Aminopropylated MCMs as base catalysts: a comparison with aminopropylated silica

Duncan J. Macquarrie* and Dominic B. Jackson

Department of Chemistry, University of York, Heslington, York, UK YO1 5DD

Aminopropyl-functionalised MCMs, prepared *via* a one-pot method, are found to be effective base catalysts for the Knoevenagel reaction, with significant improvements in terms of turnover number and solvent dependence to the ostensibly similar aminopropylsilica.

We, and others, recently reported a simple one-pot method for the preparation of surface-modified monodisperse MCM-type silica.[1,2] This method can be used to prepare organically modified materials in high yield, which have very high surface areas (650–1600 $m^2\ g^{-1}$) and are functionalised with a variety of organic groups. The pore size distribution of these materials is very narrow and in the mesoporous region (1.8–3.9 nm). Such properties would make these materials potentially very interesting as novel catalysts. We have recently reported that aminopropylated silica is an effective base catalyst, which is limited in its usefulness by an unusual solvent dependency, and which is poisoned by amide formation at the NH_2 groups.[3] We now wish to report our findings on aminopropylated MCMs, materials which display considerable differences in catalytic activity to the apparently similar aminopropylsilicas.

The aminopropylated MCMs were prepared according to known methods.[1] Three catalysts were prepared, whose structural and compositional characteristics are shown in Table 1. The ability to increase loading of these materials by changing the ratio of the two silanes [aminopropyl(trimethoxy)silane and tetraethoxysilane] used in their preparation makes this methodology more flexible than the post-modification of silica, where maximum loadings are in the region of 1 mmol g^{-1}. The surface area and pore size distributions are as expected for such materials, and their surface polarity, as measured using adsorption of Reichardts dye[4] is significantly higher than that of the corresponding silica-derived materials, and approaches that of underivatised silica [E_N^T (SiO_2) = 0.89–0.96, depending on drying conditions. Similar values are obtained for unmodified MCMs]. This difference can be ascribed to the larger amount of exposed, unfunctionalised surface in the case of the MCM materials, and, in agreement with this, the 2.5 mmol g^{-1} loading catalyst has a value lower than that of the 1.2 mmol g^{-1} material. Such a difference might be expected to lead to different solvent dependency in reactions catalysed by the MCMs compared to the silica-derived catalysts, owing to different partitioning of reactants between the catalyst surface and the bulk solution.

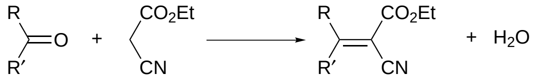
The catalysts were then evaluated in a series of reactions. Reactions used were the Knoevenagel condensation of aldehydes and ketones with ethyl cyanoacetate, a model reaction which has been studied in some detail.[3,5,6,7] The CH acid and the ketone (20 mmol of each) were added to a suspension of the catalyst (0.25 g) in the appropriate solvent (25 ml) at reflux. All reactions were run with continuous removal of water. Reactions were followed by GC using *n*-dodecane as internal standard, and products were isolated using conventional techniques. Results are shown in Table 2. Yields are generally high and compare favourable well with those in the literature.[3,5,6,8] As

Table 1 Selected physical parameters of catalysts

Catalyst	Pore diameter/nm	SSA/ $m^2\ g^{-1}$	Loading/ mmol g^{-1}	E_N^T
1	3.6	756	1.2	0.90
2	3.7	745	2.5	0.82
3	1.8	715	1.2	0.86
AMPS[a]	8.0 (br)	254	0.95	0.56

[a] Aminopropyl-substituted silica.

Table 2 Selected reaction data for reactions catalysed by aminopropyl-MCMs



R	R′	Catalyst	Solvent	*T*/°C	*t*/h	Yield (%)[a]	TON[b]
Ph	H	**1**	cyclohexane	82	36	94	
n-C_7H_{15}	H	**1**	cyclohexane	82	0.5	93	> 6000
cC_5H_{10}		**1**	cyclohexane	82	4	96	2450 (650)
cC_5H_{10}		**1**	cyclohexane	82	12	70[c]	
cC_5H_{10}		**1**	toluene	110	2	92	
cC_5H_{10}		**1**	EtOAc	78	4	11	
cC_5H_{10}		**1**	$CHCl_3$	61	4	18	
cC_5H_{10}		**1**	DCE[d]	81	4	16	
cC_5H_{10}		**3**	cyclohexane	82	4	49	
Et	Et	**1**	cyclohexane	82	30	89	1127 (265)
Et	Et	**1**	toluene	110	18	95	
Et	Et	**2**	toluene	110	4	97	
Me	Bu^n	**2**	toluene	110	4	95	1244
Me	Ph	**1**	toluene	110	72	49	55 (250)
Me	Ph	**2**	toluene	110	36	48	47

[a] GC yields with *n*-dodecane as internal standard. Isolated yields are 3–7% lower. [b] Number of moles product per mole of NH_2 groups. Figures in brackets are for reactions using 1.0 mmol g^{-1} aminopropylsilica as catalyst. [c] Reaction carried out without removal of water. [d] 1,2-Dichloroethane.

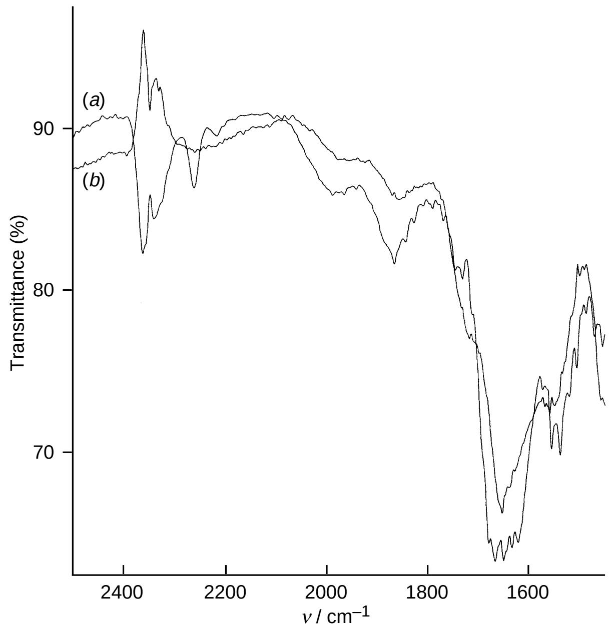


Fig. 1 IR spectra of spent catalysts recovered from Knoevenagel reactions: (*a*) spent aminopropylsilica and (*b*) spent aminopropyl-MCM

can be seen, the overall reactivity bears some similarity to that of aminopropylated silica.[3,5] Aldehydes and ketones both react with ethyl cyanoacetate, chosen as a carbon acid of moderate activity and synthetic utility. Surprisingly, benzaldehyde reacts extremely sluggishly with the MCM catalysts, despite being a facile substrate with both the silica-derived catalysts and with homogeneous amines such as piperidine. Otherwise, the relative reactivity of ketones is typical of both aminopropyl-modified silica and of most homogeneous systems. For reactions of ketones, the rates of reaction in cyclohexane, the optimum solvent for the silica variant, are typically 20–30% slower with the catalysts described here. However, as will be discussed later, the MCM-type catalysts are less restricted by solvent than their amorphous silica equivalents. Immediately obvious is the generally increased turnover numbers (TONs), although the reactivity and TON of acetophenone is disappointingly low. This, coupled with the remarkably low activity of benzaldehyde, may suggest that the reduced electrophilicity of the aromatic carbonyl, relative to the aliphatic, plays an unusually significant role in reactions catalysed by these materials.

Other points of interest are that the small pore (1.8 nm) catalyst **3** gives a poor conversion compared to the larger pore analogue **1**. However, it is interesting to note that the rate of reaction caused by both catalysts is essentially identical, the difference being that **1** remains active for longer. Increasing the loading from 1.2 mmol g^{-1} to 2.5 mmol g^{-1} causes a corresponding increase in reaction rate. Such an increase in loading is readily achieved by altering the ratio of silanes in the preparation of the MCM catalysts, but is not possible with the post-functionalisation of silica, where 1.0 mmol g^{-1} is the maximum loading achievable. In connection with TON, the mode of catalyst deactivation also differs between the two catalyst types. For the silica catalysts, there is clear evidence for a slow, irreversible formation of surface-bound amide groups, arising from the reaction of the surface-bound primary amine and the ester of the ethyl cyanoacetate [Fig. 1(*a*)]. In the case of the MCM catalysts, recovered spent catalyst does not display bands for nitrile or amide groups, but rather indicates the presence of some adsorbed organics [Fig. 1(*b*)]. The identity of the species responsible is currently the subject of investigation.

A further point of divergence between the two types of catalyst is their behaviour in different solvents. Whereas the silica-based catalyst has a very limited range of solvents in which it is effective,† the activity of the MCM catalyst seems to follow a simpler trend with respect to reflux temperature of the solvent. However, it is clear that more polar solvents are disadvantageous (Fig. 2). While the reasons for this behaviour are still under investigation, it may be the case that the rate of reaction is influenced by the partitioning of the (polar) reactants between the catalyst surface (polar) and the bulk medium (non-polar). The silica-based catalysts have a significantly lower polarity, as measured by the Reichardts dye method[4] (Table 1). This might mean that partitioning away from the catalyst is pronounced even in moderately polar solvents such as toluene, whereas the much more polar MCM catalysts can more effectively compete for the substrate, thus effectively extending the range of useful solvents, leading to reaction rates greater than those achievable with the silica-based materials.

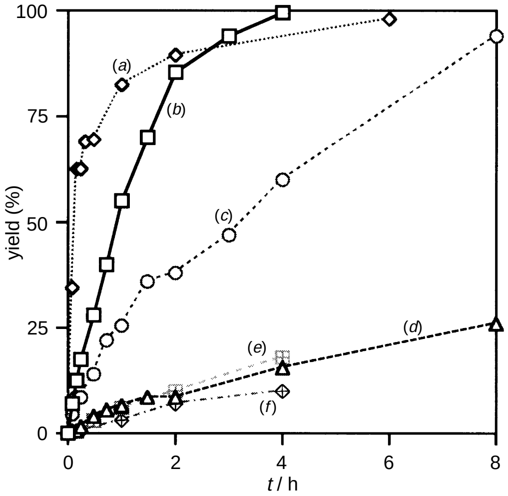


Fig. 2 Effect of solvents on the rate of reaction with aminopropyl-MCM **1**: (*a*) toluene, (*b*) cyclohexane, (*c*) hexane, (*d*) 1,2-dichloroethane, (*e*) chloroform, (*f*) ethyl acetate

In conclusion, the novel organofunctionalised MCM catalysts described here represent novel catalytic materials, differing significantly in many respects from their post-functionalised silica counterparts. Under optimum conditions they can outperform the silicas, in terms of both activity and catalyst turnover.

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Footnotes and References

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* E-mail: djm13@york.ac.uk

† The relative rates of reaction at reflux in various solvents are as follows: octane > heptane > cyclohexane > hexane > toluene > pentane ≫ chlorobenzene, 1,2-dichloroethane. Octane and heptane, however, lead to rapid deactivation of the catalyst. Initial rate studies with the alkane solvents indicate an Arrhenius-type behaviour, showing a simple temperature dependence of rate. More polar solvents such as toluene, PhCl and other chlorinated solvents show rates much reduced from those achieved in a hydrocarbon of similar boiling point.

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