

Mesoporous Aluminosilicate MCM-41 as a Convenient Acid Catalyst for Friedel–Crafts Alkylation of a Bulky Aromatic Compound with Cinnamyl Alcohol

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Owing to its large molecular size, alkylation of 2,4-di-*tert*-butylphenol with cinnamyl alcohol does not take place using HY zeolite (pore opening 7.4 Å) as catalyst even after controlled steaming treatment to increase its mesoporosity; by contrast, novel mesoporous aluminosilicate MCM-41 catalyses this reaction giving rise to 6,8-di-*tert*-butyl-2-phenyl-2,3-dihydro[4*H*]benzopyran (arising from intramolecular cyclization of the primary cinnamylphenol) together with 4-*tert*-butylphenol and small amounts of 6-*tert*-butyl-2-phenyl-2,3-dihydro[4*H*]benzopyran.

Catalysis by zeolites has been severely limited in the past by the available dimensions of their micropores and, therefore, the maximum molecular size of substrate or reaction products that can diffuse through the internal voids.¹ For typical large-pore zeolites such as Y faujasites, the pore opening is around 7.4 Å.² These limitations have been in some way overcome by the use of reagents supported onto layered aluminosilicates.^{3–5} However, these materials suffer from a small capability to incorporate nonpolar organic substrates within the highly hydrophilic interlayer regions. In this context, the recent development of novel extra large mesoporous MCM-41 aluminosilicates^{6–9} constitutes a significant breakthrough in the field of catalysis. Their structure is formed by an array of parallel hexagonal channels, the diameter of which can be varied between 25 and 100 Å. However, in spite of these favourable pore dimensions, catalytic studies using these novel aluminosilicates are scarce.¹⁰ A spectroscopic characterization by the pyridine adsorption–desorption method has established that aluminium containing MCM-41 samples exhibit only weak and mild Lewis acid sites, and in any case its acidity is weaker than that of HY zeolites.¹¹ This inherent weakness of the sites must restrict the processes that can be catalysed by MCM-41 to those with low acid requirements.

We report here that these novel mesoporous zeotypes are adequate catalysts for the Friedel–Crafts alkylation of electron-rich aromatic compounds. Thus, we have found that the reaction of bulky 2,4-di-*tert*-butylphenol with cinnamyl alcohol does not occur using acid faujasites as catalysts, while in the presence of MCM-41 the corresponding dihydrobenzopyran **3** is formed. Previous studies have demonstrated that in the case of benzene¹² and furan¹³ derivatives, alkylation with cinnamyl alcohol in the presence of acid zeolites is catalysed by sites of low and medium acid strength.

Acid faujasite HY was prepared from commercial NaY (Aldrich, LZ52) by three consecutive Na⁺-to-NH₄⁺ exchange-calcination (500 °C) cycles using aqueous solutions of NH₄AcO of increasing concentrations.¹⁴ The final Na⁺ content was less than 0.2 ppm. A sample of HY was prepared by steam calcination at 1300 K of an 80% NH₄⁺-exchanged NaY zeolite (SK-40, Union Carbide), followed by treatment with 1 mol dm⁻³ citric acid solution at 333 K for 30 min. The zeolite was then washed and dried at 403 K, the final zeolite exhibiting a well-developed supermicropore system.^{15,16} Measurement of the pore distribution of the resulting HYM sample indicated a remarkable increase in the volume of 20–60 Å compared with untreated HY. MCM-41 was obtained according to the reported procedure⁶ by using amorphous silica (Aerosil 200, Degussa) and a 25% aqueous solution of tetramethylammonium hydroxide and hexadecyltrimethylammonium bromide as templates. The Si:Al ratio determined by chemical analysis was 95:1, while the pore size distribution measured by Ar adsorption was 30 Å. The acidity of the zeolites was determined by the pyridine adsorption–desorption method.¹⁷

When an equimolar solution of 2,4-di-*tert*-butylphenol and cinnamyl alcohol in isooctane was heated in the presence of HY

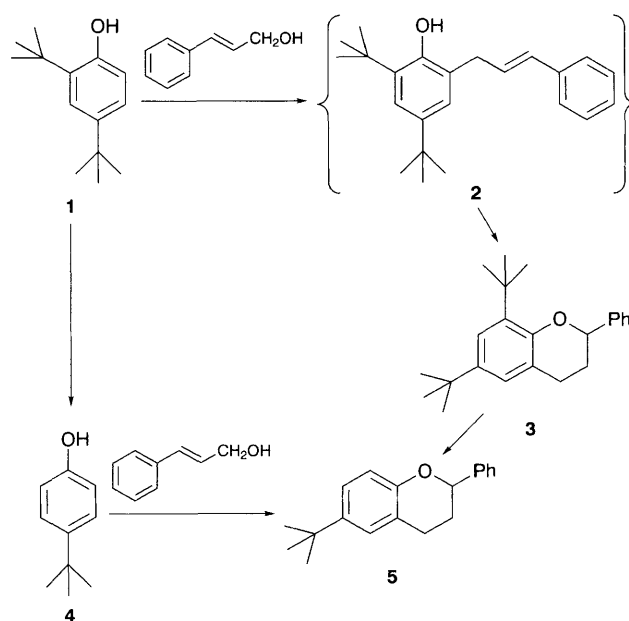
for 24 h, only very minor amounts of compounds **3** and **4** were detected. The modified HYM sample led to a substantial increase of the di-*tert*-butylated product **3**, thus indicating that the formation of mesoporosity (even though it is accompanied by a decrease in the number of acid sites due to a dealumination of the zeolite)^{15,16} does appreciably alter the accessibility of reactants and this increases its ability to catalyse the alkylation of **1**. Nevertheless, the selectivity to the Friedel–Crafts product **3** is still very low.

By contrast, working under the same conditions but using MCM-41 as catalyst, a mixture of **3**[†] and **4** together with minor amounts of **5** and unreacted starting material **1** was obtained. In fact, MCM-41 gave a much higher yield of **3** than conventional catalysis using sulfuric acid or amorphous silica–alumina

Table 1 Results of the reaction of 2,4-di-*tert*-butylphenol (206 mg) with equimolar amounts of cinnamyl alcohol (134 mg) in isooctane (50 ml) at 90 °C in the presence of solid catalyst (250 mg) or sulfuric acid (20 mg)

Catalyst	Products, yield (%)			
	1	3	4	Others
HY	89	<1	5	—
HYM	75	9	—	12 ^a
MCM-41	20	35	25	5(6)
Si/Al	56	6	—	—
H ₂ SO ₄	73	12	9	3 ^b

^a Dicinnamyl ethers plus diphenylpentadienes. ^b Tri-*tert*-butylphenol.



Scheme 1 Reaction products of 2,4-di-*tert*-butylphenol with cinnamyl alcohol in the presence of acid zeolites

(25%). The results obtained under the different catalysts studied are given in Table 1.

A possible explanation for the product formation observed is outlined in Scheme 1. Thus, dihydrobenzopyran **3** would arise through the intramolecular ring closure of the primary cinnamylphenol **2** (not detected) arising from the Friedel–Crafts alkylation of phenol **1**. On the other hand, compounds **4** and **5** would be formed by acid-catalysed dealkylation, a process that is generally observed in *tert*-butyl substituted aromatics¹⁸ and has been previously reported to occur using acid zeolites.^{19,20}

The different results achieved using Y zeolites and MCM-41 aluminosilicate can be easily interpreted assuming that the diffusion of phenol **1** through the windows of faujasites is strongly restricted, and the small amount of benzopyran **3** observed using HY must be formed on the external surface. This would be consistent with the increase in this conversion obtained when the ratio of external to internal surface in the zeolite was increased by steaming (HYM). Calculations based on molecular modelling using the Biosym Insight II package also predicts that **1** cannot enter into the faujasite supercages through the 7.4 Å opening windows. A visualization of this system is provided in Fig. 1. In contrast, the channel dimensions of the MCM-41 catalyst are large enough to allow the transit of substrate or products through the mesopores. This reaction exemplifies the new opportunities of novel MCM-41 as catalyst when the organic compound is too bulky to diffuse through the faujasite supercage.

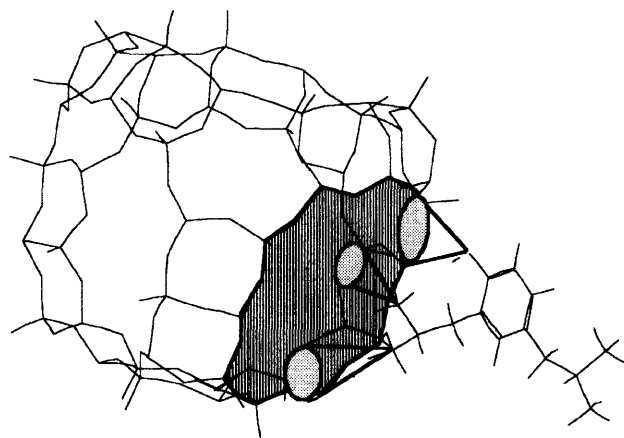


Fig. 1 Visualization based on molecular modelling of 2,4-di-*tert*-butylphenol **1** entering through the window of the faujasite supercage. The cavity opening is outlined (heavy lines), while regions where an overlapping of the van der Waals radii of methyl and OH groups of **1** with the zeolite framework atoms occurs are shadowed.

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Footnote

† IR ν/cm^{-1} : 3072, 2963, 1590, 1475, 1450, 1398, 1366, 751, 698. ¹H NMR (CDCl₃): δ 7.50–6.98 (m, 7H, ArH), 4.99 (dd, 1H, J_1 12.8, J_2 2.4 Hz, H at C2), 3.10–2.84 (m, 2H, CH₂), 2.18–2.11 (m, 2H, CH₂), 1.32–1.28 [s + s, 9H + 9H, 2 C(CH₃)₃]. MS: m/z 322(M⁺, 39), 307(100), 251(10), 203(51), 104(6).

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