CATALYSIS OF THE MICHAEL REACTIONS BY N,N'-DIMETHYLAMINOPROPYL DERIVATISED MICELLE TEMPLATED SILICA: EFFECTS OF SOLVENT AND CATALYST LOADING

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ABSTRACT. A neutral amine templating route was used to prepare dimethylaminopropyl-derivatised micelle templated silicas with various loadings. The resultant materials were characterised by various techniques and were also screened as catalysts in model Michael addition reactions. Results obtained show that materials with surface areas and organic group loading as high as 800 m^2g^{-1} and 3.4 mmol per g of silica, respectively, are obtainable. The materials show moderate to high catalytic activity as well as selectivity in a range of substrates. The activities and selectivities, however, are affected by catalyst loading and type of solvent.

KEY WORDS: Catalysis of Michael reactions, N,N'-Dimethylaminopropyl-derivatised micelle templated silicas, Effect of catalyst loading, Solvent effect

INTRODUCTION

Michael reaction is one of the carbon-carbon bond forming reactions developed over a century ago. It involves a nucleophilic addition of carbanions to α,β-unsaturated carbonyl compounds. Normally the carbanions are generated by bases that remove protons from activated methylene precursors.

Traditionally, the Michael reaction is catalysed by soluble mild to moderately strong bases such as diisopropylamine, potassium *t*-butoxide [1] and tetramethylguanidine [2, 3]. Unfortunately such bases sometimes generate significant amounts of multiple Michael adducts, involve other side reactions and are difficult to recover and recycle, aspects that are unfavourable as far as 'green chemistry' is concerned [4]. Green chemistry principles require chemical technologies that are not environmentally friendly to be replaced by cleaner and environmentally benign alternatives.

Currently there is an upsurge of interest in the development and use of heterogeneous catalysts. This is due to the fact that heterogeneous catalysts always offer many advantages over homogeneous counterparts. Such advantages include easy and safer handling of the catalyst, easy isolation of a catalyst from a reaction mixture by simple filtration or decantation and hence speedier regeneration and recovery of the catalyst, possible improvement of selectivity and hence less waste, and possible enhancement of reaction speed under mild conditions [5]. In light of the problems associated with the traditional catalysts in the Michael reaction, a number of heterogeneous catalytic systems have been developed. Examples of such systems include KF-alumina [6], potassium *t*-butoxide on xonotlite [7], and Amberlyst A-27 [8], which have been used with different degrees of success. Despite this effort the number of genuinely useful systems still remains low.

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Macquarrie *et al.* [9] reported a one-pot sol-gel method for preparing organic-silica hybrids. The method has been successful in preparing a number of such hybrids for catalytic applications [10-12]. For instance, aminopropyl-silica hybrids are very active catalysts in the Knoevenagel reaction [10, 11]. On the other hand, Mdoe *et al.* [13] reported that N,N'-dimethyl-3-aminopropyl-silica developed by both post-modification and *via* sol-gel copolymerisation processes are active catalysts in the Michael reaction. However, the latter report does not show detailed physicochemical properties of the material developed by the sol-gel method. In addition, effects of parameters such as catalyst loading and type of solvent were not investigated.

In continuation of a search for heterogeneous systems that can replace homogeneous ones in the Michael reaction, we hereby report a detailed account of the physicochemical properties of N,N'-dimethyl-3-aminopropyl-micelle templated silica hybrids and the effect of solvent and organic groups loading in the Michael reaction. Regeneration and recycling of the catalysts is also discussed.
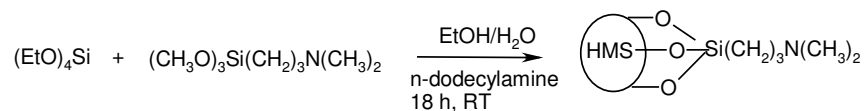
EXPERIMENTAL

3-Buten-2-one, cyclohexen-1-one, *n*-dodecane and *n*-dodecylamine were purchased from Aldrich Chemical Company, tetraethylorthosilicate (TEOS) and N,N'-dimethyl-3-aminopropyl(trimethoxysilane) were purchased from Fluorochem Ltd. Solvents were standard laboratory grade and they were used as purchased.

Characterisation

The physical structure of the materials was studied by nitrogen physisorption on a Coulter SA3100 porosimeter at 77.4 K. Scanning electron microscopy (SEM) images were obtained from an Hitachi SEM S2400 instrument, using an electron gun energy of 8 keV. Reichard's dye polarity measurements [14] were derived from diffuse reflectance ultraviolet-visible (UV-vis) spectra which were carried out on a Perkin Elmer Lambda 15 spectrophotometer. Infrared (IR) spectra were measured on a Bruker Equinox 55 FTIR spectrometer fitted with an environmental chamber diffuse reflectance unit. The samples were dried in air at 110 $^{\circ}$C prior to analysis and then run at room temperature as mixtures with KBr. Solid state ^{13}C nuclear magnetic resonance (NMR) spectra were obtained on a Bruker MSL300 spectrometer operating at 75 MHz at a rotor spinning rate of 5 kHz.

Preparation of materials

The procedure developed by Macquarrie *et al.* [9] was followed. In a typical experiment 18.8 g TEOS and 2.07 g of N,N'-dimethyl-3-aminopropyl(trimethoxy)silane were added separately, but simultaneously and rapidly to a stirred mixture of 5.08 g *n*-dodecylamine in aqueous ethanol (46 cm^3 of absolute ethanol and 53 cm^3 of deionised water) at room temperature. The mixture was stirred for 18 h after which it turned to a thick white paste. The thick solution was filtered, and the white solid washed with ethanol. The damp solid product was then refluxed in ten times its own weight of ethanol for 3 h and filtered again to remove the template. The solvent reflux was repeated twice to completely remove the template from the material. The final solid was then dried in an oven at 100 $^{\circ}$C to give material **I** (Scheme 1).

$(EtO)_4Si$ + $(CH_3O)_3Si(CH_2)_3N(CH_3)_2$ $\xrightarrow[\substack{\text{n-dodecylamine} \\ \text{18 h, RT}}]{\text{EtOH/H}_2\text{O}}$ HMS$-$O$-$Si$(CH_2)_3N(CH_3)_2$

Scheme 1. Preparation of dimethylaminopropyl-silica hybrid.

Materials of higher loading were prepared by changing the ratios of N,N'-dimethyl-3-aminopropyl(trimethoxy)silane to TEOS. The ratios used were 1:2, 1:3 and 1:4 which gave materials **II**, **III** and **IV** in that order. In each case the templates were recovered and reused in fresh experiments as explained elsewhere [12].

Reaction studies

In a typical procedure a 100 cm^3 reaction flask was charged with a catalyst (0.25 g), 25 cm^3 Michael donor, 20 mmol Michael acceptor and 0.3 cm^3 *n*-dodecane (gas chromatograph, GC, internal standard) and placed in an oil bath. The reaction mixture was then stirred while refluxing. The progress of the reaction was monitored continuously by GC. When no significant increase in product was observed, the reaction was stopped and the reaction mixture filtered off and evaporated at reduced pressure to give the crude product. Purification of the crude product was done by chromatography over silica gel with ethyl acetate/*n*-hexane (1:4) as eluent and the resulting products confirmed by gas chromatograph/mass spectrometry (GC/MS) and/or ^{1}H NMR.

5-Nitropentan-2-one. GC/MS: M[+], *m/z* (%) = 132 (10), 114 (5), 99 (20), 85 (100), 55 (10). ^{1}H NMR (CDCl$_3$): δ 2.2 (s, 3H), 2.3 (m, 2H), 2.7 (t, 2H), 4.5 (t, 2H J = 7.8 Hz).

5-Nitrohexan-2-one. GC/MS: M[+], *m/z* (%) = 130 (30), 115 (39), 99 (55), 83 (30), 73 (35), 55 (36), 43 (100). ^{1}H NMR (CDCl$_3$): δ 1.6 (d, 3H), 2.2 (s, 3H superimposed on m, 2H), 2.6 (t, 2H J = 7.8 Hz) and 4.7 (m, 1H).

5-Methyl-5-nitro-nonane-2,8-dione. GC/MS: M[+], *m/z* (%) = 200 (10), 168 (32), 153 (65), 135 (15), 125 (30), 107 (18), 43 (100).

5-Nitroheptan-2-one. GC/MS: M[+], *m/z* (%) = 160 (5), 141(3), 129 (13), 114 (100), 110 (15), 99 (48), 95 (60).

3-(Nitromethyl)cyclohexanone. GC/MS: M[+], *m/z* (%) = 158 (5), 114 (2), 110 (23), 97 (7), 82 (35), 67 (27), 55 (100).

3-(1-Nitroethyl)cyclohexanone. GC/MS of the 2 isomers: M[+], *m/z* (%) = 172 (52), 154 (5), 141 (7), 125 (100), 107 (30), 97 (65), 81 (37), 69 (22), 55 (95).

3-(1-Nitropropyl)cyclohexanone. GC/MS of the 2 isomers: M[+], *m/z* (%) = 186 (28), 168 (5), 155 (10), 139 (80), 121 (65), 109 (10), 97 (90), 81 (25), 69 (55), 55 (100). ^{1}H NMR (CDCl$_3$): δ 1.1 (t, 3H), 1.25-2.6 (m, 11H), and 4.5 (m, 1H).

In studying the effect of solvents the procedure was as follows. The reaction flask was charged with a catalyst (0.25 g), 25 cm^3 of an organic solvent, equimolar amount (20 mmol) of nitroethane and but-3-en-2-one, and 0.3 cm^3 *n*-dodecane. The reaction mixtures were then stirred and refluxed. The reactions in water were however, carried out using a slightly different method. In a typical procedure 40 mmol of nitroethane and 20 mmol of but-3-en-2-one were stirred at 60 ^{o}C in a mixture of water (25 cm^3) and 0.25 g of catalyst. In both cases the reactions were monitored by GC and products analysed by GC/MS. For the experiment conducted in a reaction mixture that had pH similar to that of the catalyst-water suspension, the pH of the mixture was adjusted using dilute NaOH or HCl.

RESULTS AND DISCUSSION

Characterisation of the materials

In order to establish the nature of the functional groups that are on the support surfaces, the developed materials were studied by diffuse reflectance Fourier transform infrared (DRIFT) and ^{13}C cross polarization magic angle spin nuclear magnetic resonance (CP MAS NMR) spectroscopies. Results on DRIFT studies showed that in addition to vibrations due to the silica lattice structure, all the important vibrations attributable to the presence of the respective supported organic groups were seen in the spectra (Figure 1). These are alkyl stretching vibrations at 2929 and 2871 cm^{-1} and alkyl CH deformation at 1467 and 1410 cm^{-1}. The vibrations arising from the silica support are those appearing at *ca*. 1830 and 1220–1030 cm^{-1} due to the Si-O-Si linkage. A strongly observable feature is the hydrogen-bonded SiOH stretching band at *ca*. 3600–3100 cm^{-1}. Other vibrations associated with groups such as C-N from the tertiary aliphatic amines appear at *ca*. 1200–1000 cm^{-1}. In the latter case however, the bands are strongly masked by the Si-O-Si stretching vibrations bands arising from the silica support.
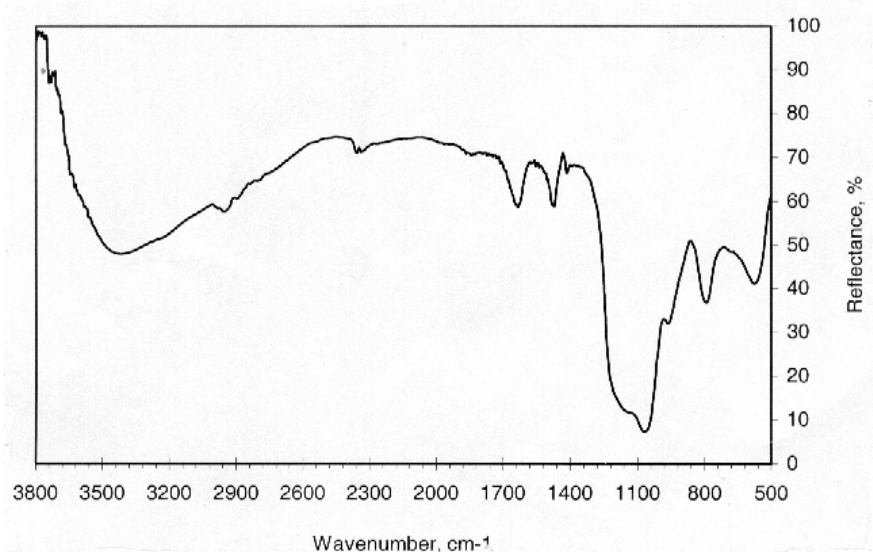
Figure 1. Diffuse reflectance FTIR spectrum of material **I**.

The ^{13}C CP MAS NMR spectra shown in Figure 2 reveal the presence of all expected carbons (see also Table 1). The peaks that appear at 61.2 and 19.9 ppm are broad and have up-field shoulders. The shoulders are likely to be due to residual -OEt groups which have been reported before with aminopropyl-silica materials [10]. Generally, the two spectroscopic techniques have proved that the targeted organic functional groups are indeed on the silica surface.

Figure 3 shows the scanning electron microscopy (SEM) images of the materials. As can be seen, there is a clear difference in the shapes and dispersity of the primary particles of the materials depending on the proportion of the organosilane. Material **I** is comprised of aggregates of small irregularly shaped particles together with roughly spherical particles with a typical size of about 0.4 μm (Figure 3a). On the other hand, material **II** (Figure 3b) is made up of aggregates

of small roughly spherical or ellipsoidal particles, but the particles are relatively more distinct and their surfaces are more regular. The majority of the particles fall in the size range of 0.3 to 0.7 μm. Further increase in the dimethylaminopropyl groups loading leads to production of a material with even larger particles (typically 30–80 μm) as shown in Figure 3c. The particles of material **III** are angular in shape and have a more solid texture like that of amorphous silica.
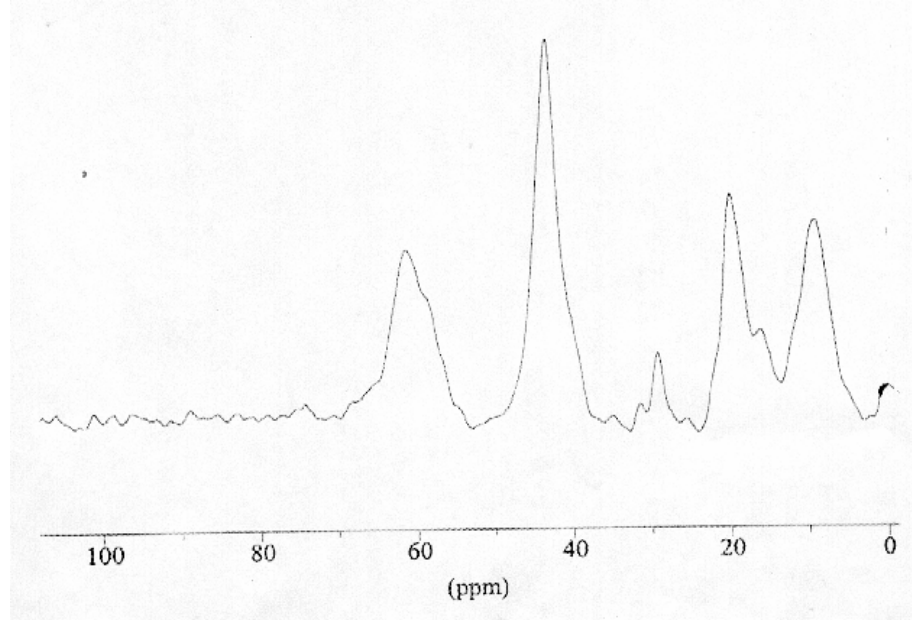

Figure 2. ^{13}C NMR spectrum of material **I**.

Table 1. Assignment of the chemical shifts of the ^{13}C NMR spectrum of material **I**.

Chemical shift/ppm	Assignment
61.2	-CH$_2$CH$_2$$\underline{C}H_2$N(CH$_3$)$_2$
43.1	-CH$_2$CH$_2$CH$_2$N($\underline{C}$H$_3$)$_2$
19.9	-CH$_2$$\underline{C}H_2CH_2$N(CH$_3$)$_2$
9.1	-$\underline{C}$H$_2$CH$_2$CH$_2$N(CH$_3$)$_2$

Table 2 summarises the physical properties of the prepared materials. The polarities of the material surfaces as indicated by E_N^T values are also shown in the table. E_N^T is a normalized Dimroth's parameter measured using Reichardt's dye [14]. As expected, the surface polarities of the materials surfaces decrease as the loading of the organic groups increases. For instance, the polarity of the surfaces decreases from 0.77 to 0.41 as the organic groups loading increases from 0 to 3.4 mmol g^{-1}. This is because as the loading is increased the surface tends to be hydrophobic due to the increase of the organic groups.

Figures 4 and 5 show the representative adsorption–desorption isotherms and the pore size distribution of the materials, respectively. The materials show type IV isotherms with a type H2 hysteresis loop. Type H2 hysteresis loop indicates a complex pore structure made up of interconnected network of pores [15]. There was no change in the shapes of the adsorption-desorption isotherm and the hysteresis loop of this material when the loading was increased

from 1.3 to 2.3 mmol g^{-1}. This implies that the increase in the proportion of the organosilane did not affect the porosity characteristic of the resultant material.
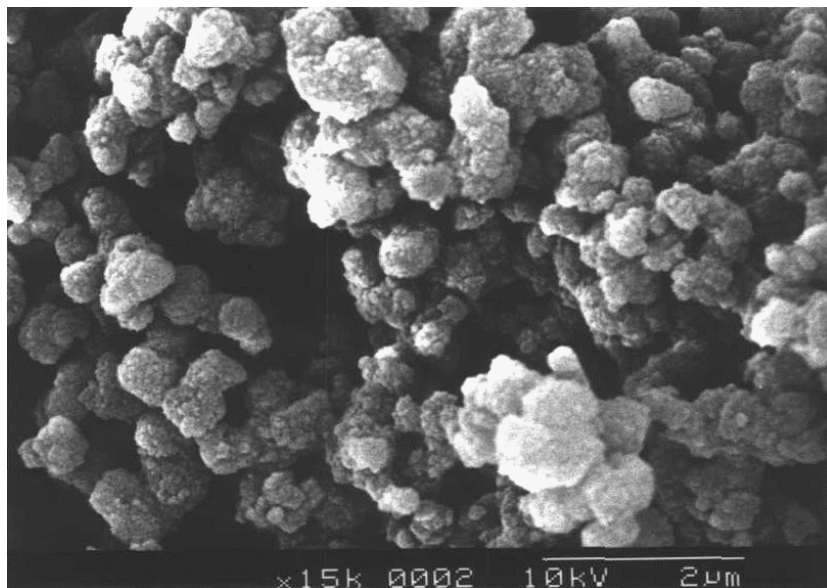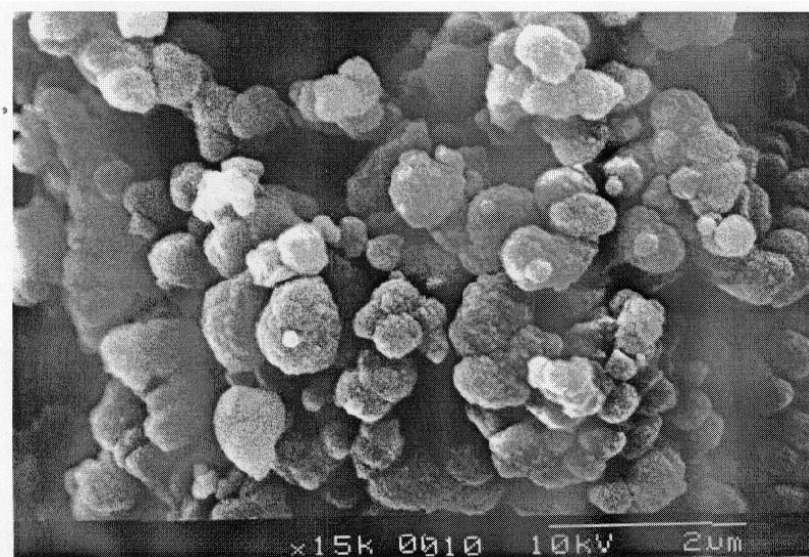

Figure 3a. Electron micrograph of material **I**.

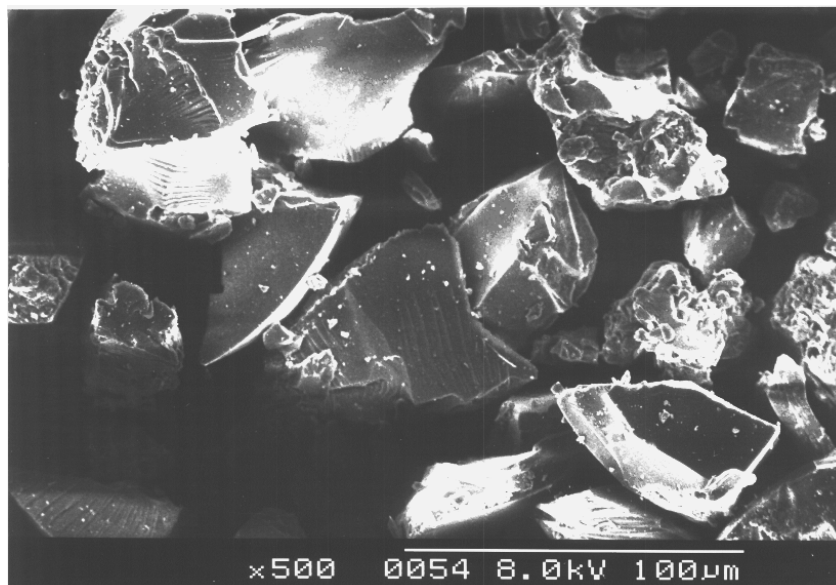Figure 3b. Electron micrograph of material **II**.

Figure 3c. Electron micrograph of material **III**.

Table 2. A summary of the physical properties of the developed materials

Material	S_{BET} (m^2g^{-1})	Average pore diameter (nm)	Total pore volume (cm^3g^{-1})	Loading $(mmol\ g^{-1})$	E_N^T value
I	790	3.5	0.69	1.2	0.74
II	707	3.7	0.65	2.2	0.68
III	395	3.5	0.34	2.9	n.d.
IV	323	n.d.	n.d.	3.4	0.41
Unmodified HMS	>1000	n.d.	n.d.	n.d	0.77

n.d. = not determined.

The pore size distribution curves (Figure 5) of the materials prepared at two different proportions of the dimethylaminopropylsilane show to a smaller extent that increasing loading leads to production of materials with pores of relatively wide range of sizes. Fewer and fewer framework confined pores are produced as a result of the increase in loading. This phenomenon is not that much significant as compared to materials based on primary aminosilane [16].

Hexagonal mesoporous silica (HMS) [17] and related family materials, materials that are prepared by one-pot sol gel method posses very large surface areas compared to amorphous silica. From Table 2 it can be seen that the surface areas of our materials are as high as 800 m^2 g^{-1}, well below that of HMS (typically > 1000 m^{2}g^{-1}). The surface areas decrease as loading increases. It has been reported before that organic-inorganic hybrids based on basic organosilanes that were developed by the sol-gel method have lower surface areas than those based on other non-basic organosilanes though the reason is still contentious [18].
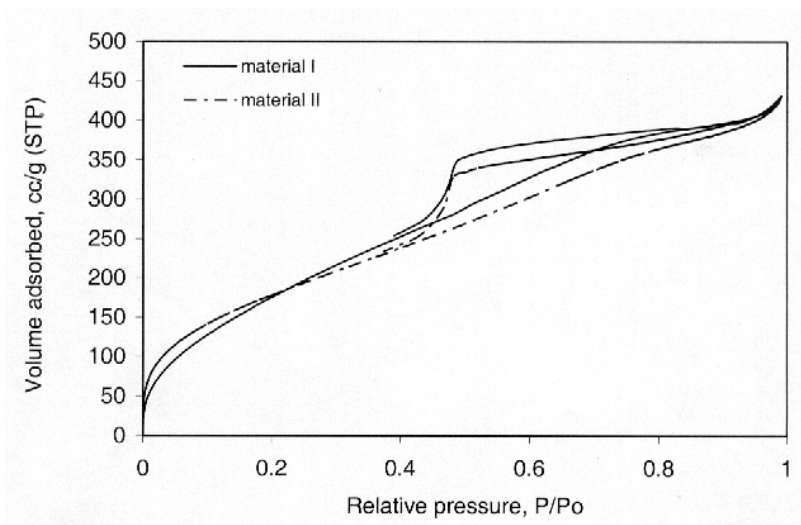
Figure 4. Adsorption-desorption isotherms of materials **I** and **II**.
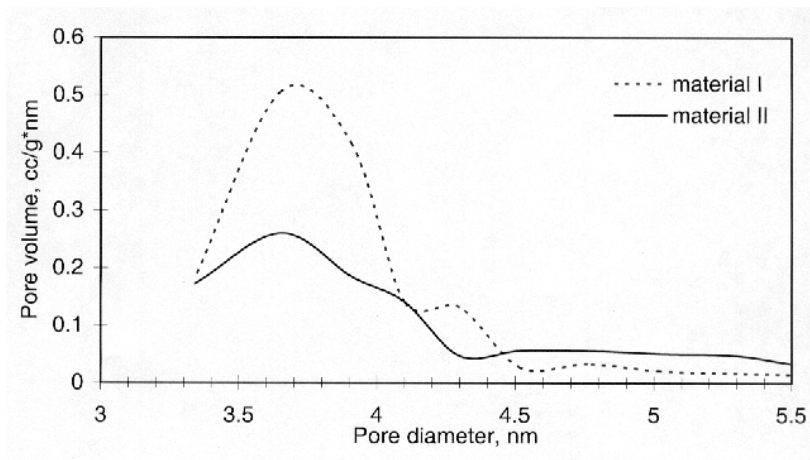

Figure 5. Pore size distribution of the materials **I** and **II**.

The average pore sizes closely match the length of the template alkyl chain, in this case *n*-dodecylamine. The typical average diameter of the pores obtained using this template is 3.6 nm. As expected, when a material with a lot of textural mesopores is produced the average diameter increases significantly. Despite the low surface areas of these materials relative to that of unmodified HMS, they are still considerably high over those of commercial amorphous silica (typically 300 m^2g^{-1}).

The thermal analysis traces of the dimethylaminopropyl-silica hybrids are shown in Figure 6. The traces indicate loss of residual solvent with a maximum at 80 °C followed by two minor weight losses of *ca*. 0.8% and 3% that are centred at 150 °C and 380 °C, respectively. A major

weight loss of *ca*. 7.8% and 16.5% for the materials **I** and **II**, respectively, occurs from *ca*. 400 ^{o}C and is accompanied by an endothermic effect centred at around 500 ^{o}C. The last two weight losses occur at temperatures characteristic of chemisorbed materials, the one occurring at around 500 ^{o}C being indicative of a robustly bound material. Studies of the gaseous products desorbed during the thermal analysis as recorded by thermogravimetry-Fourier transform infrared (TG-FTIR) spectroscopy (Figure 7) indicate the major loss above 400 ^{o}C to be due to loss of the attached dimethylaminopropyl groups. The loss is consistent with the loadings of 1.3 and 2.3 mmol g^{-1} for the materials **I** and **II**, respectively, as determined also by elemental analysis. The temperature at which the supported organic groups desorb indicate that indeed the organic groups are chemisorbed onto the support surfaces, consistent with earlier results on other HMS-supported organic groups [16].
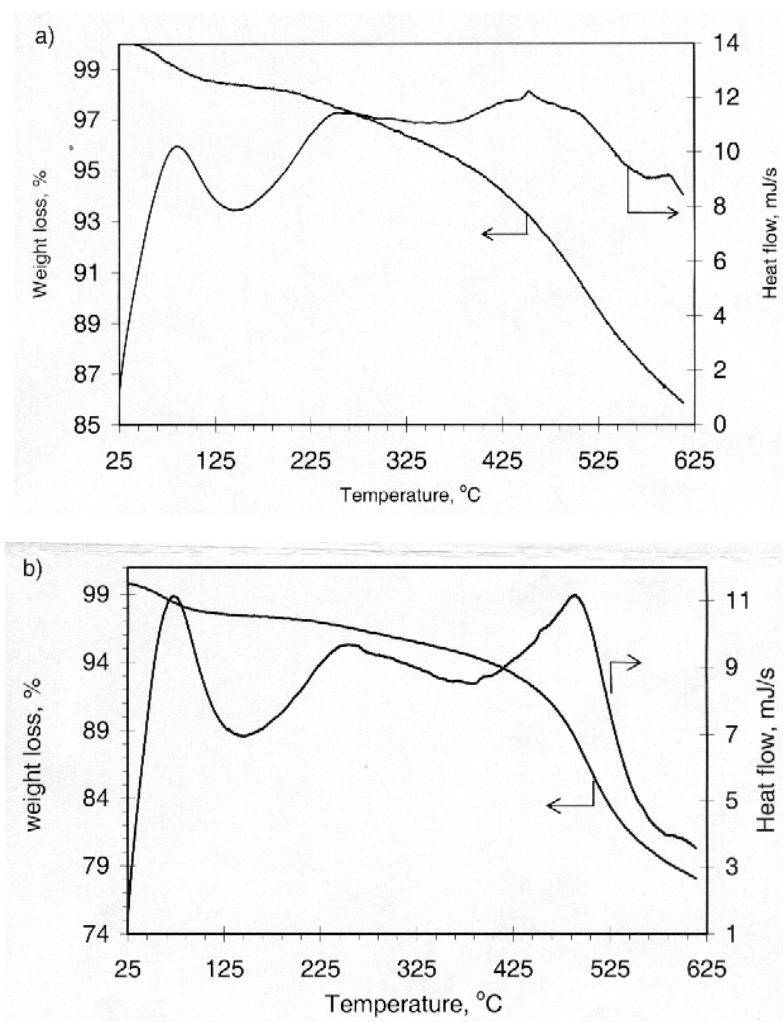
Figure 6. Thermal analysis traces of a) material **I** and b) material **II**.

The TG-FTIR studies (Figure 7) of the samples prepared show IR peaks that are believed to be associated with the degradation of the supported organic groups *via* a Hoffman elimination mechanism. In order to establish as to whether the peaks are indeed resulting from the desorption of the supported organic groups, an unmodified HMS material was studied by TG-FTIR as a control. The data obtained showed no peaks that are attributable to the presence of any organic group coming from the HMS surface. This shows that the vibrations observed earlier in the investigated dimethylaminopropyl-silica hybrids can indeed be associated with the supported organic groups.
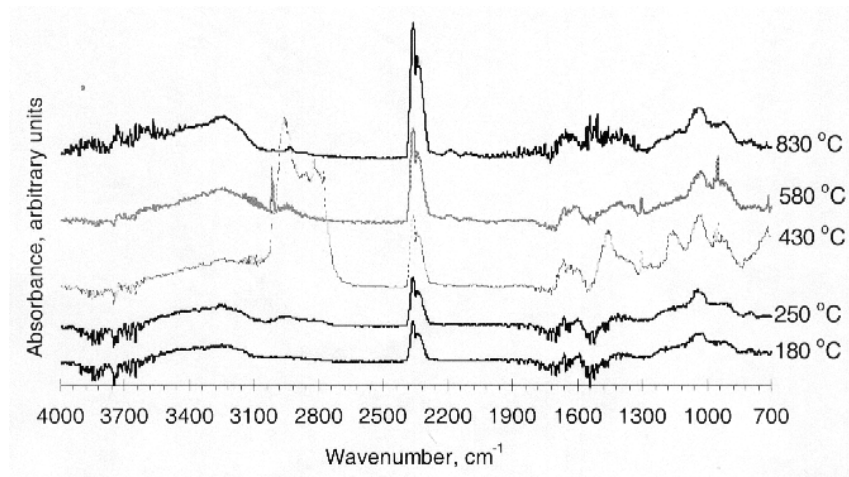
Figure 7. IR spectra of the gaseous products evolved from material **I** as recorded by TG-FTIR.

Catalysis of the Michael reaction
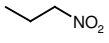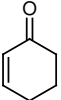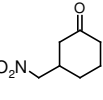
The dimethylaminopropyl-silica hybrids were screened as catalysts in the Michael reaction using a range of nitroalkanes as Michael donors. Two types of Michael acceptors, namely, but-3-en-2-one and 2-cyclohexen-1-one were used. Results obtained are given in Table 3. As seen on the table the materials are highly active in this reaction. The yield is however, slightly low when using nitromethane as a Michael donor. This shows the poor activity of this particular donor. Moreover, the catalysts show high reaction selectivities to mono Michael adduct, especially in the reactions between the nitro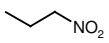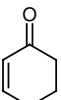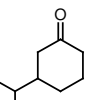alkanes and but-3-en-2-one. In the reaction between 2-cyclohexen-1-one and nitroalkanes, nitroethane and nitropropane, two diastereoisomers are obtained as products in a 1:1 ratio in both cases. In neither reaction, however, are any Knoevenagel type products observed, nor are there any double Michael additions. The diastereoisomers are consistent with the presence of two chiral centres in the products obtained. In addition, no leaching of the catalyst was observed in the reaction mixtures, and the reactions did not proceed when they were interrupted before their completion by removing the catalyst. This indicates that indeed the materials do catalyse the reactions.

Loading effects

A study of the effect of dimethylaminopropyl groups loading on activity has been conducted. Again, the model reaction was that between excess nitroethane and but-3-en-2-one under reflux

conditions. Table 4 gives the results obtained together with the catalysts loadings that range from *ca.* 1.0 to 3.4 mmol g^{-1}.

Table 3. The activities of materials I and II in catalysing the Michael reaction using various substrates.

Entry	Catalyst	Michael donor	Michael acceptor	Product	Yield[a] (%)	Time (h)
1	**I**	CH$_3$NO$_2$			70	4
2	**II**				80	3
3	**I**	NO$_2$			92	2
4	**II**				94	1.2
5	**I**	NO$_2$			90	2
6	**II**				95	1.5
7	**I**	CH$_3$NO$_2$			62	6
8	**II**				90	4
9	**I**	NO$_2$			72[b]	4.5
10	**II**				88	1.5
11	**I**	NO$_2$			86[b]	5
12	**II**				93[b]	2.5

[a]Yields of products quoted as % GC area as determined using *n*-dodecane as an internal standard.
[b]The yield is a sum of the two isomers which are obtained at a ratio of 1:1.

The evaluation of the catalytic activities of the materials in the model reaction shows the activity to increase with loading up to *ca.* 3 mmol g^{-1} and then drops off. The reasons for this observation are likely to be a complex interplay of many factors such as the physical nature of the catalysts (pore size distribution, surface area and pore shape), the relative polarity of the catalyst surface (which drops with increasing organic content) and the proportion of active groups that are available to react. In the higher loaded amorphous materials, it is likely that many dimethylaminopropyl groups are embedded within the bulk amorphous structure and hence can not take part in the catalysis process. In that case the effective catalyst loading becomes lower than that predicted by elemental analysis. The drop in activity at higher loadings has also been observed with similarly prepared aminopropyl-HMS catalysts in the Knoevenagel reaction [19]. In the latter report however, the behaviour occurs at loadings above 4 mmol g^{-1}, loadings achieved at similar organosilane to TEOS ratio as the material under discussion.

Table 4.   The loading effects on the activity of dimethylaminopropyl-HMS catalysts in the Michael reaction.

20 mmol   348 mmol
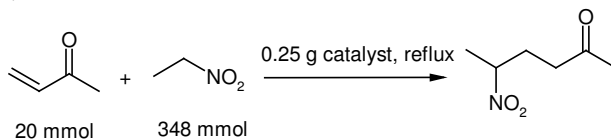
Material	Organic group loading (mmol g^{-1})	Yield (%)	Time (h)
I	1.2	92	2
II	2.2	94	1.2
III	2.9	95	1.5
IV	3.4	70	3

n.d. = not determined.

Solvent effects

The use of organic solvents. Solvents have tremendous effects on rates of reactions. The effect has been studied in the Michael reaction using our materials. A typical procedure involved mixing equimolar (0.8 mol dm^{-3}) amounts of nitroethane and but-3-en-2-one in a given solvent. The reactions were conducted at the refluxing temperatures of the respective solvents and the results are displayed in Figure 8. As seen from the figure, the solvents do have a massive influence on the rate of the reaction. The reaction is obviously not favoured by the use of solvents. When solvents are used less than 30% yield is obtained after 3 h compared to ca. 90% obtained in clean excess nitroethane in less than 2 h. In the latter case the ratio of the donor to the acceptor was nearly 20:1. The reason for the sharp decline in yield is thought to be due to a decrease in the effective concentration of the reactants on the catalyst surface resulting from competition between the reactants and the solvent for the surface, among other factors. Changing the ratio of the donor to the acceptor from 1:1 to 10:1 in the presence of solvents leads to an increase in the yield to ca. 35%, which is still not very significant. Moreover, less polar solvents show relatively better yields compared to polar solvents. A literature survey shows that a high proportion of nitroalkanes to Michael acceptors, typically at 20:1 ratios, are necessary for the reactions to give good yields [20]. The use of solvents has previously been shown to lead to a decrease in selectivity. Indeed heavy products believed to be oligomers resulting from the polymerisation of but-3-en-2-one were observed in the GC. This explains even further the cause for the decline in the yield.

Water as a solvent. Water is known to promote various organic reactions such as the Diels Alder [21], Claisen rearrangement [22] and the Michael addition [23]. The ability of water to promote the reactions is attributed to its high cohesive energy density, very large surface tension and very large heat capacity [24]. In the water promoted Michael reaction Lubineau and co-workers [23, 24] observed that the reaction between nitroalkanes and but-3-en-2-one can proceed without any catalyst to give quantitative yields, though after about 2 days. The reaction however, does not proceed without a catalyst in solvents such as tetrahydrofuran, toluene, and dichloromethane. When a homogeneous base such as NaOH is introduced into the system the reaction time is reduced significantly. In the present work water was used as a solvent in the Michael reaction catalysed by dimethylaminopropyl-silica hybrids. The interest was to investigate the effect of water in this system.
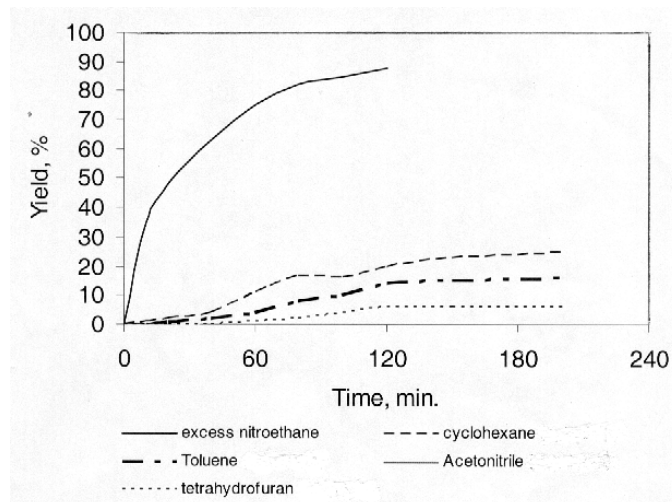
Figure 8. The solvent effects on the reaction between but-3-en-2-one and nitroethane.
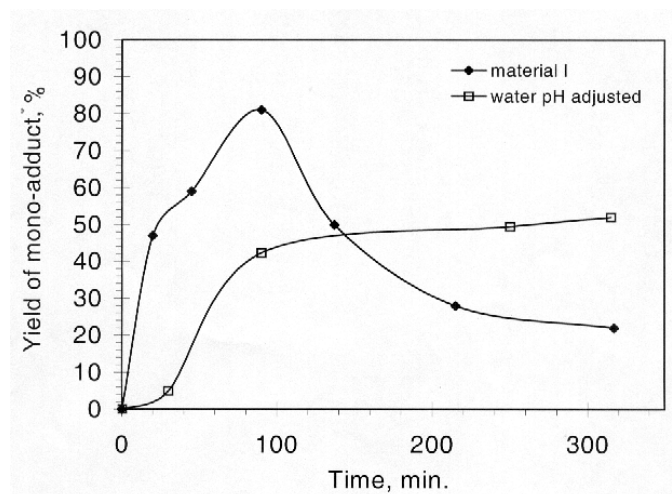

Figure 9. The effect of water as a solvent in the Michael reaction between excess nitroethane and but-3-en-2-one.

In a typical procedure nitroethane (1.6 mol dm^{-3}) and but-3-en-2-one (0.8 mol dm^{-3}) were stirred in a mixture of water and 0.5 g material **I** at 60 ^{o}C. In another experiment the reaction was run without a catalyst in a reaction mixture whose pH was adjusted to match that of the catalyst-water suspension. In both cases the reactions were monitored continuously by GC. The results obtained are presented in Figure 9. From the figure the following aspects are observable: a) The rate of reaction on material **I** is closely similar to that observed when excess nitroethane was used (*cf.* Figure 9). However, the yield of mono-adduct, **a**, starts to decrease drastically from about 90 minutes onwards (Scheme 2). The decrease is due to double Michael addition to

form a *bis*-adduct, **b**, which was observed in the reaction mixture in significant amounts together with but-3-en-2-one oligomers. b) The yield obtained in the pH adjusted reaction mixture does not go beyond 50% and no *bis*-adduct is observed. This shows that indeed the catalysts play a major role and the observation is not simply a pH effect.
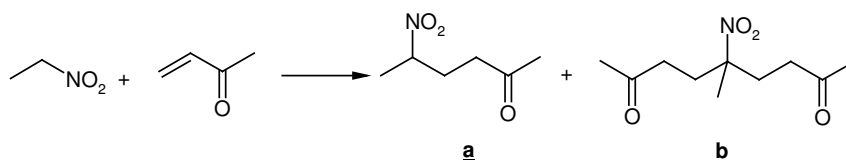
Scheme 2. A reaction between but-3-en-2-one and nitroethane to give mono- and bis-adducts.

From the above observations it is obvious that water plays a significant role in the reaction. The fact that a lot of *bis*-adduct is obtained with material **I** as a catalyst, indicates that there is an enhancement of basicity, or probably the residence time of **a** on the surface of material **I** is longer, leading to higher chance of the second reaction. The actual reason is still unclear. The main point however, is that material **I** is less selective under these conditions. Unfortunately, the data obtained in the present study do not allow a distinction to be made between the role of water and that of the catalyst in the catalysis of the reaction.

Catalyst recycling

Recycling of a catalyst is a very important aspect from an 'environ-economics' point of view. The reusabilities of material **I** in the Michael reaction were studied. After the reaction has stopped the catalyst was filtered off and washed thoroughly with nitroethane in order to remove physisorbed organics. This was followed by an immediate re-charging of fresh reactants without further treatment of the catalyst. Washing and drying of the used catalyst leads to a decrease in activity, a problem that has been observed previously with the Knoevenagel reaction [10].

The material continued to catalyse the reaction close to completion, though after progressively longer times (Figure 10). Effective reuse of the catalyst for up to 7 times is possible. After the materials had lost activity they were analysed by DRIFT spectroscopy. The spectra obtained show the presence of a lot of organic groups on the catalyst surface. The peaks were however, too complex to attribute to specific organic molecules. Nevertheless, this suggests that deactivation of the catalysts is likely to be due to blockage of the pores resulting from the accumulation of such groups.
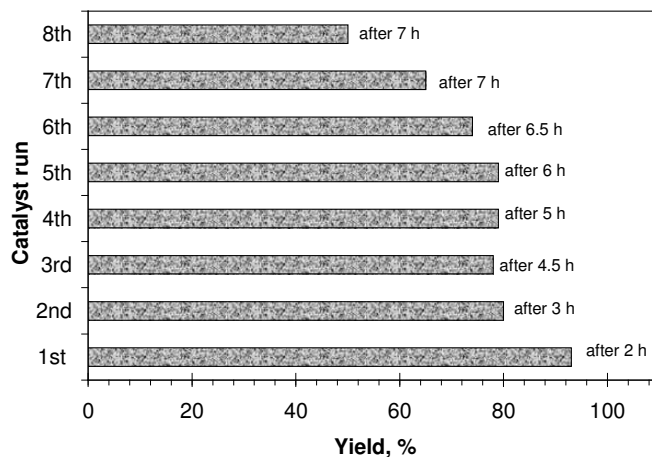
Figure 10. Studies on the reusability of material **I** on the reaction between excess nitroethane and but-3-en-2-one.

CONCLUSION

Our results show that one-pot sol-gel method carried out over a neutral templating amine provides a simple and versatile way of preparing dimethylaminopropy-silica hybrids. Materials with surface areas and organic group loading as high as 800 m^2g^{-1} and 3.4 mmol per g of silica, respectively, are obtainable. The materials have good to excellent activities and selectivities in model Michael additions using a range of substrates. The selectivity is best achieved if excess nitroalkanes are used. Furthermore, the use of organic solvents leads to a decrease of both activity and selectivity. Water however, promotes the activity of the catalysts although there is a possibility of a double Michael addition with these materials. As expected, increase in loading leads to an increase in the rate and conversion of the reaction if physicochemical properties of the catalyst are not a hindrance.

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