MCM-41–Quaternary organic tetraalkylammonium hydroxide composites as strong and stable Brønsted base catalysts

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Quaternary organic tetraalkylammonium hydroxide grafted on MCM-41 is a strong Brønsted base catalyst, and represents a useful alternative to soluble bases in reactions such as Knoevenagel condensations, Michael additions and aldol condensations because of their high catalytic activity under mild conditions, and good stability.

The development of environmentally friendly solid catalysts for the production of fine chemicals is becoming an area of growing interest, and recyclable solid base catalysts are needed. Alkali ion-exchanged zeolites,[1,2] sepiolites,[3] alkaline oxides supported on microporous [4,5] and mesoporous aluminosilicates,[6] alkaline earth solids such as magnesium oxide,[7] aluminium–magnesium mixed oxides derived from hydrotalcites[8] and organic resins[9] can cover a wide range of basic strengths. The recently discovered family of mesoporous MCM-41 materials, with the possibility of being prepared with a wide range of pore dimensions, provides a unique inorganic support for introducing basic sites in a post-synthesis step and expanding the possibilities of the above described solid catalysts. Indeed, the reported anchored amines on MCM-41,[10] *e.g.* the immobilized 1,5,7-triazabicyclo[4.4.0]dec-5-ene on MCM-41,[11] have been shown to be efficient base catalysts. However, excluding anionic resins, the basicity of the solid inorganic catalysts developed up to now is associated with Lewis sites, and there is a need for stable catalysts containing Brønsted basic sites.

Here we report the preparation of a strong Brønsted basic catalyst obtained by preparing an inorganic–organic composite formed by an organic ammonium quaternary salt anchored on the surface of pure silica MCM-41. The truly catalytic behaviour of this material as well as the recycling characteristics is shown for Knoevenagel condensations, Michael additions and aldol condensations.

Pure silica MCM-41 with 3.7 nm pore diameter was synthesised following a well-known method from the literature.[12]

The functional tetraalkylammonium groups were anchored on the Si-MCM-41 surface by reacting 3-trimethoxysilylpropyl(trimethyl)ammonium chloride ($SiNR_4Cl$) with hydroxy groups located at the surface. This was achieved by contacting the dehydrated MCM-41 material with a solution of the appropriate amount of $SiNR_4Cl$ (provided by ABCR GMBH, 50 wt% in MeOH) in $CHCl_3$. This slurry was stirred for 1 h to allow the $SiNR_4Cl$ to diffuse inside of the pores. Then, Et_3N (molar ratio $Et_3N/SiNR_4Cl = 2$) in $CHCl_3$ was added to the above slurry. The final liquid/solid mass ratio was 20. The reaction was performed for 12 h and functionalized MCM-41 was obtained by filtration, exhaustive washing with $CHCl_3$ and CH_2Cl_2 and drying at 60 °C overnight. The MCM-41 structure was preserved.

The exchange of chloride by hydroxide anions was carried out by contacting the functionalized MCM-41 samples with a 0.21 M methanolic solution of NMe_4OH at room temperature for 10 min using a liquid/solid mass ratio of 50. The solid was recovered by filtration and extensively rinsed with MeOH, followed by vacuum drying, and the MCM-41 structure was preserved. The degree of exchange was calculated by titration of the NMe_4OH solution after exchange. The OH/N ratio found for all samples was close to 1. ^{29}Si MAS NMR spectroscopy and elemental analysis of the catalysts in the chloride and hydroxide forms show that no leaching of the anchored tetraalkylammonium occurs during the anionic exchange of chloride by hydroxide anions.

Table 1 Knoevenagel condensation between benzaldehyde **1** (10 mmol) and ethyl cyanoacetate **2a** (8 mmol) in the presence of MCM-41OH (80 mg) at 60 °C under N_2

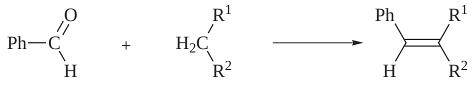
Catalyst	Anchored NMe_4OH[a]	Intial rate[b]/ 10^{-4}	TON[c]/ 10^{-3}	Yield of **3a**
MCM-41OH1[d]	1.22	17.8	1.45	88[e]
MCM-41OH2[d]	0.88	11.0	1.25	77[e]
MCM-41OH1[f]	1.22	217	17.8	95[g]
MCM-41OH2[f]	0.88	163	18.6	90[g]
NMe_4OH[f]	0.064[h]	208[i]	32.5	100[g]

[a] In millimoles of NMe_4OH per gram MCM-41. [b] In moles of product per minute per gram of catalyst. [c] Turn over number in moles of product per minute per millimole of NMe_4OH. [d] $CHCl_3$ as solvent (5 ml). [e] 2 h reaction time. [f] Without solvent. [g] 0.5 h reaction time. [h] NMe_4OH added (in mmol). [i] In mol min^{-1}.

MCM-41OH1 was tested as a basic catalyst for the Knoevenagel condensation of benzaldehyde **1** with ethyl cyanoacetate **2a**. The reaction progress was monitored by withdrawing aliquots which were analyzed by GC, and the products were identified by GC–MS. The reaction was carried out in $CHCl_3$ at 60 °C under nitrogen atmosphere using the conditions shown in Table 1. After 2 h the conversion of ethyl cyanoacetate was 88% with 100% selectivity for the condensation product **3a** (Scheme 1).

When the condensation was carried out under the same reaction conditions described above, but in the presence of an MCM-41 sample containing a different amount of anchored tetraalkylammonium quaternary salt (MCM-41OH2), it was possible to see that the initial rate was proportional to the amount of anchored tetraalkylammonium hydroxide (Table 1), indicating that a highly homogeneous strength distribution of basic sites is obtained on these catalysts and there is total accessibility of reactants to the active centres.

The condensation was also carried out without solvent under the reaction conditions described above, and the yield, initial rate and TON obtained are given in Table 1. When the Knoevenagel condensation was carried out using other active methylene compounds, *i.e.* phenylsulfonylacetonitrile **2b**, in the presence of MCM-41OH1 at 70 °C, the reaction was completed within 1 h with 100% selectivity for phenylsulfonylcinnamonitrile **3b**.



1 **2a,b** **3a,b**

a $R^1 = CN$, $R^2 = CO_2Et$
b $R^1 = CN$, $R^2 = SO_2Ph$

Scheme 1

Table 2 MCM-41OH1 as a catalyst for Michael reactions[a]

Entry	Donor	Acceptor	T/°C	t/h	Yield (%)[b]
1	Ethyl 2-oxocyclopentanecarboxylate	Methyl vinyl ketone	20	1	85
2	Ethyl cyanoacetate	Methyl vinyl ketone	20	2	72 (30)
3	Ethyl cyanoacetate	Methyl vinyl ketone	60	1	58 (37)
4	Ethyl cyanoacetate	Cyclopentanone	80	2	50 (10)
5	Ethyl cyanoacetate	Cyclohexanone	80	2	35
6	Diethyl malonate	Methyl vinyl ketone	60	2	10

[a] Reaction conditions: 8 mmol of donor, 8 mmol of acceptor, 60 mg of catalyst, 2 ml MeCN under N_2. [b] Molar yield of double-addition product in parentheses.

For comparison purposes, the reaction between ethyl cyanoacetate and benzaldehyde was also carried out using NMe_4OH as a homogeneous basic catalyst (Table 1), and the initial rate per mmol of OH^- is almost twice than with the heterogeneous catalyst. Taking into account the fact that the accessibility of the reactants to the active sites on MCM-41 must be almost unrestricted, the smaller intrinsic activity shown by the heterogeneous catalyst could be explained by considering that the hydroxide group might be interacting with the remaining silanol groups located on the inner part of the MCM-41 channels.

Michael additions using different donor and acceptor substrates and requiring stronger basicities than Knoevenagel condensations were also carried out (Table 2). In all cases, products coming from side reactions such as rearrangements, dimerizations or other condensations were not observed, and extremely high selectivities for the 1,4-adduct can be achieved. This excellent selectivity must be attributed to the well-defined strong basicity of the MCM-41OH.

These results show that MCM-41OH is an efficient catalyst for Michael additions with acceptable yields and selectivities when working under mild conditions with large substrates. This is in contrast with other modified MCM-41 materials reported previously, such as Cs-MCM-41 materials, which only catalyse Michael reactions under much more drastic conditions,[6] or the MCM-TBD catalyst,[11] where the bulky immobilized 1,5,7-triazabicyclo[4.4.0]dec-5-ene reduces the pore size of the catalyst inducing a transition state shape selectivity or even limiting the accessibility of bulky reactants to the active sites.

MCM-41OH1 was also tested as a basic catalyst for the aldol condensation between benzaldehyde and 2′-hydroxyacetophenone (10 mmol and 8 mmol, respectively; 15 wt% relative to the catalyst). The solid was able to catalyse the successive aldol condensation and intramolecular Michael addition to flavanone in a solvent-free system at 130 °C. After 8 h reaction time a conversion of 65% with a selectivity of 78% for flavanone was obtained.

The MCM-41OH1 catalyst used in the Knoevenagel reaction between ethyl cyanoacetate and benzaldehyde in EtOH was reused three times, after Soxhlet extraction with CH_2Cl_2, and no leaching and/or deactivation of the catalyst was observed.

Our results prove that it is feasible to introduce strong Brønsted basic sites into the MCM-41 structure by anchoring tetraalkylammonium hydroxide salts. This new solid base catalyst is a useful alternative to soluble bases in reactions such as Knoevenagel condensations, Michael additions and aldol condensations because of its high catalytic activity under mild liquid phase conditions. The mechanical stability of the inorganic support materials ensures easy separation of the solid catalyst together with waste minimisation and the possibility of recycling.

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