Grafting Metalorganic Species into Mesoporous Silica from the Vapour Phase

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MCM-41 silica are mesoporous materials with uniform, non-interconnected channels arranged in a 2-D hexagonal array. Pores several nanometers wide with numerous pending Si-OH groups are well fitted to nanoscale chemical reactions leading to a wide range of modified MCM-41 materials. Grafting metal complexes according to the elementary process $\equiv$Si-OH + $ML_n \rightarrow$ $\equiv$Si-OML_{n-1} + HL currently allows to prepare hybrid organic/inorganic compounds or precursor compounds subsequently transformed into inorganic materials. Whereas wet impregnation has been widely used for grafting metal complex species, the CVD technique remains marginally used.

We present here preliminary results concerning the grafting of europium β-diketonato species by using the CVD technique. As part of a wider work on luminescent materials using MCM-41 as a host for Eu(III) complexes, and besides compounds prepared by wet impregnation, compounds were prepared by reacting vapours of $Eu(dik)_3$ with MCM-41, in sealed ampoules [$Eu(thd)_3$, $Eu(fod)_3$] and in a continuous flow reactor [$Eu(thd)_3$]. The study was completed by a similar work using $Cu(thd)_2$, in view of potential applications in magnetism. Results presented here deal with the characterisation of the products according to the precursor and the way of preparation.

In the static vapour phase (SVP) method, weighed out samples of activated MCM-41 (typically 15 to 50 mg treated under vacuum at 200 °C for 4 hrs) and of $M(thd)_n$ (typically 10 to 30 mg) were placed in two separate glass-containers and sealed under vacuum in a Pyrex glass tube. The ampoule was heated at 185 °C for a period of time going from a few hours to a few days depending on the experiment. Then it was quenched in the air, so that remaining vapour phase could condense on the wall, not in the containers. The containers were weighed immediately after opening the ampoule, and kept in a desiccator.

In the dynamic vapour phase (DVP) method, the reactor is a vertical Pyrex-glass tube (internal ϕ = 24 mm; length = 600 mm) placed in a vertically sliding oven equipped with a temperature controller. MCM-41 (typically 150 mg) is placed on a sinter-glass filter in the middle of the tube. The precursor (typically 300 mg) is placed in a glass container (internal ϕ = 18 mm ; length = 20 mm) below the sinter-glass, on the top of a sliding thermocouple. The precursor container may be lifted up to the position corresponding to the desired temperature. The lower part of the reactor is connected to a nitrogen delivery system. The upper part is connected to a manometer, a liquid nitrogen trap and a rotary pump. Reaction temperature is monitored by means of a thermocouple fixed outside the reactor on a level with MCM-41 sample. MCM-41 is first activated at 200 °C under vacuum for 4 hours. After cooling, N_2 is progressively admitted at about 2 mln/min. so as to fluidise MCM-41. The reaction temperature is maintained at 185 °C, and the precursor temperature at 150 °C. After one hour, the precursor container is lifted down to the cool part. The reactor temperature is maintained at 185 °C for an other 30 minutes, and then let to cool down under flowing N_2.

The expected overall reaction is as follows: $SiO_{2-x}(OH)_{2x} + t\,M(dik)_m \rightarrow SiO_{2-x}(OH)_{2x-y}(O^s)_y M_z(dik)_{mz-y} + (t\text{-}z)\,M(dik)_m + y\,Hdik$, meaning that a fraction z of the t $M(dik)_m$ precursor molecules (M = Eu, m = 3; M = Cu, m = 2) reacts with one mole of mesoporous silica to give chemisorbed species, the remaining ($t - z$) molecules being physisorbed.

Formation of Hthd has been proved by RMN analysis of the product condensed in the liquid N_2 trap in DVP experiments run with $Eu(thd)_3$ and $Cu(thd)_2$.

The comparison of X-ray diffraction patterns for starting MCM-41 and the products showed that the ordered hexagonal structure of MCM-41 was conserved upon reaction. Examination of the large Bragg angles region showed either no appreciable or trace amounts of the crystalline form of relevant precursor metal complex.

The nitrogen sorption measurements on some samples gave further evidence for pore filling. BET surface area of 951 ± 1, 338 ± 9, and 545 ± 16 m^2/g were recorded respectively for pure MCM-41, a sample prepared from $Eu(thd)_3$ and one prepared from $Eu(fod)_3$.

None of the compounds prepared from $Eu(fod)_3$ or from $Eu(thd)_3$ released free metal complex upon heating under vacuum, which means that no physisorbed species formed with these precursors.

The mean atomic ratios Eu/Si are in the range 8.0 - 8.3 %, whatever the precursor, for compounds prepared by the SVP method. It amounts to 9.3 % for the compound prepared by the DVP method from $Eu(thd)_3$.

For samples prepared from $Eu(fod)_3$ at 185 °C, it has been established that two plateaux of compositions are reached depending upon the length of the thermal treatment. The first one, corresponding to Eu/Si $\cong$ 0.07, is obtained for treatment lasting from 17 to 36 hours. The second one, above 41 hours, corresponds to Eu/Si $\cong$ 0.08. Structural modifications suggested by a dramatic increase in BET surface area are upon investigation. Intermediary compositions are obtained for treatments lasting between 36 and 45 hours.

Compounds prepared from $Cu(thd)_2$ by the SVP method proved to contain both chemisorbed and physisorbed metal complex species. Maximum Cu/Si atomic ratios for the total amount of adsorbed copper and of chemisorbed copper are 0.11 and 0.04 respectively. Whatever the amount of precursor engaged in the reaction with MCM-41, the same ratio of 4/11 is observed for chemisorbed to totally adsorbed copper. The use of the DVP method leads to chemisorbed only species with Cu/Si = 0.05.