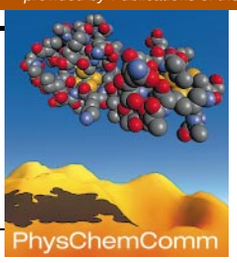

Entrapment and catalytic activity of gold nanoparticles in amine-functionalized MCM-41 matrices synthesized by spontaneous reduction of aqueous chloroaurate ions

Paper

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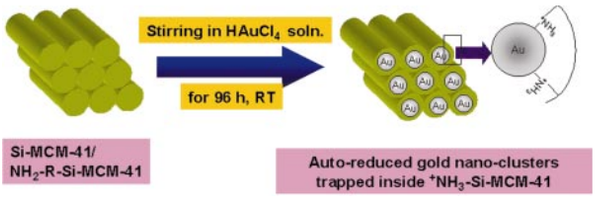
There is tremendous current interest in the generation of nano-hybrid materials using silicate mesoporous materials. We describe herein a new process for the synthesis of gold nanoparticle–amine functionalized MCM-41 hybrid materials by the spontaneous reduction of chloroaurate ions within the silicate matrix. The gold nanoparticles thus formed are bound to the pores of the MCM-41 framework by amine functional groups and show excellent catalytic activity in hydrogenation reactions.

Since the discovery of mesoporous silicate materials such as MCM-41,[1] there has been tremendous interest in interfacing these materials with nanoparticles to form novel, advanced hybrid materials.[2–5] The well-defined cavity size of MCM-41 makes it particularly attractive for size-selective entrapment of nanoparticles as has been demonstrated for CdS quantum dots[5] and silver nanoparticles.[6] We demonstrate in this communication that nanoparticles of gold may be synthesised within the pores of amine-derivatized MCM-41 material by spontaneous reduction of $AuCl_4^-$ ions present in solution (Scheme 1). To the best of our knowledge, this is the first report on the formation of nano-hybrid materials of MCM-41 wherein the inorganic host actively participates in the reduction of the metal ions as well as entraps the resulting nanoparticles within its framework. Reduction of the metal ions occurs *via* hydroxy groups on the inner surface of the cavities while the grafted amine groups residing inside the channels of MCM-41 bind the gold particles to the silicate matrix (Scheme 1). The entrapped gold particles show excellent catalytic activity in the conversion of styrene to ethylbenzene.

The syntheses of the silicious MCM-41 material (Si-MCM-41) and the amine-modified MCM-41 material (NH_2-MCM-41) have been described in detail in ref. 7 and 8 respectively. The Si-MCM-41 and NH_2-MCM-41 materials (before and after the autoreduction process) were characterized by X-ray diffraction (XRD, Rigaku D Max III VC instrument with Cu Kα radiation). The XRD measurements yielded the (100), (110) and (200) Bragg reflections for all the samples indicating a high degree of ordering even after *in-situ* formation of the gold nanoparticles. The surface area of the Si-MCM-41 and NH_2-MCM-41 samples were found to be 1000 and 600 $m^2\ g^{-1}$ with mean pore diameters of 40 and 30 Å respectively. After autoreduction of the $AuCl_4^-$ ions, it was observed that the nature of the N_2 adsorption isotherms remained the same and even yielded a decrease in surface area (920 $m^2\ g^{-1}$ for Si-MCM-41 and 480 $m^2\ g^{-1}$ for NH_2-MCM-41) indicating filling of the pores by gold nanoparticles while maintaining the intactness of the mesoporous structure.

The procedure for the formation of nano-Au–MCM-41 hybrid materials proceeded along the following lines. In a typical experiment, 1.0 g of each of the Si-MCM-41 and NH_2-



Scheme 1 The probable structure of the NH_2-MCM-41 material before and after immersion in $HAuCl_4$ solution for 96 h. The magnified view of the cross-section shows the entrapped gold nanoparticles formed by spontaneous reduction of chloroaurate ions by the MCM-41 material.

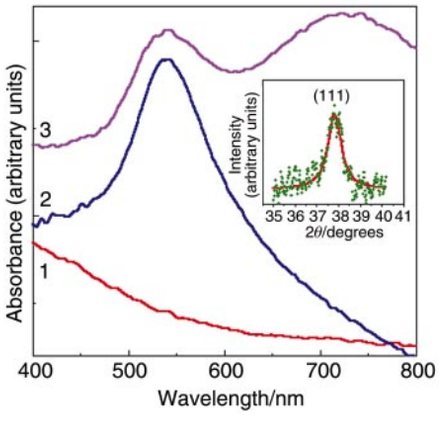


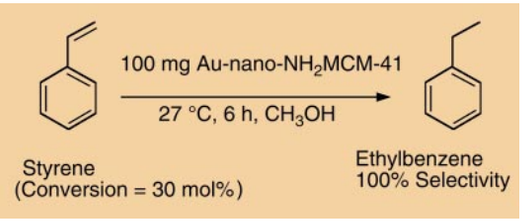
Fig. 1 UV-vis spectra recorded from the as-prepared NH_2-MCM-41 material (curve 1); the Si-MCM-41 material after immersion in $HAuCl_4$ solution for 96 h (curve 2) and the NH_2-MCM-41 material after immersion in $HAuCl_4$ solution for 96 h (curve 3). The curves have been displaced vertically for clarity. The inset shows the (111) Bragg reflection from the entrapped gold nanoparticles in the NH_2-MCM-41 material. The solid line is a Lorentzian fit to the XRD pattern and was used to estimate the nanoparticle size (see text for details).

MCM-41 materials were separately treated with 100 ml of 10^{-4} M $HAuCl_4$ solution for 96 h (Scheme 1). After the specified duration, the samples were filtered, washed thoroughly with copious amounts of water and acetone and finally vacuum dried. It could immediately be seen that both materials had acquired a deep pink color, clearly indicating the presence of gold nanoparticles in the cavities of the silicate bundles. This is illustrated in Schematic 1 for the NH_2-MCM-41 material but a similar structure is expected to hold for the Si-MCM-41 material as well. Gold nanoparticles have a characteristic absorption band in the visible region of the electromagnetic spectrum (around 520–550 nm) which is responsible for the striking violet–blue color of the nanoparticles.[9] Fig. 1 shows the UV-vis spectra[10] recorded from the as-prepared NH_2-MCM-41 material (curve 1) and the Si-MCM-41 (curve 2) and NH_2-MCM-41 materials (curve 3) after immersion in $HAuCl_4$ solution for 96 h. A strong resonance at *ca.* 540 nm is observed for the mesoporous materials after immersion in chloroauric acid solution and is clear indication of reduction of the chloroaurate ions in both the amine-derivatized and as-prepared Si-MCM-41 samples (Fig. 1, curves 1 and 2). Note that this resonance is clearly missing in the as-prepared mesoporous material (curve 1). An interesting observation is the presence of an additional resonance at *ca.* 725 nm in the case of the nano-Au–NH_2-MCM-41 material. This feature arises due to excitation of longitudinal surface plasmon vibrations and is a consequence of close-packing of the gold nanoparticles in open, string-like networks[11] within the channels of this material. This may be a consequence of the fact that the amine groups anchor the gold nanoparticles to the inner surface of the silicate cavities while such an interaction does not occur in the case of the nano-Au–MCM-41 material. It has been reported that primary amines bind to gold nanoparticles *via* a weak covalent linkage[12] and this is believed to be the binding mechanism in this study as well.

Esumi *et al.*[13] have shown that the reduction of chloroaurate ions by sugar balls (sugar persubstituted (amidoamine)dendrimers) occurs *via* the hydroxy groups in the sugars. We believe that a similar mechanism is operative in this study and that the reduction of the chloroaurate ions within the channels of the silicate mesoporous material occurs through silanol groups on the inner surface of the silicate material.

In order to estimate the size of the gold nanoparticles formed by spontaneous reduction of chloroaurate ions, X-ray diffraction (XRD) measurements of the nano-Au–MCM-41 and nano-Au–NH_2-MCM-41 were carried out on a Philips PW 1830 instrument operating at 40 kV voltage and a current of 30 mA with Cu Kα radiation. The diffraction pattern obtained from the NH_2-MCM-41 material is shown in the inset of Fig. 1 in the region of the (111) Bragg reflection ($2\theta = 38.2$ degrees). The solid line is a Lorentzian fit to the XRD (111) reflection and an analysis of the width of the (111) peak using the Debye–Scherrer equation[14] yielded a nanoparticle size of *ca.* 35 ± 5 Å. This value is in good agreement with the maximum possible particle size that can be accommodated within the pores of the present mesoporous material.

There have been recent reports on the catalytic activity of gold particles of nanoscale dimensions (diameters less than 50 Å).[15,16] We have investigated the catalytic activity of the gold nanoparticles immobilized in the MCM-41 structure in a hydrogenation reaction. The catalytic hydrogenation reaction was carried out in a quartz vessel at atmospheric pressure and at room temperature wherein 100 mg of the nano-Au–NH_2-MCM-41 sample was reacted with 250 mg of styrene in 8 mL of methanol solvent (Aldrich 99.8%) for 6 h under constant stirring. The products were analyzed by high resolution capillary gas chromatography (Shimadzu 17A instrument) using a flame ionization detector. The results of the catalytic



activity studies are summarized below.

It can be seen that 100% selectivity for the hydrogenated styrene product (ethylbenzene) is obtained with a total conversion of 30 mol% for the hydrogenation reaction. We would like to point out here that the dimensions of the gold nanoparticles required for high catalytic activity occur naturally for nanoparticles synthesized within the MCM-41 material framework and these nano-hybrid materials are thus ideal candidates for catalysis applications.

In conclusion, it has been shown that nanoparticles of gold may be synthesized and entrapped within the channels of silicious MCM-41 material by spontaneous reduction of aqueous chloroaurate ions. The reduction occurs *via* silanol groups on the inner surface of the silica pores. The dimension of the pores in the mesoporous material is commensurate with the size range of gold nanoparticles where they show maximum catalytic activity. This makes such metal nanoparticle-MCM-41 hybrid materials exciting systems for application in catalysis.

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