously described by Oppolzer and coworkers.[12]

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