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Ordered mesoporous CoO_x/MCM-41 materials exhibiting long-range self-organized nanostructured morphology

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Abstract

A novel class of nanostructured silicious materials of MCM-41 type containing cobalt, CoO_x/MCM-41, and exhibiting remarkable long-range self-organized morphology has been developed. The method of synthesis is *a one step procedure* and includes the use of poly-acrylic acid, complexed with CTAB by a zip-type mechanism, as a backbone of the structure. On the external surface of this meso-structure, hydrolysis of TEOS and $Co(NO_3)_2$ takes place at various pH values. The loading of cobalt ($9 < Si/Co < 37$) in the final solid can be controlled by the pH values at which the material is isolated in the range $5.5 < pH < 9.5$. The isolated mesostructures, after drying (80 °C), as well as the resulting mesoporous solids after calcination (600 °C), exhibit remarkable self-organized morphology of the order of μm. In XRD, both the dried mesostructured as well as the calcined solids, exhibit typical patterns of MCM-41 type, which are blurred as the amount of cobalt increases. The surface area of those nanostructured mesoporous solids CoO_x/MCM-41 was determined in the range 910–1250 m^2/g by nitrogen porosimetry and their pore volume in the range 0.7–0.9 cm^3/g. The pore diameter D was found to be around 3.1 nm while the pore anisotropy $b = L/D$, where L—the length of the pores, was determined in the range 15–380 depending on the sample.
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1. Introduction

The incorporation of transition metal ions (t.m.i.) into the framework of mesoporous materials, like MCM-41 [1,2], MCM-48 [3,4] and SBA-1 [5,6] has attracted enormous interest due to potential applications of such solids as heterogeneous catalysts [7–12] or electrochemical sensors [13,14]. The most common heteroatoms, which have been incorporated into the silicate framework of silicate mesoporous solids, include Al [15–17], Ga [18,19], Ti [20–22], Mn [23,24] and Co [25–31]. The incorporation of cations like Al and Ti into the SiO_2 matrix results in a substantial increase of surface acidity [32–34], as happens with zeolites too [35,36], and such solids can be employed as acid catalysts. On the other hand incorporation of cations like Mn, Ni and Co leads to materials with sites suitable for redox catalytic operations. In relation to cobalt, which is the subject of this work, its incorporation into mesoporous materials has been achieved by direct one pot synthesis [25–27], by post synthesis ion exchange [28–30] as well by gas phase deposition of $Co_2(CO)_8$ into the silicate porous network [31]. The content of cobalt loading in the cases of direct synthesis or cation exchange reaches an upper limit of about 10% [25–30] and only in the case of deposition from the gas phase the loading increases to almost 40% for reasons which can be easily understood.

The direct one-pot-synthesis methods are relatively easy procedures, which provide mesostructures or mesoporous solids into which CoO or Co_3O_4 species are observed depending on the preparation method. In a recent study

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by Vralstad et al. it was suggested that the amount of cobalt incorporated into the final MCM-41 ($0.45 <$ wt.%Co < 4.66) and the MCM-48 ($0 <$ wt.%Co < 9.35) solids depends on the pH values which affect the precipitation of cobalt hydroxide $Co(OH)_2$ in a mixed gel with oxyhydroxy-silicates [25]. The same authors observed that the addition of increasing amounts of cobalt salt into the MCM-48 synthesis gel causes a change of the mesoporous structure from cubic to hexagonal for reasons related to the charge density matching between the divalent cobalt(II) and the negatively charged silicate species.

In a relevant work by Haskouri et al. on CoO–MCM-41 nanocomposites [27] with ratio Si/Co > 23 it was shown that the ordered hexagonal structure is degenerated to a wormhole-like structure as the cobalt content increases. Furthermore, independently of the Si/Co ratio, it was observed by UV–vis and NMR techniques that cobalt is organized into the silicate framework in well-dispersed, uniform CoO superparamagnetic nanodomains of size approximately 3 nm.

Finally in another publication by Lim et al. [26] highly ordered Co–MCM-41 materials were synthesized as catalysts for the production of single wall carbon nanotubes. The local environment of cobalt, as determined by UV–vis spectroscopy, was a mixture of tetrahedral and distorted tetrahedral structures similar to those observed in Co_3O_4. Cobalt appears uniformly distributed at nearly atomic dispersion as probed by XAFS.

In the present paper we communicate a different one-pot-synthesis-method of CoO_x–MCM-41 materials, in which, apart from the usual ingredients, i.e. a surfactant CTAB, a silica source TEOS and a source of Cobalt, employed in the above mentioned cases [25–27], we employed poly-acrylic acid as a directing agent of the structure [37–39]. The most remarkable result of this methodology is that it leads to self-organized solid particles, which in the μm *level* exhibit long-range decorated patterns of specific morphology, while in the nm *level* they are typical ordered MCM-type mesoporous solids. We mention that in the literature there are various examples of morphogenetic systems developed usually via a self-organized mechanism [40–53], including cases where poly-acrylic acid was employed as a component of the hybridic system [44d,45d,54]. Nevertheless such systems are not usually porous. As far as we know morphogenesis effects in porous systems have become apparent only in silicate ordered mesoporous solids prepared by the group of Ozin et al. [42]. In the present case the morphogenesis of the ordered mesoporous silicate structure is generated by the addition of a transition metal ion, namely cobalt.

2. Experimental section

2.1. Preparation of the samples

The preparation of the mesoporous solids took place according to a methodology developed recently [37–39]

which makes use of poly-acrylic acid—Pac in the next— as a stabilizing agent of the micelle structure. The synthesis took place as follows: Pac (0.7 g, 2000 MW, 99% Aldrich) was dissolved in water (100 ml) under stirring. The pH of the solution was adjusted at 1.7 by the use of HCl 1 M (3 ml). Then CTAB (3.58 g, 99% Merck) was added. The mixture was heated to 30 °C where a clear solution was obtained. Then TEOS (6 ml, 98% Merck) was introduced as a source of silicon and $Co(NO_3)_2 \cdot 6H_2O$ (0.884 g, 98% Fluka) as a source of cobalt with atomic ratio Si/Co $= 9$. Then the pH of that mixture was slowly increased by dropwise addition of NaOH 0.1 M. The procedure was repeated four times and the final value of pH was set equal to 5.5–6.5–7.5–8.5–9.5, respectively. Each mixture was aged under stirring for 18 h, filtrated and washed with water (30 ml). The samples were dried for 6 h at 80 °C, then heated up to 600 °C with a heating rate $3° \text{min}^{-1}$ and stayed there for 1 h under atmospheric conditions.

The materials prepared in this way are designated in the next as CoO_x–A–B–C–D–E/MCM-41 where each capital letter corresponds to the pH value (5.5–6.5–7.5–8.5–9.5) where the particular sample was isolated.

2.2. Characterization

The characterization of the precursors (uncalcined samples) as well as of the calcined solids took place with the following techniques:

TG–DTA: The uncalcined materials were checked for their thermal behaviour by detecting simultaneously the TG and the DTA signals in a STA 449 C *Jupiter* system by Netzsch under air flow (30 ml/min) in the temperature range 300 K $< T <$ 1273 K and a heating rate of 10 K/min.

X-ray diffraction: The dried precursor materials, as well as the calcined solids, were characterized by XRD in a Bruker Advance P8 system using CuKα radiation ($\lambda = 1.5418$) with step 0.02°/s.

Diffuse reflection UV–visible spectroscopy: The diffuse reflectance spectra of dried and calcined solids were recorded in the range 250–850 nm at room temperature using a UV–vis spectrometer type UV-2401PC by Shimadzu.

Nitrogen adsorption–desorption porosimetry: The calcined samples were tested for their surface area and porosity by N_2 adsorption–desorption porosimetry (77 K) in a Sorptomatic 1990 Fisons porosimeter. Before each measurement the sample was degassed at 150 °C for 6 h.

SEM–EDS: The dried precursor materials, as well as the calcined solids, were photographed by scanning electron microscopy (SEM) in a Jeol JSM 5600 system operating at 20 kV. The atomic ratio between Si/Co for each calcined sample was calculated by the average of six measurements of energy dispersive spectra (EDS), which were analysed by the ISIS Oxford Microanalysis system.