PREPARATION, CHARACTERISATION AND APPLICATION OF POLYAMINE-SILICA HYBRIDS IN THE EPOXIDATION OF α,β-UNSATURATED OLEFINS

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ABSTRACT. Polyamine-silica hybrids were prepared by a one-pot sol-gel method *via* a neutral amine templating route. At low loadings (*ca*. 1 mmol organic group per g of silica) the resultant materials displayed properties typical of M41S-type materials, namely, high surface area (typically 600 m^2 g^{-1}) and controlled porosity with an average pore diameter of 3.6 nm. However, the materials were amorphous at loading above 1.2 mmol organic group per g of silica. The materials were used as heterogeneous base catalysts in the epoxidation of electron deficient olefins. The yields of the epoxide product ranged between 52% and 76%, depending on the loading of the catalytic group.

KEY WORDS: Polyamine-silica hybrids, Heterogeneous base catalysts, Epoxidation of α,β-unsaturated olefins

INTRODUCTION

The majority of publications [1-3] on organically modified M41S-type materials have involved post-synthesis modification of the pre-formed materials. Such materials usually display higher loadings than grafted amorphous silica, and they retain high surface areas and pore structures typical of a M41S-type material. However, it is expected that they may suffer from the same disadvantages as the grafted silicas, namely little control over loading, relative lack of stability due to partial cross-linking of the silane coupling agent to silica surface and the possibility of formation of a variety of surface bound species [4].

Macquarrie [5] and others [6-9] have independently developed routes to organically modified M41S-type materials by a one-pot co-polymerisation of a silica precursor and an organosilane in the presence of a templating agent. This method is thought to be a good alternative to grafting because the organic group is incorporated during the condensation of the silica framework, and is therefore likely to be fully integrated into the final material. 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 the silica precursor to the organosilane, respectively. From an environmental point of view the method also offers an advantage in that 98% of the template used in the preparation process can be recovered and reused [10].

Interest in heterogenization of soluble catalysts is currently on the increase. This is because conventional homogeneous catalysts often present separation and recycling problems, setbacks that need to be overcome as far as 'environ-economics' is concerned. The one-pot preparation of organically modified micelle templated silicas has made available a range of heterogeneous materials that have been used successfully in the Knoevenagel [11] as well as the Michael [12] reactions.

As part of a continuing program on the development of the organically modified micelle templated silicas, we have developed polyamine-micelle templated silica hybrids by using the one-pot sol-gel method. In this paper we report results on the physicochemical properties of the

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materials and their activity in the epoxidation of α,β-unsaturated olefins. The latter reaction is traditionally carried out in alkaline hydrogen peroxide [13, 14] or using soluble bases such as 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) with *tert*-butyl hydroperoxide (TBHP) [15]. Such systems, as explained above, present separation and recycling problems.

EXPERIMENTAL

Chemicals such as sodium sulphate, dichloromethane, 30% (v/v) hydrogen peroxide, 2-cyclohexen-1-one, methanol, absolute ethanol (97%) and *n*-dodecylamine were obtained from Aldrich whereas tetraethylorthosilicate, (3-trimethoxysilylpropyl)-ethylenediamine, and (3-trimethoxysilylpropyl)-diethylenetriamine were obtained from Fluorochem Ltd. All chemicals were used as received.

Instrumentation

Porosimetry was carried out on a SA3100 porosimeter using nitrogen as an adsorbate at 77.4 K whereas SEM images were obtained from an Hitach SEM S2400 instrument, using an electron gun energy of 8 keV.

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 ^{o}C prior to analysis and then run at room temperature as mixtures with KBr. On the other hand, solid state ^{13}C NMR spectra were obtained on a Bruker MSL300 spectrometer operating at 75 MHz at a rotor spinning rate of 5 kHz.

Preparation and recycling of template

The materials were prepared using a method described elsewhere [5, 10, 16]. 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). Precipitation started between 5 and 15 min after mixing. The stirring was continued and after 18 h, the thick mixture 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 reflux with fresh amounts of ethanol was repeated twice to completely remove the template from the material. The final solid was then dried in an oven at 100 ^{o}C to give product **1** (Scheme 1). The ^{13}C chemical shifts for product **1** are as follows: 10.4 ppm (-Si-C̲H$_2$R); 15.1 ppm (Si-OC̲H$_2$CH$_3$); 20.0 ppm (-Si-CH$_2$C̲H$_2$R); 48.6 ppm [-Si-(CH$_2$)$_2$C̲H$_2$-]; 51.2 ppm [-Si-(CH$_2$)$_3$NHC̲H$_2$CH$_2$-] and 59.1 ppm [-Si-(CH$_2$)$_3$NHC̲H$_2$- and -Si-OC̲H$_2$CH$_3$].

Materials of higher loading were also prepared using organosilane to TEOS ratios of 1:4 and 1:2, giving products **2** and **3**, respectively. A different material, hereinafter product **4**, was prepared in a similar manner as product **1** but using (3-trimethoxysilylpropyl)-ethylenediamine as an organosilane (Scheme 1). The ^{13}C chemical shifts for product **4** are: 10.3 ppm (-Si-C̲H$_2$CH$_2$-); 15.6 ppm (-Si-OCH$_2$C̲H$_3$); 20.5 ppm (-Si-CH$_2$C̲H$_2$CH$_2$-) and 58–40 ppm (broad) (-Si-CH$_2$C̲H$_2$C̲H$_2$NHC̲H$_2$C̲H$_2$NHC̲H$_2$C̲H$_2$NH$_2$ and -OC̲H$_2$CH$_3$).

In every 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 ^{1}H NMR, IR and melting point. The recovered templates could be reused successfully in fresh experiments.
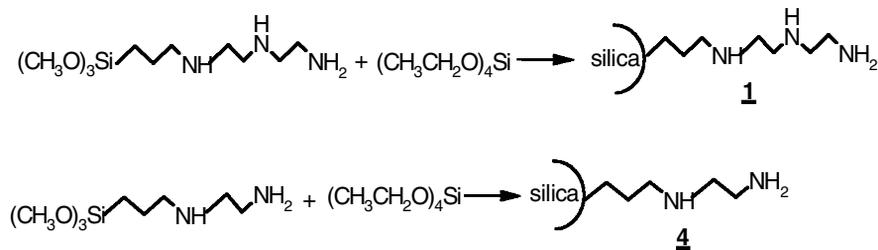
Scheme 1. Preparation of polyamine-silica hybrids.

Reaction studies

Typical reaction involved addition of catalyst (0.25 g) to a mixture of methanol (15 cm^3) and 10 mmol of 2-cyclohexen-1-one in a 100 cm^3 two-necked round-bottomed flask. This was followed by a drop-wise addition of 5 cm^3 of 30% v/v H_2O_2 at a rate of 0.05 cm^3 per min. The reaction mixture was stirred at room temperature and monitored by GC. After the reaction was complete the crude product was extracted using dichloromethane, dried with Na_2SO_4 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).

RESULTS AND DISCUSSION

Preparation

The materials were synthesized using a literature method [5, 10-12, 16]. Generally, the method involves the simultaneous and rapid addition of an organosilane and a silica precursor, typically 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 about 18 h, the resulting solid was filtered, and the template extracted by using hot ethanol. The removal of the neutral template is generally considered to be more straightforward than the removal of the quaternary ammonium salts templates, which are known to be difficult to remove entirely [17].

As seen from Table 1 loadings as high as 2.4 mmol g^{-1} are obtainable. The latter loading was obtained at a ratio of 1:2 (organosilane to silica precursor), a ratio that is reported to give loadings *ca*. 4 mmol g^{-1} in the case of short-chained monoamines [10]. Probably the long chain of the organic part in our case interferes with close packing of the Si atoms during the co-polymerisation process, thus lowering the overall loading. Despite the relatively low maximum loading (*i.e.*, 2.4 mmol g^{-1}) achieved with long chain polyamines compared to the short-chain monoamines, there is a significant improvement over the conventional grafting method that gives only about 1.9 mmol of a monoamine per g of MCM-type material [18]. Efforts to synthesize structured polyamine-silica hybrids with loadings higher than 2.4 mmol g^{-1} were not successful. Incomplete polymerisation was observed even after a reaction time of one week when a ratio of propyldiethylenetriamine silane to TEOS was changed to 1:1. This ratio produced a material that was non-porous and had a specific surface area of only *ca* 3 m^2 g^{-1}.

Table 1. A summary of the properties of the polyamine-silica hybrids.

Material	Organic group attached	Ratio*	Loading (mmol g^{-1})	S_{BET} (m^2 g^{-1})	Av. pore diameter (nm)
1	-(CH$_2$)$_3$NH(CH$_2$)$_2$NH(CH$_2$)$_2$NH$_2$	1:9	1.1	366	3.7
2	-(CH$_2$)$_3$NH(CH$_2$)$_2$NH(CH$_2$)$_2$NH$_2$	1:4	1.8	460	9.9
3	-(CH$_2$)$_3$NH(CH$_2$)$_2$NH(CH$_2$)$_2$NH$_2$	1:2	2.4	97	14.8
4	-(CH$_2$)$_3$NH(CH$_2$)$_2$NH$_2$	1:9	1.2	575	3.5

*Organosilane to TEOS ratio.

In order to establish the nature of the functional groups that are on the support surfaces, the developed organic-inorganic hybrid solid bases were studied by diffuse reflectance-FTIR spectroscopy as well as solid state ^{13}C NMR. As stated earlier the organic groups that were attached onto the silica surface by the one-pot sol-gel method are propylethylenediamine and propyldiethylenetriamine.
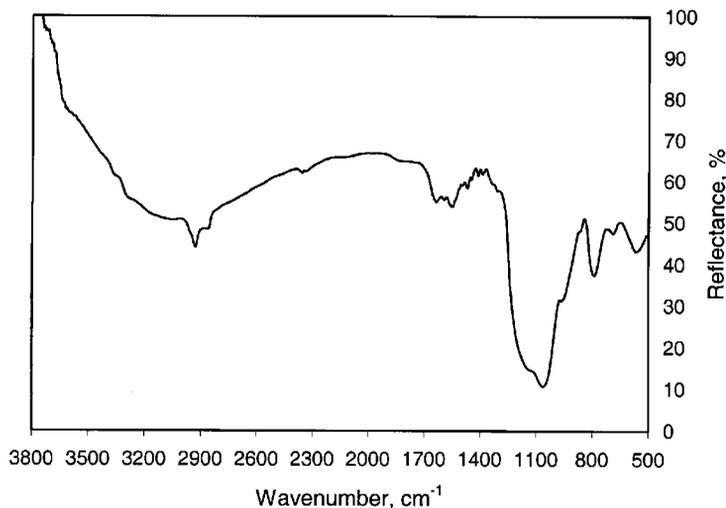

Figure 1. The IR spectrum of polyamine-silica hybrid.

Figure 1 shows the IR spectra of material **1**, as an example of the spectra that were obtained. As expected all the important vibrations attributable to the presence of the supported organic groups are observable. These include ν(N-H) and ν(C-H) bands at 3280 (broad) cm^{-1} and 2925 cm^{-1}, respectively, both associated with the aliphatic chains of the polyamino groups. Also observed are bands at 1610 cm^{-1} and 1450 cm^{-1} attributable to N-H and C-H deformation vibrations, respectively. The spectra of all other materials showed similar bands or peaks implying that the attached organic groups were not destroyed in the course of preparation. In addition to the vibrations attributable to the supported organic groups, vibrations associated with the silica lattice structure are also present. These are observed at *ca*. 1830 cm^{-1} and 1220 –1030 cm^{-1} and are due to the Si-O-Si linkage. A strongly observable feature in almost all the IR spectra is the hydrogen-bonded SiOH stretching band at *ca*. 3600–3100 cm^{-1}. The N-H

stretching band appears in a similar region but is masked by the SiOH band. The N-H bending mode at *ca.* 1600 cm^{-1} proved very useful in identifying primary amines on the silica surface.

The ^{13}C NMR study further proved the presence of the respective organic groups on the silica surface (*cf.* section *Instrumentation*). One important feature arising from the obtained data is the occurrence of peaks attributable to residual –OEt groups, peaks that were also observed in supported monoamines prepared via a similar route [13]. This suggests that the polymerisation process was incomplete. Moreover, some peaks in the spectrum of product **1** were clustered together, giving broad peaks with many shoulders. Despite this setback the peaks of interest could be identified thus confirming the presence of the polyamine groups on the silica surface.

Nitrogen physisorption studies

Figure 2 shows the representative adsorption–desorption isotherms of the materials synthesized. Generally, the results show that for a well-templated material (usually one with a loading *ca.* 1 mmol g^{-1}), a type IVc isotherm [19] is usually obtained (see for example product **4** in Figure 2). Such isotherms exhibit a characteristic inflection point at a relative pressure of about 0.2, consistent with the adsorption isotherms observed for MCM-type materials [20, 21]. This is indicative of capillary condensation in the framework-confined mesopores. The isotherms show little or no hysteresis loops although there are slight up turns at very high relative pressures suggesting that the majority of the pores are framework-confined.
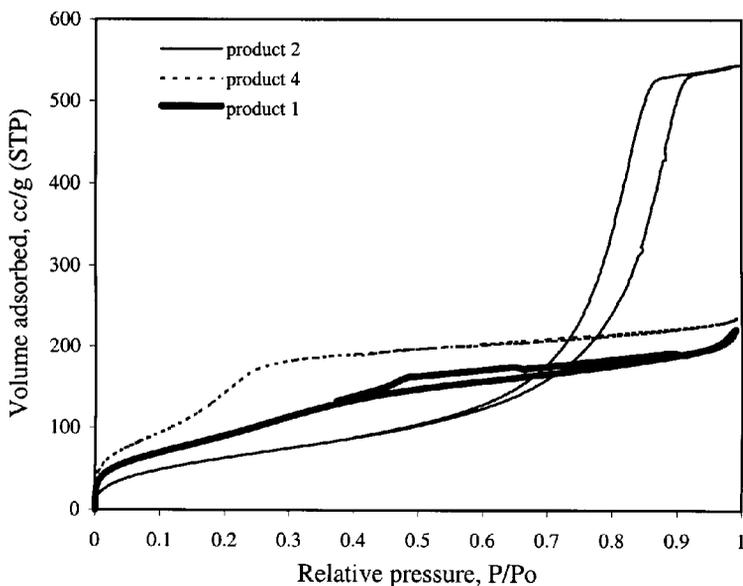

Figure 2. Adsorption-desorption isotherm of products **1**, **2** and **4**.

On the other hand, the adsorption-desorption isotherm of product **1** (Figure 2) has a pronounced hysteresis loop at high relative pressures and a very weak inflection point at relative pressure around 0.2. This implies that there are more textural mesopores than framework-confined ones.

Table 1 gives a summary of the 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^2 g^{-1}. Although the range is generally lower than that for MCM-type

materials [20, 21], the upper limit of this range approaches that for materials developed by the same route using short-chained organosilanes [11, 12]. In addition, only materials produced at an organosilane to silica precursor ratio of 1:9 has a narrow range of pore sizes. All other ratios produce materials with a wide range of pore sizes as evidenced in Figure 3. This figure compares the pore size distributions of materials produced at organosilane to TEOS ratios of 1:9 and 1:4, respectively. As seen from the figure, product **1** (organosilane to TEOS ratio of 1:9) has a narrow range of pore sizes relative to that of product **2** (organosilane to TEOS ratio of 1:4).
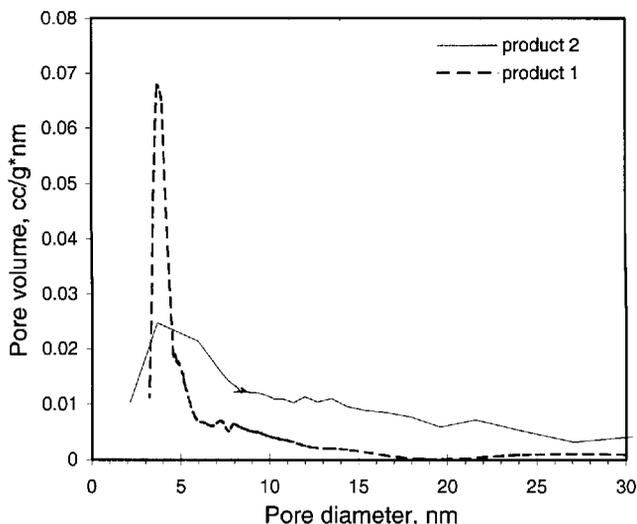

Figure 3. Pore size distribution curves of products **1** and **2**.

Scanning electron microscopy studies

As the method of preparing hexagonal mesoporous silica (HMS) [22] and our polyamine-silica hybrids differs only in the ingredients added, one would expect the morphologies of the particles of these two products to be similar. Figure 4 compares the micrographs of polyamines-silica hybrid and that of HMS material. The shapes of the primary particles of both materials are roughly spherical and they appear in aggregates. Their dimensions are however, different. Whereas the majority of the primary particles of the polyamine-silica hybrid have diameters of about 0.4 μm, most of the HMS particles have diameters of 0.3 μm, with the expection of very few particles. The shapes of the two materials however, differ markedly from the hexagonal particles observed for MCM-41 materials [20, 21].
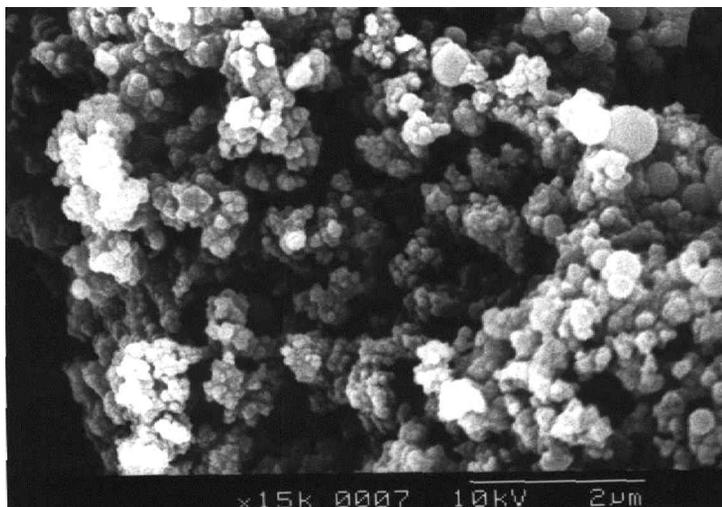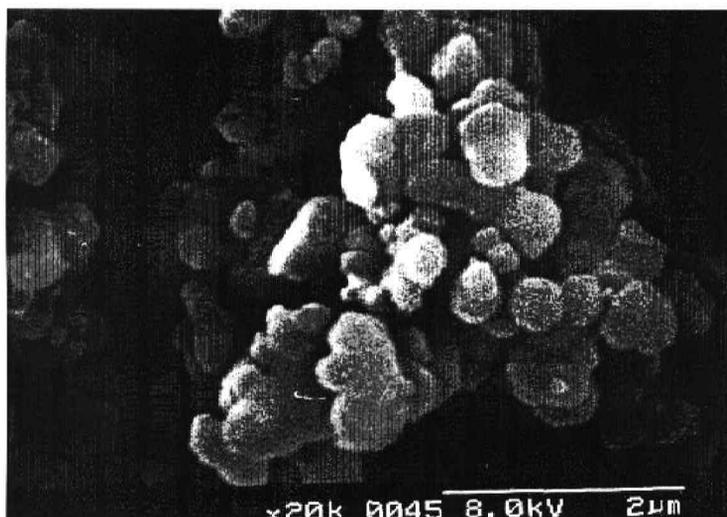
Figure 4a. Electron micrograph of HMS.

Figure 4b. Electron micrograph of product **1**.

Thermal analysis

Thermal studies of the polyamine-silica hybrids display very interesting results. Figure 5 shows the simultaneous thermal analysis (STA) profile of product **1**, a material with a loading of 1.1 mmol g^{-1}. Three weight loss regions are clearly observable in the figure. The first loss (*ca.* 3%) is centered at 90 ^{o}C and is due to loss of residual solvents. The second linear weight loss (*ca.* 6%) occurs in the region from 120 to 320 ^{o}C, followed by another linear loss (*ca.* 11%) at a relatively slow rate up to 600 ^{o}C. Whereas the former weight loss is due to loss of physically bound organic groups, the latter is attributable to desorption of the chemically bound organic

groups as confirmed by thermogravimetry-infrared studies. Elemental analysis of the material showed that it has a loading of 1.1 mmol organic group per g of silica, results that are consistent with the weight that was lost from 120 to 320 °C (*i.e.*, *ca.* 11%). Generally, these long-chain supported polyamines have lower thermal stability than short-chain supported monoamines [18] that are prepared by a similar route. This may be due to the greater length of the organic molecule that has many possible weak points.
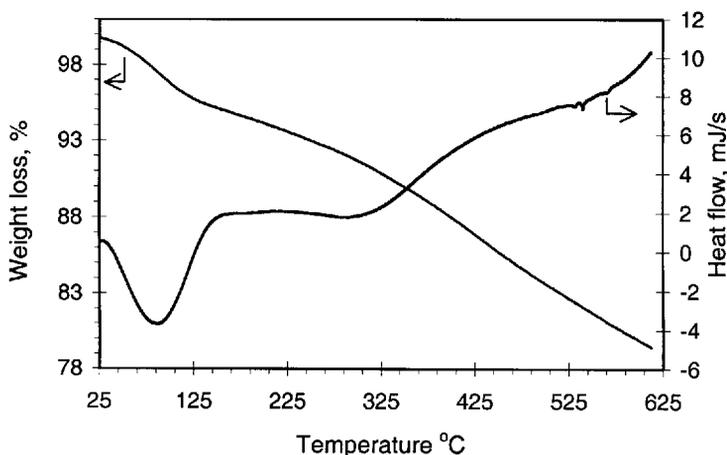

Figure 5.STA profiles of product **1**.

Activity and selectivity in the epoxidation of electron deficient olefins

The prepared materials were screened in the epoxidation of electron deficient olefins to establish their catalytic activity. The epoxidation of 2-cyclohexen-1-one was used as a model reaction. The results obtained are collated in Table 2. The results in the table show the materials have moderate to good activities. The results also show the supported diamine material, **4**, to have a relatively lower activity compared to the triamine versions, organic loadings not withstanding (Table 1). For instance, whereas product **4** (loading 1.2 mmol g^{-1}) gives an epoxide yield of 52% in the test reaction, product **1** gives a yield of 63%. This is probably due to the higher number of active centers per mole in the triamine-based material (*i.e.*, 2NH and 1NH$_2$ groups for triamine versions versus 1NH and 1NH$_2$ groups in the diamine material). Other supported monoamines reported elsewhere [12] to be very active in the Michael reaction (the mechanism of which is similar to our model reaction) showed very little activity in this reaction. The reason for this observation is not clear. The yields obtained in this study are lower than those obtained using DBU as a homogeneous catalyst, although in the latter case recycling, selectivity and separation were not good [15]. Nevertheless, our materials show excellent selectivities to the epoxide product, with typical values being above 90%.

As expected, an increase in loading leads to an increase in activity (see products **1** and **2**, Table 2). However, a further increase in loading up to 2.4 mmol g^{-1} (product **3**) results in a drop in activity. As noted earlier, products **2** and **3** with loadings of 1.8 mmol g^{-1} and 2.4 mmol g^{-1}, respectively, are mostly amorphous, especially the latter one. In addition, the specific surface area of the latter material is very low compared to that of the former (Table 1). The drop in the activity of the catalyst that has a loading of 2.4 mmol g^{-1} is therefore likely to be due to, among other reasons, the low specific surface area and hence low number of active sites available for catalysis. This phenomenon has been reported before with similarly prepared materials [10].

Table 2.   Activities of HMS-supported polyamines in the epoxidation of 2-cyclohexen-1-one.

Material	Epoxide yield* (%)	Time (h)
1	63	12
2	76	10
3	66	15
4	52	12

*GC yields using *n*-dodecane as internal standard.

Catalyst reusability

Studies on the reuse of the materials as catalysts were conducted using product **1** in the epoxidation of 2-cyclohexen-1-one. When the reaction reached completion, the material was retrieved by filtration and washed thoroughly with methanol. The catalyst was then re-used 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; a situation that calls for further study.

The loss of activity is attributed to oxidation of the primary and secondary amino groups present on the material surface as a result of their reaction with hydrogen peroxide, to give aldoximes and hydroxylamines, respectively (Scheme 2). This was further confirmed by the fact that when a fresh material was stirred with hydrogen peroxide, and then recovered and used as a catalyst, it lost its catalytic activity. Diffuse reflectance IR studies of the spent material showed a disappearance of a peak at 1610 cm^{-1} (attributed to NH bending vibration) and appearance of a strong peak at 1640 cm^{-1} attributed to molecular water which persisted even upon dying indicating a probable overlap of peaks due to aldoximes and water. The fresh material treated with hydrogen peroxide shows similar peaks.

$$RCH_2NH_2 \ + \ 2H_2O_2 \longrightarrow RCH=NOH \ + \ 3\,H_2O$$

$$RNHR' \ + \ H_2O_2 \longrightarrow RR'NOH \ + \ H_2O$$

Scheme 2. Reactions of hydrogen peroxide with primary and secondary amines.

As long as the deactivation is due to the oxidation of the active sites by the peroxide it is envisaged that if non-oxidative systems are employed the chances of regenerating the materials will be increased. Hence a systematic study of the use of these materials as heterogeneous base catalysts in non-oxidative systems will be conducted.

CONCLUSION

Our results show that the one-pot sol-gel synthesis method can be used to prepare polyamine-silica hybrids. At low loading (*ca*. 1 mmol organic part per g of silica) it is possible to obtain structured materials that have properties typical of M41S-type materials, namely, high surface area (typically 600 m^2 g^{-1}) and controlled porosity. When the loading is increased however, only amorphous materials are obtained that have low surface areas and a wide pore size distribution. Initial studies on the use of the materials as base catalysts for the epoxidation of electron

deficient olefins showed moderate to good activity depending on the loading. However, the active sites were prone to oxidation by hydrogen peroxide and hence loss of activity.

ACKNOWLEDGEMENTS

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