



# One-pot preparation of polyamine–silica hybrids and their use in the epoxidation of cyclohex-2-ene-1-one

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## Abstract

Micelle templated silica–amine hybrids have been prepared using a clean and efficient method, and have been shown to be effective catalysts for the epoxidation of enones.

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## 1. Introduction

Micelle templated silicas (MTS) are a group of silicas with very high surface areas ( $500\text{--}1100\text{ m}^2\text{ g}^{-1}$ ) and tightly defined cylindrical pores, making them ideal for use as catalysts and/or catalyst supports [1–3]. The majority of publications on organically modified MTS-type materials have involved post-synthesis modification (grafting) [4,5] of the pre-formed materials. Such materials usually display higher loadings than grafted amorphous silica, and they retain the high surface areas and pore structures typical of MTS-type material. However, such grafting processes suffer from some drawbacks: there is a need for excess silane during the grafting process, there exists the possibility of a lack of stability due to partial cross-linking of the silane coupling agent to the silica surface and the possibility of a variety of surface bound species [6].

Macquarrie [7], Macquarrie et al. [8] and others [9–12] have independently developed routes to or-

ganically modified MTS-type materials by one-pot co-polymerisation of a silica precursor (tetraethoxysilane, TEOS) and an organosilane ((MeO)<sub>3</sub>SiR) in the presence of a templating agent (in our case a long-chain amine). This method is thought to be a good alternative over grafting because the organic group is incorporated during the condensation of the silica framework, and is therefore likely to be fully integrated into the material—indeed <sup>29</sup>Si NMR studies previously carried out indicate that this is the case [8]. In addition, the porosity properties of the resultant material and the organic loading can be tailored by changing the alkyl chain length of the template and the ratio of TEOS to the organosilane, respectively. This is illustrated for amine-containing materials in Fig. 1, but is generally valid.

From the environmental point of view the method also offers an advantage in that all the silane is incorporated, and the template used in the preparation process is easily and completely recovered and reused [13]. Furthermore, the process takes place at room temperature and ambient pressure in a few hours, rather than the higher temperatures and pressures often used for many alternative preparations. The benefits of such

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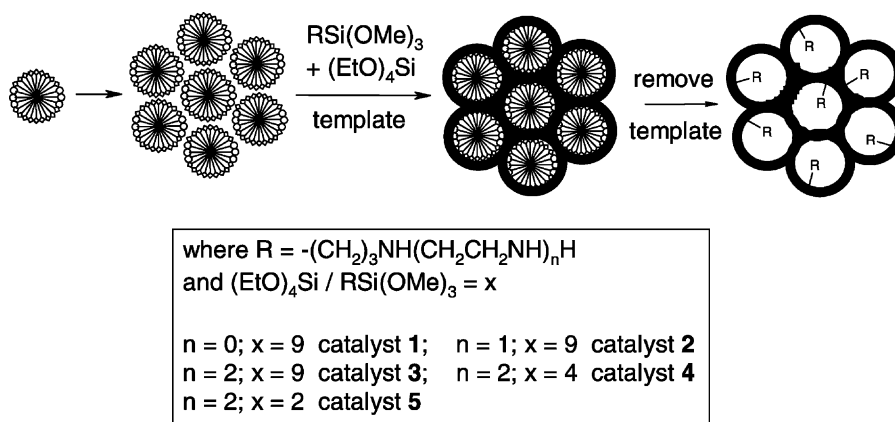


Fig. 1. Formation of amine-containing MTS materials.

heterogeneous catalysts over homogeneous catalysts include the ease of separation of the catalyst after use, facilitating the isolation of product and, in the case of acid and basic catalysts, the obviation of a neutralisation step prior to disposal of aqueous effluent (which is further minimised by the elimination of a washing step). In the case of simple epoxyketones, such a washing/neutralisation step may lead to further hydrolysis of the product.

The one-pot preparation of organically modified micelle templated silicas has made available a range of heterogeneous basic materials that have been used successfully in catalysis of the Knoevenagel condensation [14] with **1** as well as the Michael [15] (*N,N*-dimethyl-**1**) and aldol [16] reactions. The latter material is based on aminoethylaminopropyl groups, and appears, on the basis of its activity in the aldol reaction, to be somewhat more basic than the corresponding monoamine materials. As part of a continuing program on the development of such materials, we have developed polyamine–micelle templated silica hybrids by using the one-pot sol–gel method, and here we report results on their physicochemical properties and activity in the epoxidation of cyclohex-2-ene-1-one, an example of a reaction class which does not take place with the monoamine materials (Fig. 2).

The latter reaction is traditionally catalysed by strong homogeneous bases, [17–19] but recent work has involved the use of supported guanidines, [20–23] some of which work very well in the reaction, but

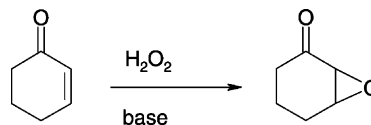


Fig. 2. The epoxidation of cyclohex-2-ene-1-one under basic conditions.

which have relatively complex and somewhat wasteful syntheses.

## 2. Results and discussion

### 2.1. Preparation

The materials were synthesised using a literature method [8]. Generally, the method involves a simultaneous and rapid addition of an organosilane and a silica precursor, typically tetraethylorthosilicate (TEOS), to a stirred solution of a neutral amine surfactant and aqueous ethanol. The organosilane and the silica precursor are added at a particular ratio that can be varied as desired. After ageing the mixture for 18 h, the resulting solid is filtered, and the template extracted by using hot ethanol.

As can be seen from Table 1, loadings as high as  $2.4 \text{ mmol g}^{-1}$  are obtainable. Despite the relatively low maximum loading (i.e.  $2.4 \text{ mmol g}^{-1}$ ) achieved with long-chain polyamines compared to short-chain monoamines (over  $4 \text{ mmol g}^{-1}$ ), this is a significant

Table 1

A summary of the properties of the catalysts

Catalyst	Organic group attached	Ratio <sup>a</sup>	Loading (mmol g <sup>-1</sup> )	RSiO <sub>3</sub> :SiO <sub>4</sub>	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Average pore diameter (nm)
<b>2</b>	–(CH <sub>2</sub> ) <sub>3</sub> NH(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>	1:9	1.2	0.1	575	3.5
<b>3</b>	–(CH <sub>2</sub> ) <sub>3</sub> NH(CH <sub>2</sub> ) <sub>2</sub> NH(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>	1:9	1.1	0.1	366	3.7
<b>4</b>	–(CH <sub>2</sub> ) <sub>3</sub> NH(CH <sub>2</sub> ) <sub>2</sub> NH(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>	1:4	1.8	0.25	460	9.9
<b>5</b>	–(CH <sub>2</sub> ) <sub>3</sub> NH(CH <sub>2</sub> ) <sub>2</sub> NH(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>	1:2	2.4	0.33	97	14.8

<sup>a</sup> Organosilane to TEOS ratio.

improvement over the conventional grafting method that gives only about 1.9 mmol of a monoamine per gram of MTS-type material [5,24]. It may be that the long triamine chains interfere with the packing processes in the forming material, leading to lower loadings, or that the size of the groups precludes higher site densities. Efforts to synthesise structured polyamine–silica hybrids with loadings higher than 2.4 mmol g<sup>-1</sup> were futile. Incomplete polymerisation was observed even after a reaction time of 1 week when a ratio of diethylenetriaminopropyl silane to TEOS was changed to 1:1. This ratio produced a material that was non-porous and has a specific surface area of only ca. 3 m<sup>2</sup> g<sup>-1</sup>.

## 2.2. N<sub>2</sub> physisorption studies

For a well-templated material, a type IVc isotherm [25] is usually obtained. Such isotherms exhibit a characteristic inflection point at a relative pressure of about 0.2, consistent with the adsorption isotherms observed for MTS-type materials. This is indicative of capillary condensation in the template-defined mesopores. The isotherms show little or no hysteresis although there are slight upturns at very high relative pressures, suggesting that the majority of the pores are framework-confined. Such an isotherm is obtained for **2**.

On the other hand, the adsorption–desorption isotherm of **3** has a pronounced hysteresis loop at high relative pressures (reminiscent of a Type H isotherm) [25] and a very weak inflection point at relative pressure around  $p/p_0 = 0.2$ . This implies that the majority of pores are slit-shaped rather than cylindrical, indicating that the templating mechanism has broken down. Catalysts **4** and **5** display isotherms similar to amorphous silicas, again indicating that the templating mechanism is not operative.

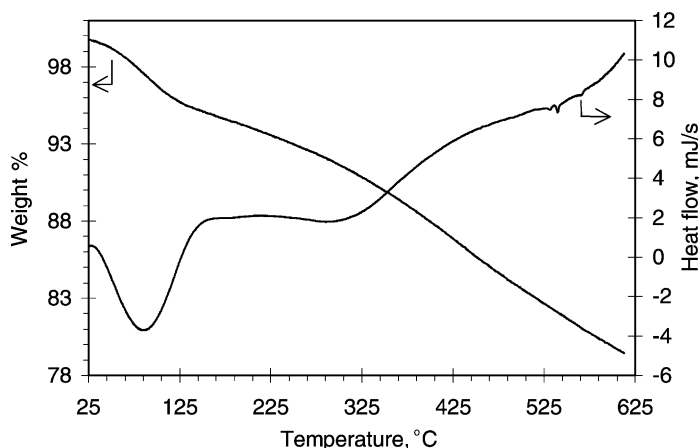
Table 1 gives a summary of the BET specific surface areas and average pore diameters of the prepared organic–inorganic hybrids. As seen in the table the specific surface areas range between 360 and 600 m<sup>2</sup> g<sup>-1</sup>, a range that is slightly lower than that of the parent MTS as well as of materials developed by the same route using shorter-chained organosilanes. In addition, only material produced at an organosilane to silica precursor ratio of 1:9 has a narrow range of pore diameter. All other ratios produce materials with a wide range of pore diameter.

## 2.3. Scanning electron microscopy studies

As the method of preparing the parent all-silica micelle templated silica (MTS) and our polyamine–silica hybrids differs only in the ingredients added, one would expect the morphology of their particles to be similar. This was indeed found to be the case. The shapes of the primary particles of both materials are roughly spherical and they appear in aggregates. Their dimensions are broadly similar. Whereas the majority of the primary particles of the polyamine–silica hybrid have diameters of about 0.4 μm, most of the MTS particles have diameters ca. 0.3 μm, with very few exceptions. The shapes of the two materials, however, differ markedly from the hexagonal particles observed for MCM-41 materials [1]. The non-templated materials also had similar roughly spherical morphologies and particle sizes were in the same range.

## 2.4. Thermal analysis

Thermal studies of the polyamine–silica hybrids display very interesting results. Fig. 3 shows the simultaneous thermal analysis (STA) profile of **3**, a material with a loading of 1.1 mmol g<sup>-1</sup>. Three weight losses are clearly observable in the figure. The first

Fig. 3. STA profile of **3**.

loss (ca. 3%) is centred at 90 °C and is due to loss of residual solvents. The second loss (ca. 6%) occurs at a linear rate from 120 to 320 °C, followed by another linear loss (ca. 11%) at a relatively slow rate up to 600 °C. This weight loss is attributable to desorption of the attached organic groups as evidenced by thermogravimetry–infrared studies. The percentage weight loss of ca. 11% is consistent with the loading of 1.1 mmol g<sup>-1</sup> as determined by elemental analysis. Generally, these long-chained supported polyamines have somewhat lower thermal stability than short-chained supported monoamines [8] that are prepared by a similar route.

### 2.5. Activity and selectivity in the epoxidation of electron deficient olefins

The catalysts were screened in the epoxidation of electron deficient olefins to establish their catalytic activity. The epoxidation of cyclohex-2-ene-1-one was used as a model reaction. The results obtained are collated in Table 2. Without catalyst, almost no conversion was achieved. The results in the table show the catalysts to have moderate to good activities. The results also show the supported diamine catalyst **2** to have a relatively lower activity compared to the triamine versions. This is probably due to the higher number of active centres per unit mass in the triamine based catalyst. Other supported monoamines, such as **1** and *N,N*-dimethyl-**1** reported elsewhere to be very

active in the Michael reaction [15] (the mechanism of which is similar to our model reaction) showed very little activity in this reaction. This is consistent with the fact that the diamine catalyst has been found to be active in the aldol reaction, [16] while the monoamine catalysts are not, indicating that the polyamine catalysts may have somewhat higher basicity. As might be expected on the basis of the relative p*K*<sub>a</sub> values of hydrogen peroxide and the CH acids typically used in these C–C bond forming reactions, a polyamine system is very effective for the epoxidation reaction too. As expected, an increase in loading leads to an increase in activity (see catalysts **3** and **4**, Table 2). However, further increase in loading up to 2.4 mmol g<sup>-1</sup> (catalyst **5**) results in a drop in activity. As noted earlier, catalysts **4** and **5**, with loadings of

Table 2  
Activities of HMS-supported polyamines in the epoxidation of cyclohex-2-en-1-one

Catalyst	Epoxide yield <sup>a</sup> (%)	Time (h)	Selectivity	
			Organic (%)	Oxidant (%)
<b>2</b>	52	12	90	39
<b>3</b>	63	12	92	41
<b>4</b>	76	10	90	41
<b>5</b>	66	15	89	38
<b>6</b>	48 (66) <sup>b</sup>	10	88	45
None	10	24	–	–

<sup>a</sup> GC yields using *n*-dodecane as internal standard.

<sup>b</sup> Conversion in brackets.

1.8 and 2.4 mmol g<sup>-1</sup>, respectively, are mostly amorphous, especially the latter. In addition, the BET surface area of the latter catalyst is very low compared to that of the former (Table 1). The drop in the activity of **5** is therefore likely to be due to, among other reasons, the low BET surface area and hence low amount of active sites accessible for catalysis. A similar phenomenon has been reported before with monoamine materials [13].

Selectivity is also good with the di and triamine catalysts. Two selectivities are important to characterise an effective catalyst in these systems. Selectivity based on conversion of enone to epoxide (“organic” selectivity) is excellent, being around 90%. The remaining 10% of organics is distributed amongst a range of products, most of which are <1%, and have not been characterised fully. It is likely that hydrolysis of the epoxyketone represents one of these pathways, Michael addition of methanol is another (2–3%); the others are not established. Baeyer–Villiger oxidation of the ketone does not occur as far as the sensitivity of our analysis allows. This compares well with other published heterogeneous systems, with traces of a range of other products being found. Selectivity towards hydrogen peroxide (“oxidant” selectivity) is also important, with an efficient transfer of oxygen to substrate (with minimal non-productive decomposition) minimising the volume added and reducing side reactions due to excessive quantities of water being added with the oxidant. In this case, heterogeneous catalysts based on silicas can be a problem, since the bare surface of most silicas appear to cause extensive decomposition of the peroxide without product formation (20% selectivity [21] and 10% [13] for non-passivated materials). Surface passivation can increase this efficiency significantly, but adds a step to the catalyst preparation and increases the associated waste. With the catalysts described here, there is no passivation step, yet the selectivity towards peroxide is already ca. 40%, significantly better than that found in other cases, and almost as good as for the passivated guanidine catalyst [13]. Given the very clean preparation of the catalyst, compared to the more complex synthesis required for the guanidines, it may be that this slight drop in selectivity towards peroxide is preferable to the waste generated in the passivated guanidine catalysts. The use of (3-trimethoxysilylpropyl)-diethylenetriamine (**6**)

directly (i.e. without formation of the solid material) led to a conversion of 66%, with selectivity towards organics of 88% and towards oxidant of 45%. Separation of the product from the catalyst was complicated by the homogeneous nature of the system, and thus the process, and the efficiency of recovery was considerably lower. However, from the point of view of conversion and selectivity, little difference was observed. This indicates that the formation of a solid catalyst is beneficial from the point of view of the simplicity and efficiency of the process, rather than just of the reaction.

### 2.6. Catalyst reusability

Studies on the catalyst reuse were conducted using catalyst **3** in the epoxidation of cyclohex-2-ene-1-one. When the reaction reached completion, the catalyst was retrieved by filtration and washed thoroughly with methanol. The catalyst was then reused without further treatment. Upon reuse the catalyst suffered a very strong deactivation, giving only ca. 15% of the epoxide product in the second use. Efforts to regenerate the catalyst proved futile.

The loss of activity is attributed to oxidation of the primary and secondary amino groups present on the catalysts surfaces as a result of their reaction with hydrogen peroxide to give aldoximes and hydroxylamines, respectively. This was further confirmed by the fact that fresh catalyst stirred with hydrogen peroxide lost activity upon retrieval. Diffuse reflectance IR studies of the spent catalyst showed a disappearance of a peak at 1610 cm<sup>-1</sup> (attributed to NH bending vibration) and appearance of a strong peak at 1640 cm<sup>-1</sup> attributed to molecular water which persisted even upon drying indicating a probable overlap of peaks due to aldoximes and water.

## 3. Experimental

All chemicals were obtained from Aldrich or Fluo-rochem Ltd. and were used as received. Porosimetry was carried out on a SA3100 porosimeter using nitrogen as an adsorbate whereas SEM images were obtained from a Hitachi SEM S2400 instrument, using an electron gun energy of 8 keV.

### 3.1. Preparation and recycling of template

The materials were prepared using a method described elsewhere [8]. In a typical process tetraethylorthosilicate (TEOS) (0.09 mol) and (3-trimethoxysilylpropyl)-diethylenetriamine (0.01 mol) were added separately, but simultaneously and rapidly at room temperature to a stirred solution of *n*-dodecylamine (0.0275 mol) in aqueous ethanol (0.789 mol of absolute ethanol and 2.94 mol of deionised water). In either case precipitation started between 5 and 15 min and reaction was continued for 18 h. The thick solution was then 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 °C to give catalyst **3**. Materials of higher loading were also prepared using the latter organosilane at ratios of (3-trimethoxysilylpropyl)-diethylenetriamine to TEOS of 1:4 and 1:2 giving catalysts **4** and **5**, respectively. Another material (catalyst **2**) was prepared in a similar way using (3-trimethoxysilylpropyl)-ethylenediamine instead of the triamine.

In each case the templates were recovered by combining the filtrates and extracts solutions and evaporating the solvent under reduced pressure. Yields of ca. 98% *n*-dodecylamine were obtained as proved by <sup>1</sup>H NMR, IR and melting point. The recovered templates could be reused successfully in fresh experiments.

### 3.2. Diffuse reflectance IR and solid state <sup>13</sup>C NMR studies

IR spectra were measured on a Bruker Equinox 55 FTIR spectrometer fitted with an environmental chamber diffuse reflectance unit. The results showed, as expected,  $\nu(\text{N-H})$  and  $\nu(\text{C-H})$  bands at 3280 cm<sup>-1</sup> (broad) and 2925 cm<sup>-1</sup>, respectively, both coming from the aliphatic chains of the polyamino groups. Also observed were bands at 1610 and 1450 cm<sup>-1</sup> attributable to N-H and C-H deformation vibrations.

Solid state <sup>13</sup>C NMR spectra were obtained on a Bruker MSL300 spectrometer operating at 75 MHz at a rotor spinning rate of 5 kHz. Two catalysts, namely **2** and **3** were studied and their results are as follows:

Catalyst **2**: 58–40 ppm (broad) [ $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}-\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$  and  $-\text{OCH}_2\text{CH}_3$ ]; 20.5 ppm  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$ ; 15.6 ppm  $-\text{OCH}_2\text{CH}_3$ ; 10.3 ppm  $-\text{CH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$ .

Catalyst **3**: 59.1 ppm  $-(\text{CH}_2)_3\text{NHCH}_2\text{CH}_2\text{NH}_2$  and  $-\text{OCH}_2\text{CH}_3$ ; 51.2 ppm  $[-(\text{CH}_2)_3\text{NHCH}_2\text{CH}_2\text{NH}_2]$ ; 48.6 ppm  $-(\text{CH}_2)_2\text{CH}_2\text{NH}(\text{CH}_2)_2\text{NH}_2$ ; 20.0 ppm  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}(\text{CH}_2)_2\text{NH}_2$ ; 15.1 ( $-\text{OCH}_2\text{CH}_3$ ); and 10.4 ppm  $-(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}(\text{CH}_2)_2\text{NH}_2)$ .

One important feature arising from the above data is the occurrence of peaks attributable to residual  $-\text{OEt}$  groups, peaks that were also observed in supported monoamines prepared by the same route [26].

The spectrum of **3** shows most of the peaks to be clustered together, giving very broad and shouldered peaks. Despite this observation, the data still confirm the presence of the polyamine groups on the silica surface.

### 3.3. Epoxidation studies

Typical conditions involved the use of methanol as solvent and 20 °C as reaction temperature. Hydrogen peroxide (30% (v/v)) was used throughout, and was added slowly over the period of the reaction. The reaction mixture was stirred at room temperature and monitored by GC. After the reaction the catalyst was separated by filtration, and the crude product extracted using ethyl acetate, dried with Na<sub>2</sub>SO<sub>4</sub>, evaporated under reduced pressure and then purified by column chromatography (ethyl acetate: hexane 1:4 as eluent). The product was identified by GC/MS as 2,3-epoxy-cyclohexanone:  $M^+$ ,  $m/z$  (%) = 112 (8), 97 (5), 85 (10), 83 (18), 67 (40), 57 (8), 55 (100). Hydrogen peroxide selectivities were calculated by the ratio of organic product/amount of hydrogen peroxide added.

## 4. Conclusion

The versatility of one-pot synthesis has been shown in the preparation of long-chained polyamine-micelle templated silica hybrids. However, in contrast to hybrids based on short-chained monoamines, these materials are only partially templated except for a diamine version at a loading of ca. 1 mmol g<sup>-1</sup>. The materials



exhibit moderate thermal stability, the organic groups being desorbed at temperature ranging between 320 and 600 °C. Generally these materials possess BET surface areas that are lower than their monamine counterparts. As to their catalytic performance, the materials showed excellent selectivity and moderate to good activity in the epoxidation of electron deficient olefins, though oxidation of the active sites was a major drawback to recycling (as is also the case for other catalysts used in this reaction). While results are slightly less impressive than those obtained with the best guanidine catalysts, the advantages of simplicity of preparation may make these catalysts of interest in the clean epoxidation of electron-deficient alkenes.

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