Base and Acid Catalysis by the Alkali-containing MCM-41 Mesoporous Molecular Sieve

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Sodium and caesium cation-exchanged mesoporous MCM-41 are shown to be mild, selective, water-stable and recyclable catalysts for the base-catalysed Knoevenagel condensation and acid-catalysed acetalization and aldol condensation, whereas caesium acetate-impregnated MCM-41 shows strong base activity in the Michael addition.

The development of clean and economical processes for the production of fine chemicals is becoming an area of growing interest. Solid inorganic catalysts, especially zeolites, have the advantage of being tunable and recyclable and are easily separated from liquid reaction mixtures. The recently developed family of mesoporous molecular sieves, M41S,[1] and the related kanemite-based materials,[2] have enlarged the field of possible applications.[3] So far the focus is on one member of the M41S family: MCM-41 with a pore size of *ca.* 40 Å. Until now only a few papers have been published about its acid catalytic properties.[3–6]

Besides acid catalysts, there is a need for recyclable, water-stable solid base catalysts. Inorganic solid catalysts such as clays have been advanced in this respect.[7] Regarding base catalysis by zeolites, it is generally known that the average oxygen charge or basicity increases with increasing aluminium content of the zeolite and with increasing ionic radius of the exchanged alkali cation.[8,9] Also, zeolites containing intrazeolitic caesium oxide particles[10] or sodium clusters[11] have been advanced as base catalysts. Here we report on the basic properties of alkali cation-exchanged/impregnated MCM-41.

MCM-41 was synthesized according to the literature method.[12] The calcined material, denoted HNa-MCM-41, containing Si : Al and Na : Al ratios of 13.0 : 1 and 0.5 : 1, respectively, was ion-exchanged with 0.1 mol dm^{-3} NaCl at room temperature for 2 d, recovered by filtration, washed with distilled water and dried under vacuum at 80 °C. In this way the Na : Al ratio of the resulting Na-MCM-41 was raised to 1.0 : 1. H-MCM-41 was prepared by ion-exchange with 1 mol dm^{-3} NH_4NO_3 at 80 °C for 20 h and calcined at 450 °C for 6 h. Cs-MCM-41 materials were obtained by stirring MCM-41 at room temperature for 20 h with a 0.1 mol dm^{-3} solution of CsCl or a 1 mol dm^{-3} solution of caesium acetate (CsOAc). The Cs : Al and Na : Al ratios of the two Cs-MCM-41 samples (denoted A and B, respectively) were 0.8, 0.2 and 3.8, 0.1, respectively, indicating for the latter that an appropriate amount of the CsOAc is incorporated inside the pores. All MCM-41 samples were calcined at 450 °C for 10 h prior to use.

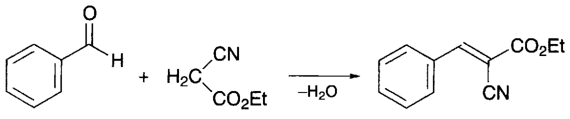
Na-MCM-41 was tested as a base catalyst in the Knoevenagel condensation (Scheme 1) of benzaldehyde with ethyl cyanoacetate (pK_a = 9),[9] with the reaction progress monitored by GC and the products identified by GC-MS and reference samples. Carrying out the reaction without solvent resulted in a conversion of 81% with a selectivity of 75% to the dehydrated product being obtained within 7 h. When testing the reaction in water at 100 °C with Na-MCM-41 a conversion of *ca.* 90% within 3 h with a selectivity of nearly 100% was obtained. Homogeneous catalysis by leached basic particles can be excluded. In contrast to the recovered catalyst, the filtered reaction mixture demonstrated no activity after adding fresh substrate. Likewise, H-MCM-41 is inactive. Na-MCM-41 also showed a high activity in bi-phased systems like THF–H_2O at 70 °C (Table 1). Na-MCM-41 is also able to abstract a proton from the less acidic diethyl malonate (pK_a = 13.3) in a solvent-free system at 150 °C, but only a 6% conversion after 3 h could be obtained. Unexpected solvent effects in Knoevenagel condensations have been found by several workers.[13,14]

Various alkali-containing MCM-41 materials can be compared by expressing their specific activity A as mol h^{-1} mol$^{-1}_{\text{alk. met.}}$ (A_{alk}) or as mmol h^{-1} g$^{-1}_{\text{MCM-41}}$ (A_{wt}). Table 1 illustrates that Cs-MCM-41A is about twice as active as Na-MCM-41. However, a five times higher A_{alk} was found when using the unexchanged HNa-MCM-41, though the A_{wt} is comparable.

A completely different reaction occurred when Na-MCM-41 (5% *m*/*m*) was suspended in a refluxing ethanolic solution of benzaldehyde and ethyl cyanoacetate. The latter remained unreacted in solution, while benzaldehyde was acetalized with 2 equiv. ethanol. Within 30 min the reaction reached equilibrium conversion (60%) with a selectivity of 100% to the diethyl acetal. The acetalization was also catalysed by H-MCM-41 with essentially the same selectivity and A_{wt}. We conclude that in both cases the acetalization is acid catalysed.

Another reaction that was found to be acid-catalysed by MCM-41 was the aldol condensation of benzaldehyde with acetophenone to chalcone [Scheme 2(*a*); R = H].[15] Table 2 shows that H-MCM-41 and Na-MCM-41 were both able to catalyse these reactions in the absence of any solvent at 150 °C, although the latter was slightly less active. The selectivities of around 90% at 6 h and virtually unchanged conversions after one day under air suggest that the catalyst deactivates.[15] A significant improvement of the aldol condensation could be obtained by performing the reaction under nitrogen.

Table 3 illustrates that bulky substrates like α-tetralone can also easily be converted to benzylidenetetralone[16] with a high



Scheme 1

Table 1 Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate with different MCM-41 catalysts

Catalyst	Amount (% *m*/*m*)	*t*/h	Conversion (% *m*/*m*)	Selectivity (%)	A_{alk}/ mol h^{-1} mol$^{-1}_{\text{alk. met.}}$	A_{wt}/ mmol h^{-1} g^{-1} [c]
Na-MCM-41[a]	5	7	81	75	2.3	11.8
Na-MCM-41[b]	5	3	72	99	4.7	15.5
HNa-MCM-41[b]	5	3	61	95	24.9	14.1
Cs-MCM-41A[a]	1.6	7	67	60	5.3	12.9
Cs-MCM-41A[b]	5	3	72	98	7.5	18.4

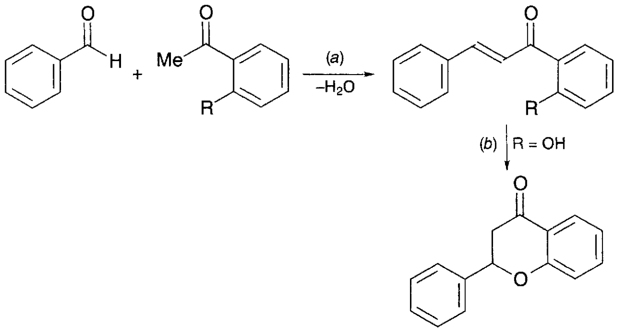
[a] Solvent-free at 150 °C, 20 mmol of ethyl cyanoacetate and 26 mmol of benzaldehyde. [b] THF–H_2O at 70 °C, 15 ml of each and 10 mmol of each reactant. [c] Specific activity at *t*.

selectivity. Allylic ketones like isophorone were converted less easily to benzylideneisophorone[16] and the reaction was accompanied by the production of a substantial amount of by-products. Na-MCM-41 and H-MCM-41 were also capable of catalysing the successive aldol condensation and intramolecular Michael addition to flavanone [Scheme 2(*a*) and (*b*); R = OH].

Table 2 Aldol condensation of benzaldehyde (26 mmol) and acetophenone (10 mmol) with H- and Na-MCM-41 catalyst (5% *m*/*m*) in the absence of solvent at 150 °C

Catalyst	*t*/h	Conversion (% *m*/*m*)[a]	Selectivity (%)[a]	A_{wt}/ mmol h^{-1} g^{-1} [a,b]
H-MCM-41	1	21	96	28.8
	3	50	92	21.9
	6	72	90	14.6
Na-MCM-41[b]	1	18 (15)	97 (99)	24.3 (23.1)
	3	34 (56)	92 (98)	14.9 (17.9)
	6	53 (73)	89 (98)	9.9 (14.2)

[a] Values in parentheses are the results of the reaction under nitrogen. [b] Specific activity at *t*.



Scheme 2

Table 3 Aldol condensation of benzaldehyde and different ketones with Na-MCM-41 catalyst (5% *m*/*m*) at 150 °C without solvent

Ketone	*t*/h	Conversion (% *m*/*m*)[b]	Selectivity (%)[b]
α-Tetralone	6	60	98
Isophorone	6	20	55
2′-Hydroxyacetophenone	2	10 (8)	72 (77) : 28 (23)[c]
	8	25 (27)	52 (62) : 48 (38)
	24	35 (56)	33 (37) : 67 (63)
2′-Hydroxyacetophenone[a]	2	9	63 : 37
	8	26	55 : 45
	24	36	31 : 69

[a] H-MCM-41 as the catalyst. [b] Values in parentheses are the results of the reaction under nitrogen. [c] Selectivities 2′-hydroxychalcone : flavone [Scheme 2(*a*), (*b*); R = OH].

The strongly basic Cs-MCM-41B was able to catalyse the Michael addition of chalcone and diethyl malonate (26 mmol and 20 mmol, respectively; 1.8% *m*/*m* catalyst) in a solvent-free system at 150 °C. Within 30 min a conversion of 87% and a selectivity of 91% to the product were obtained. In the case of ethyl cyanoacetate the reaction was completed within 5 min. Also, zeolites X and Y impregnated with CsOAc showed a stronger basicity than caesium cation-exchanged with CsCl.[11] This difference is attributed to the formation of Cs_2O particles, probably *via* caesium carbonate intermediates and loss of CO_2 upon thermolysis of CsOAc.

In conclusion, H-MCM-41 and Na-MCM-41 both contain acid sites, but given the results on the Knoevenagel condensation the latter also contains basic sites having a $pK_b < 9$ and a few of them having a $pK_b < 13.3$. The indistinct influence of the larger caesium cations suggests that the structure of the basic active sites is essentially cation-independent. On the other hand, MCM-41 impregnated with CsOAc seems promising for superbase catalysis.

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