A Novel Route towards Iron- and Chromium-containing MCM-41 Materials through Melt-exchange of the Template

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Solid state treatment of an MCM-41 hybrid with molten iron(III) and chromium(III) salts, afforded the corresponding metal-containing MCM-41 materials free of the organic template and with high metal contents and thermal stability.

Mesoporous silica of the MCM-41 type is an important class of self-assembled inorganic materials consisting of an hexagonal arrangement of cylindrical pores between which an amorphous silicon dioxide network is interposed. As these materials show large specific surface area, high pore volume, uniform pore diameter, and thermal stability, they are promising as effective absorbents and catalysts in processes involving large molecules that can diffuse freely through their pores. However, due to the inactive chemical composition of the MCM-41 materials, incorporation of metal centers in the silica framework or grafting of metal oxide nanoparticles on its surface are necessary for their use in catalysis.[1] Therefore, several methods have been advanced in preparing metal-containing MCM-41 structures.[2–9] In this communication we report a novel route for the preparation, for instance, of iron- and chromium-containing MCM-41 materials that is based on melt exchange reactions between the positively charged template molecules in an as-synthesized MCM-41 material of the S^+I^- type (S^+ stands for ionic surfactant and I^- for the silica network) and positively charged metal-containing oligonuclear clusters derived from low melting point iron(III) and Cr(III) salts. The method proceeds in the solid state without use of solvents[9] and enables a uniform loading of the silica surfaces with a high amount of metal without destroying the organized architecture of the parent MCM-41 material.

The synthesis of the MCM-41 material (S^+I^- type) comprises alkaline hydrolysis of silicon alkoxides in the presence of surfactant molecules $[C_{16}H_{33}N(CH_3)_3Cl]$ according to a known procedure.[6,7] The salts $Fe(NO_3)_3 \cdot 9H_2O$ (mp: 56 °C) and $CrCl_3 \cdot 6H_2O$ (mp: 83 °C) were employed for the melt exchange reactions. In a typical preparation, 0.2 g of MCM-41 solid were well ground with a large excess of the corresponding salt (1 g) and the solid mixture was heated either at 80 °C for 3.5 h (iron case) or at 100 °C for 2 h (chromium case). Following, each mixture was cooled down to room temperature and subsequently washed very well with ethanol prior drying (MCMFe: yellowish, MCMCr: greenish). Portions of the samples were finally calcined in air at 400 °C for 2 h via steps of 1 °C min^{-1} resulting to MCMMe/400 samples [Me: Fe (orange), Cr (yellowish)]. ICP analysis of the calcined samples revealed metal contents (w/w) of 3.4% Fe and 3.1% Cr.

Evidence for the surfactant extraction after the melt exchange reactions with the metal salts comes from IR spectroscopy. For example, Figure 1 shows the IR spectra of as-synthesized MCM-
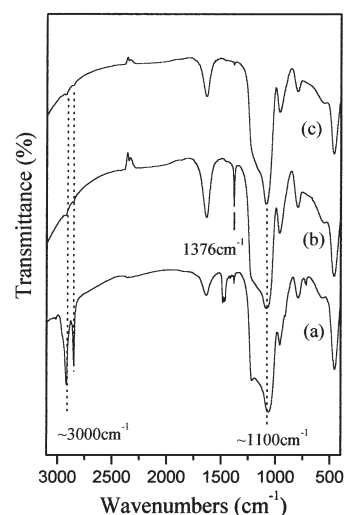

**Figure 1.** IR spectra of MCM-41 (a), MCMFe (b), and MCMFe/400 (c) samples.

41 (a), MCMFe (b) and MCMFe/400 (c). Thus, the parent MCM-41 solid exhibits strong absorption bands below 3000 cm^{-1} assigned to the –CH$_3$ and –CH$_2$– aliphatic moieties of the surfactant cations that are totally vanished after the melt exchange reaction with $Fe(NO_3)_3 \cdot 9H_2O$. In addition, a new band at ≈ 1380 cm^{-1} emerges and it is attributed to the presence of compensated NO$_3^-$ ions in the solid (absent when $CrCl_3 \cdot 6H_2O$ is employed). These data clearly point to template removal and simultaneous grafting of mobile, melt derived, charged oligonuclear iron(III) clusters onto the MCM-41 surfaces through its –Si–O$^-$ and –Si–OH groups. Additionally, they signify the uniform distribution of the inserted species mainly over the internal walls of the silica support where the majority of the surfactant molecules was protruded. Upon thermal treatment of the MCMFe solid, no significant changes were observed in the IR spectra except of combustion of the nitrate ions. At this point we must stress that the melt state of the salts during an exchange procedure is a crucial condition. Otherwise, no template removal and insertion of metal centers were observed.

The low angle XRD patterns of the as-made and calcined metal-containing MCM-41 derivatives are presented in Figure 2, left. It is seen that the metal-containing materials retain the typical for an MCM-41 solid hexagonal symmetry throughout the entire synthesis. These results suggest that upon replacement of the surfactant cations by the inserted oligonuclear species, the latter act as effective scaffolds in stabilizing the porous silica walls. In Figure 2, right, we depict the XRD patterns of the calcined samples in the region 10–60°, where no XRD detectable metal
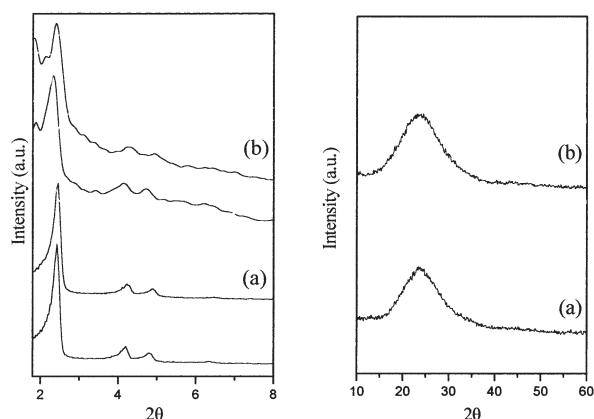
Figure 2. The left figure depicts the low angle XRD patterns of the as-made (lower) and calcined (upper) samples containing Fe (a) and Cr (b). The d_{100} values are ~36 Å for both MCMFe and MCMFe/400, and ~37 Å for MCMCr and MCMCr/400. The right figure depicts the XRD patterns of the calcined samples containing Fe (a) and Cr (b) in the 2θ region 10–60°.

oxidic phases are observed. The BET surface areas for the MCMFe/400 (uniform pore size distribution) and MCMCr/400 (non-uniform pore size distribution) were found to be $1000\,m^2\,g^{-1}$ and $360\,m^2\,g^{-1}$, respectively. The relatively small surface area of MCMCr/400 can be attributed to the high chromium content of the sample which in turn causes partial collapse of the structure associated with the formation of macropores in the solid.[10] In Figure 3 we present the TEM micrograph of the MCMFe/400 sample. Apparently, the sample displays the characteristic honeycomb structure of an MCM-41 material exhibiting uniform structural features. The mean pore diameter and wall thickness are 25 Å and 20 Å, respectively. Notice the absence of any iron oxide nanoparticles in the sample.
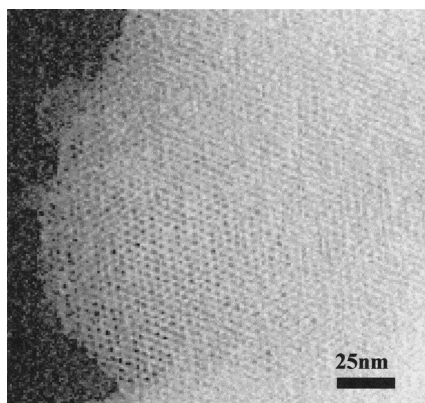
Figure 3. TEM image of the MCMFe/400 sample.

The nature of the iron and chromium species in the as-made and calcined samples was probed by Mössbauer measurements at 20 K and ESR spectroscopy, as shown in Figure 4. The ESR spectra of MCMFe and MCMFe/400 at room temperature (not shown) consist of a broad, asymmetric signal at g ≈ 2.00, typical for the presence of iron oxidic clusters in the solid.[11] In agreement with this, the Mössbauer spectrum of MCMFe at 20 K is composed of one paramagnetic doublet with isomer shift $(0.47\,mm\,s^{-1})$ and quadrupole splitting $(0.82\,mm\,s^{-1})$ values typical of trivalent iron in octahedral coordination. The absence of any magnetic hyperfine splitting in the spectrum indicates the formation of small iron oxidic clusters. The presence of silicon
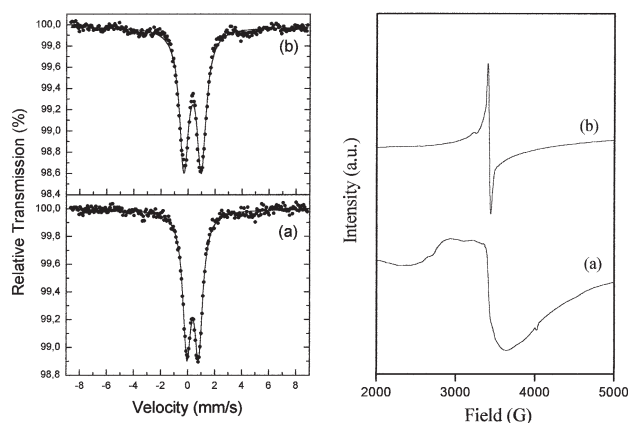
Figure 4. Mössbauer spectra of MCMFe (a) and MCMFe/400 (b) at 20 K (left), and ESR spectra of MCMCr (a) and MCMCr/400 (b) at 30 K (right).

and nitrogen in the local environment may favor the formation of ferrihydrite.[12] The spectrum of MCMFe/400 at 20 K consists again of one paramagnetic doublet having similar isomer shift value but quadrupole splitting value $(1.14\,mm\,s^{-1})$ much higher than that expected for hematite. This fact combined with the observed small deviation of the base line from the horizontal due to the onset of magnetic interactions, indicates the formation of highly defective superparamagnetic iron oxide particles of grain size less than 20 Å.[13] It is reasonable to assume that this particles reside within the pore channels of the silica since the majority of the initially loaded species were located there. Concerning the chromium-containing samples, the ESR spectrum of MCMCr at 30 K consists of a broad signal at g ≈ 1.95 which is assigned to superexchange coupling between Cr–O–Cr pairs from oligo-nuclear Cr(III) clusters dispersed on the MCM-41 surfaces.[10,14] After calcination in air, a sharp signal at g ≈ 1.95 is appeared indicating the formation of Cr(V) units.[10]

In conclusion, solid state treatment of an MCM-41 material with molten iron(III) and Cr(III) salts, leads to exchange reactions between the surfactant cations of the parent MCM-41 and positively charged, melt derived, oligonuclear metal clusters. In this way, we receive fine structured iron- and chromium-containing MCM-41 materials free of the organic template and with high metal contents and thermal stability. Most importantly, we believe that the same principles can be also applied for a wide range of hybrid materials and low melting point organic or inorganic salts.

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