

Preparation, characterization and condensation of novel metal chalcogenide/MCM-41 complexes

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Hexagonally ordered mesoporous MCM-41 with 3 nm pores has been impregnated with the metal chalcogenolate $\text{Cu}_6(\text{TePh})_6(\text{PPh}_2\text{Et})_5$ **1**: the analysis and condensation of this material is a step toward the synthesis of semiconducting nanowires.

The ability of mesoporous materials to act as hosts for quantum structures has been the focus of numerous research efforts as exemplified with reports on the absorption and subsequent polymerization of aniline,¹ the encapsulation of semiconducting Ge filaments,² the preparation of ferrocenophane polymer³ and the fabrication of nanostructured Pt clusters and wires.⁴

The independent development of the chemistry of mesoporous materials and metal chalcogenide clusters over the past decade have seen dramatic growth.^{5–7} The union of these two fields, the encapsulation of metal chalcogenide clusters and their subsequent condensation into size limited semiconductor particles, should provide novel one-directional nanostructures.

The copper–chalcogenolate cluster $\text{Cu}_6(\text{TePh})_6(\text{PPh}_2\text{Et})_5$ **1** can be accessed in high yields *via* the reaction of CuCl and $\text{Te}(\text{Ph})\text{SiMe}_3$ with an excess of the phosphine PPh_2Et .⁸ Cluster **1**, like many metal–telluroate complexes⁹ undergoes a series of condensation reactions *via* the photochemical elimination of TePh_2 . For **1**, this yields the cluster $[\text{Cu}_{50}(\text{TePh})_{20}\text{Te}_{17}(\text{PEtPh}_2)_8]^{4-}$.⁸ Our efforts in this area are to exploit these facile condensation processes within the channels of nanoporous MCM-41. Pure silica MCM-41, prepared with cetyltrimethylammonium bromide, has a pore size easily large enough to accommodate clusters such as **1**.¹⁰

The synthesis of **1**/MCM-41[†] was achieved using sublimation techniques under an inert atmosphere. During impregnation, maintaining an inert atmosphere is extremely important since at these elevated temperatures rapid cluster decomposition is otherwise observed. However, after loading, these materials are stable under atmospheric conditions for an extended period of time.

TGA data provide important information about the loading features. Characteristic decomposition curves of **1** and **1**/MCM-41 are shown in Fig. 1. For pure **1** [Fig. 1(a)] a single decomposition is observed, produced by two distinct endothermic steps obtained by DTA. This decrease in mass results from the loss of 3 equivalents of TePh_2 and 5 equivalents of PPh_2Et per cluster molecule as determined by TGA and subsequent GC–MS analysis. The observed 70.5% weight loss is close to the calculated loss of 71.5%. Since no strong interaction between the outer surface of the host and copper cluster is expected, the thermal decomposition of **1** adsorbed onto the MCM-41 exterior surface should be very similar to that observed for pure **1**. The TGA of a sample **I** of MCM-41 combined with **1** (70 °C, 10^{-3} Torr) [Fig. 1(b)] displays a weight loss at low temperature (onset = 150 °C) due to **1** adsorbed on the external surface. A 150 °C onset decomposition temperature is consistently observed for externally adsorbed **1** on MCM-41 and is identical to that observed for pure **1**. The high temperature (250 °C) weight loss can thus be attributed to cluster loaded inside the MCM-41 channels. The TGA results indicate some impregnation at 70 °C (10^{-3} Torr), with cluster **1**

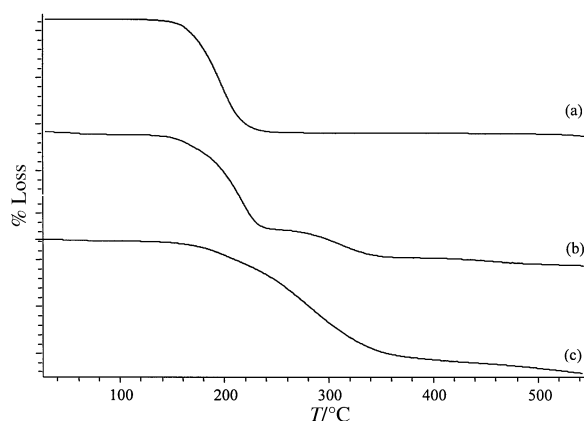


Fig. 1 TGA decomposition in the range 25–550 °C at a heating rate of 10 °C min^{-1} : (a) pure **1**; (b) **1**/MCM-41 treated at 70 °C at 10^{-3} Torr (sample **I**); (c) **1**/MCM-41 treated at 110 °C at 10^{-3} Torr (sample **II**).

being only partially loaded inside of MCM-41. In contrast, a sample of **1**/MCM-41 complex **II** prepared by heating at 110 °C (10^{-3} Torr) [Fig. 1(c)] displays only one, high temperature decomposition suggesting complete loading of **1** inside of the MCM-41 host.

The actual weight percent loading may be calculated from these curves. It is observed that loading is virtually time independent. Factors such as temperature and **1**/MCM-41 ratio affect the loading percent if loading is carried out for a minimum time of 12 h. For mechanical mixing under atmospheric conditions, a maximum of 5% loading is observed and can be attributed to a small quantity of cluster blocking the entrance to the pores. At 70 °C the loading increases to 11%. An increase in temperature leads to higher loading with a maximum of 34% achieved at 110 °C.

Nitrogen adsorption studies confirm that **1** is indeed loaded into the channels of MCM-41. The adsorption curve for pure MCM-41 [Fig. 2(a)] with a type IV isotherm and distinct capillary condensation characteristic of MCM-41 has a BET surface area of 1126 $\text{m}^2 \text{g}^{-1}$. The BET surface area decreases to 272 $\text{m}^2 \text{g}^{-1}$ for **II** [Fig. 2(b)]. No significant lattice contraction

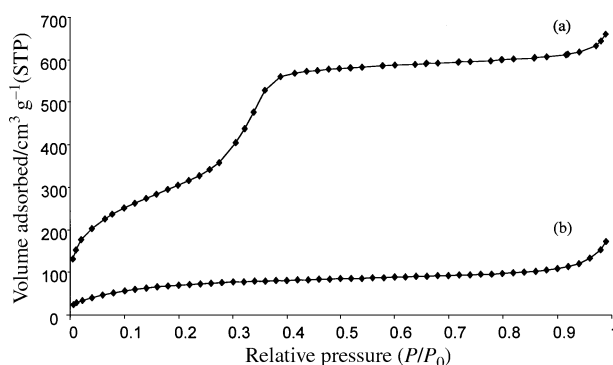


Fig. 2 Nitrogen adsorption curves: (a) MCM-41; (b) **1**/MCM-41 treated at 110 °C at 10^{-3} Torr (sample **II**).

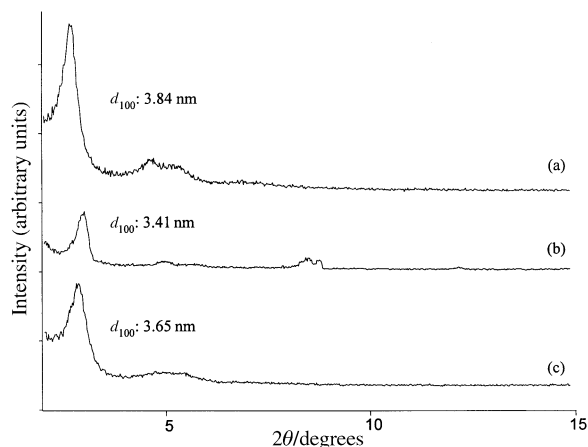


Fig. 3 PXRD patterns in the range $2\theta = 2\text{--}15^\circ$ (intensities normalized to the d_{100} reflection intensity of calcined MCM-41): (a) pure MCM-41; (b) **I**/MCM-41 treated at 70°C at 10^{-3} Torr (sample **I**); (c) **I**/MCM-41 treated at 110°C at 10^{-3} Torr (sample **II**).

was observed by powder X-ray diffraction (PXRD) and thus we conclude that this decrease in surface area is a result of the loaded cluster. The inflection point of the loaded sample becomes less sharp and shifts to lower relative pressure. This shift indicates the presence of smaller mesopores due to the impregnation of **I**. However the mesoporous structure is maintained as indicated by the overall shape of the isotherms and from PXRD.

The powder pattern of samples of MCM-41 has a characteristic diffraction pattern (h_{100} , h_{110} , h_{200}) with a calculated d_{100} of 4.4 nm.¹⁰ The partial impregnation of **I** into MCM-41 [Fig. 3(b)] gives rise to diffraction patterns for host and guest species, with reflections of **I** due to crystallites of the cluster adsorbed on the external surface of MCM-41. With **II**, only the diffraction pattern of MCM-41 is observed [Fig. 3(c)]. We therefore conclude that the structural integrity of MCM-41 is maintained during impregnation and the clusters are dispersed within the channels with no long range ordering. A decrease in the intensity of the d_{100} diffraction and a smaller d -spacing are observed in both loaded samples **I** and **II**. The loading of **I** into the pores of MCM-41 causes a decrease in the mean electron density of silicate walls compared to the pores, thus decreasing the d_{100} diffraction.¹¹ The smaller d -spacing in Fig. 3(b) and (c) suggests the loading process slightly decreases the size of the pore walls.

The IR spectrum of **I**/MCM-41 in the $\nu(\text{CH})$ stretching region suggests that cluster integrity is maintained during impregnation as the number of $\nu(\text{CH})$ bands and their position of **II** are virtually identical to those for **I**. CP MAS ^{31}P NMR spectra of **II** display only a single peak at -11.8 ppm in close agreement with the observed solution shift (-10.4 ppm)⁸ of the free cluster, as expected when the cluster is 'diluted' in the solid framework.

The photolysis of **I** and the **I**/MCM-41 complex provides evidence of cluster condensation, in agreement with its

developed solution chemistry.⁸ The UV-VIS spectra of non-photolysed **I**/MCM-41 in hexane show two distinct maxima at 210 and 249 nm.

Since **I** has low solubility in hexane, a slurry of **II** was prepared and the suspension was photolysed.[‡] A darkening of the sample and a red shift is observed for both **I** and **II**. The observed red shift in the UV-VIS spectra suggests cluster condensation, as previously observed.¹² Increasing the irradiation time increases the red shift for both samples and yields a new absorbance at 440 nm for irradiated **I**. No further change is observed after 10 h of irradiation. Although identical condensation as that observed in solution, which results in the formation of $[\text{Cu}_{50}(\text{TePh})_{20}\text{Te}_{17}(\text{PEtPh}_2)_8]^{4-}$, from **I** inside the pores of MCM-41 is unlikely, a condensation process is nonetheless occurring. Thermally activated condensation of **I** inside the pores of MCM-41 is also possible with complete loss of TePh_2 and PPh_2Et moieties with only copper telluride remaining as characterized by PXRD. We are currently perusing the characterization of the condensed materials and the general applicability of this method to metal chalcogenolate complexes.

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Notes and references

[†] 0.1 g of calcined MCM-41 was dehydrated at 130°C under dynamic vacuum (10^{-3} Torr) for 3 h. Homogeneous samples of cluster:MCM-41 (weight ratios 1:4, 1:2) were prepared by mechanical mixing under atmospheric conditions producing a yellow microcrystalline powder. These samples were then heated at 70 or 110°C under a static vacuum (10^{-3} Torr) for a minimum of 12 h.

[‡] Preparation of UV-VIS samples: 0.05 g samples of **I** and **I**/MCM-41 (**II**) were charged in quartz UV cells with glass-distilled hexane and a stir bar to prepare a suspension. The samples were irradiated at room temperature with a low-pressure Hg lamp ($\lambda > 254$ nm).

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