Calcined and silylated K10 montmorillonites as catalysts of pericyclic reactions of *trans*-anethole

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Cation-exchanged K10 montmorillonites are calcined and silylated in order to eliminate acid sites. The solids obtained promote the Diels–Alder reaction of cyclopentadiene with *trans*-anethole and the cyclodimerization of *trans*-anethole.

In 1981 Bauld and co-workers discovered the first radical cation-catalysed Diels–Alder reaction of a normal diene and an electron-rich dienophile, which takes place *via* a radical cation mechanism.[1] An aminium salt was used to initiate the reaction and the same method was used to promote other cycloadditions.[2] The mechanistic aspects of these reactions have also been studied,[3] and aminium salts supported on poly(styrene) have shown their effectiveness in catalysing the dimerization of cyclohexadiene.[4]

Several inorganic solids are able to generate radical cations in the presence of suitable organic molecules,[5] and this ability has been used to promote hole-catalysed Diels–Alder reactions using zeolites[6] or Fe[III]-doped K10 montmorillonite.[7] However, the use of heterogeneous catalysts to promote reactions of electron-rich dienophiles has not been described to date, which may be due to the presence of acid sites in these catalysts. Brønsted catalysis promotes the cyclodimerization of some dienes, such as 2,4-dimethylpenta-1,3-diene,[2,6,7] but in the presence of electron-rich alkenes, such as *trans*-anethole **1**, it leads to the formation of acyclic dimers and polymers.[8]

It has been reported[9] that calcination of cation-doped K10 montmorillonites eliminates acid sites and increases the Lewis–Brønsted acidity ratio, but the solids obtained are able to form radical cations in the presence of suitable compounds.[10] As a consequence, it was of interest for us to test these solids as catalysts in the reaction of cyclopentadiene **6** with *trans*-anethole **1**.

Unfortunately, *trans*-anethole polymerizes easily in the presence of these clays and dimers are obtained in less than 10% yield (Table 1). The major dimers are not cyclobutanes, but cyclopropanes **2** and **3** (Table 1, entries 1 and 2). Although it can be expected that polymerization was mainly promoted by Brønsted acid sites, two solids with very different Lewis–Brønsted acidity ratio, namely the Fe[III]- and Cu[II]-exchanged K10 montmorillonites calcined at 550 °C, lead to almost the same results (Table 2). This fact suggests that Lewis acid sites also promote the polymerization. In fact, *trans*-anethole quickly polymerizes in the presence of AlEtCl₂ and TiCl₄.

In order to reduce the rate of polymerization, we tried to reduce the acidity of the clays by treatment with trimethylchlo-

Table 2 Cation content and Lewis–Brønsted acidity ratio of the non-silylated and silylated clays

Clay[a]	mmol Fe g⁻¹[b]	mmol Cu g⁻¹[b]	Lewis : Brønsted[c]
Fe[III]-K10	0.66	—	5.2
Cu[II]-K10	0.21	0.08	27.4
Fe[III]-K10-EC	0.29	—	0.9
Cu[II]-K10-EC	0.20	0.08	1.2
K10-EC	0.24	—	0.9
Bentonite	0.12	—	—

[a] X-Ray diffraction patterns were recorded using Cu-Kα1 radiation for the K10 clays and do not change upon silylation. [b] Determined by Plasma Emission Spectroscopy. [c] Obtained from the intensity of the IR bands at 1450 and 1550 cm⁻¹ of pyridine adsorbed onto the clays.

Table 1 Results obtained in the dimerization of *trans*-anethole **1** and in its reaction with cyclopentadiene **6** at 25 °C in the presence of several clays[a]

Entry	Clay[b]	6 : 1	t/h	Conversion of 1 (%)[c]	% Conversion (dimer)[c,d]		% Conversion (adduct)[c,d]	
1	Fe[III]-K10	0	6	98	5 (2+3)[e]		—	
2	Cu[II]-K10	0	24	82	7 (2+3)[e]		—	
3	Fe[III]-K10-EC	0	1	70	10 (4)	3 (5)	—	
4	Cu[II]-K10-EC	0	1	74	17 (4)	3 (5)	—	
5	K10-EC	0	1.5	71	12 (4)	3 (5)	—	
6	Fe[III]-K10-EC	4	5.5	94	—		15 (7)	4 (8)
7	Cu[II]-K10-EC	4	5.5	95	—		10 (7)	2 (8)
8	K10-EC	4	6.5	96	—		18 (7)	5 (8)
9	Bentonite[f]	6	24	0	—		—	
10	Fe[III]-K10-EC	18	24	17	—		12 (7)	3 (8)
11	Fe[III]-K10-EC[g]	12	5.5	60	—		11 (7)	2 (8)
12	Fe[III]-K10-EC[g,h]	12	24	83	—		42 (7)	9 (8)

[a] 0.75 mmol of **1** and the corresponding amount of **6** with 250 mg of clay in CH₂Cl₂. [b] Clays calcined at 550 °C; EC indicates that after calcination the clay is silylated (end-capped) with TMCS. [c] Determined by gas chromatography using decane as internal standard. [d] Products were separated by column chromatography and identified by ¹H NMR. [e] **2** and **3** are the major products, but a very small amount of **4** and **5** together with some open-chain dimers were detected by GC–MS and ¹H NMR of reaction mixtures. [f] Purchased from Aldrich. [g] Reactions carried out without a solvent. [h] Reaction carried out at 0 °C.

rosilane (TMCS). The IR spectra of pyridine adsorbed on these end-capped clays show a reduction of the bands corresponding to Brønsted and Lewis acid sites. Unexpectedly, the Lewis–Brønsted acidity ratio decreases (Table 2), which indicates that the silylation blocks some of the Lewis acid sites, or that some of these sites correspond to hydroxy groups, whose Lewis acid properties are related to the formation of hydrogen bonds. The polymerization of trans-anethole in the presence of silylated clays is slower, and dimers are obtained in slightly higher yields. Under these conditions cyclobutanes **4** and **5** are the major dimers, and the trans, anti, trans **4** is the stereoisomer preferentially obtained (Table 1, entries 3–5, Scheme 1).

The role of silylated clays was tested in the reaction of cyclopentadiene **6** with trans-anethole **1** (Scheme 2). The results obtained (Table 1, entries 6–8) show that the higher proportions of Diels–Alder cycloadducts are obtained with the K10 itself and the Fe^{III}-exchanged K10 clays treated with TMCS. Table 2 shows that both clays have very similar iron contents and the same Lewis–Brønsted acidity ratio, which indicates that most of the exchanged iron is eliminated during the silylation. The similarity between both clays is reflected by the similarity of the results obtained in the reactions studied (Table 1, entries 3, 5, 6 and 8).

Given that the main lateral reaction is the polymerization of trans-anethole **1**, it can be thought that the yield of the Diels–Alder cycloadducts, **7** and **8**, would be increased in the presence of a larger excess of cyclopentadiene **6**. In fact, under these conditions, the disappearance of trans-anethole **1** is slower and the selectivity of the reaction with cycloadducts **7** and **8** increases (Table 1, entry 10). However, the reaction is too slow.
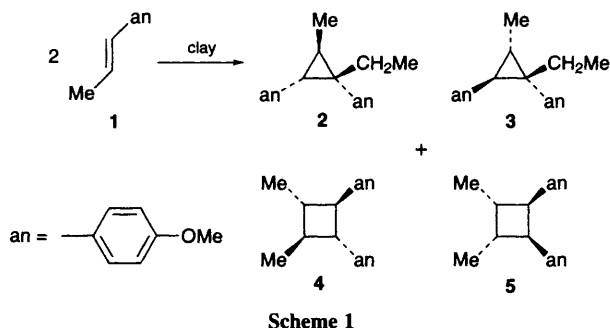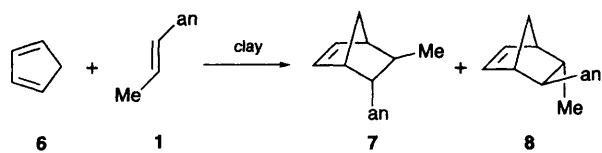
The reaction carried out in the absence of solvent is much faster, but the selectivity of the cycloadducts decreases (Table 1, entry 11). Finally, the reaction carried out without a solvent and a lower temperature is fast and selective enough to increase the yield of the Diels–Alder cycloadducts (Table 1, entry 12).

The role of the clays in these reactions could be due to both the formation of radical cations with reducible species in the solid and to the residual acidity. The activity of the non-exchanged K10 clay seems to point to the second mechanism. In order to test this hypothesis, we carried out EPR spectroscopic studies of these clays in the presence of trans-anethole **1**. All the K10 clays showed a narrow signal at $g = 2.004$, characteristic of organic radicals. This result indicates that the structural Fe^{III} of the K10 can be reduced by the trans-anethole. However, an acid-untreated bentonite did not show this signal in the presence of this compound, and did not promote the Diels–Alder reaction (Table 1, entry 9), which indicates that the acid treatment carried out to prepare the K10 clay makes structural Fe^{III} more accessible to the reagents.

In a typical sylilation procedure, 1 g of the clay was heated under reflux in toluene with 1 ml of TMCS for 24 h. The solid was separated by filtration and washed with toluene and then with methylene chloride.

Scheme 1

Scheme 2

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