Synthesis and characterization of MCM-41 coatings on stainless steel grids

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Abstract

Innovative structured catalytic packings have been prepared by in situ hydrothermal synthesis of mesoporous MCM-41 on stainless steel grid. After a one-step synthesis, the metal support was observed to be homogeneously covered by a dense layer ($\sim$80 µm) of the mesoporous material. © 2002 Published by Elsevier Science B.V.

Keywords: MCM-41; Coatings; Structured bed; One-step synthesis

1. Introduction

Recently discovered mesoporous molecular sieves of M41S type [1–5] are materials of interest for catalytic applications. These materials possess ordered pores ranging from 2 to 30 nm with narrow size distribution, high surface area (up to 1200 m^2/g) and are thermally stable. The pore sizes allow catalytic transformations of large molecules to be carried out, which could not diffuse inside the microporous zeolites. A defined length of the alkyl chain in template used during the preparation controls the pore size of M41S. Catalysis taking place within the porous space depends on the active sites, which are formed by purposeful modification of silica. For example, the doping of aluminium into the silica framework generates Brönsted acid sites, which are known to be active in many catalytic reactions. M41S-type solids can be loaded by different cations (V, Ti, Mo, etc.) to meet the requirements of chemical transformations. Thus, the control of the chemical composition and of porous structure is ensured during the catalyst synthesis, but the macrostructure of mesoporous packings is relatively undefined. MCM-41 catalysts are used in catalytic fixed beds, randomly packed by powdered micro-granules or extrudated pellets with a few millimeters in size. The main disadvantages of randomly packed beds are the limited heat and mass transfer, high-pressure drop and flow maldistribution, leading to a poor reactor performance.

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During the last decade, there has been a growing interest on structured catalytic beds as an alternative to conventional fixed-beds [6]. Various procedures have already been tested for in situ synthesis of zeolites on various structured substrates [7–11]. Zeolite coatings on stainless steel grids have been shown as effective catalysts in different reactions [12–14].

The objective of this work is to prepare mesoporous structured catalytic packings via in situ synthesize of MCM-41 coating on stainless steel grid.

2. Experimental

2.1. Support pre-treatment

The structured packing consisted of the stainless steel grid (AISI 316 type, wire diameter of 250 μm, mesh size of 800 μm) as a support for mesoporous coating, was arranged by a superposition of five plates separated from each other by steel rings of 4 mm length. The whole packing was pre-treated in boiling toluene and in hydrochloric acid solution to remove surface contaminations [9]. After ultrasonication in distilled water, the support was immersed in a cetyltrimethylammonium bromide (CTABr) solution (0.1 M) for 1 h at room temperature. The CTABr adsorbs on the grid surface guiding the mesopores synthesis selectively on the support and not in the solution, as already reported for zeolite coatings [9].

2.2. Synthesis of MCM-41 coating

The chemicals: tetraethoxysilane (TEOS, 98%, Merck–Suchardt), ethanol (EtOH, 96%, Fluka), NaOH (98%, Fluka), Cetyltrimethylammonium bromide (CTABr, 99%, Merck) were used as received. Deionized water was employed for the synthesis. MCM-41 molecular sieves were prepared via S^+/I^- templating route as described elsewhere [1].

The gel used for the MCM-41 synthesis was prepared from tetraethylorthosilicate (TEOS) as the silicon source. The TEOS (0.047 mol) was mixed with a solution containing CTABr (0.032 mol) and NaOH (0.04 mol) in H_2O (4.167 mol) and ethanol (0.086 mol) as co-solvent. After ageing for 3 h under vigorous stirring, the gel was poured in a Teflon-lined (100 ml) autoclave containing a vertically positioned stainless steel support.

The temperature was increased within one hour to 423 K and the synthesis was continued for another 24 h under autogenous pressure. Afterwards, the packing was kept in an ultrasonic bath (45 kHz) for 20 min to remove loosely attached particles and dried overnight at 400 K. The catalytic packing was calcined in air at 823 K for 5 h to burn out the organic template.

The yield of the synthesis is defined as the ratio between the amount of Si incorporated into MCM-41 and the initial amount of Si present in the synthesis gel.

2.3. Characterization

The specific surface area (SSA) of the supports and the catalysts were measured using N_2 adsorption–desorption at 77 K by a Sorptomatic 1990 (Carlo Erba) instrument. Samples before the measurements were heated in vacuum at 523 K for 2 h. The SSA of the samples was calculated employing the BET method while the Dollimore/Heal method was applied for the calculation of pore volume and pore-size distribution (PSD).

The X-ray diffraction (XRD) spectra were acquired on a D500 Siemens powder diffractometer $(\theta/2\theta)$ using monochromatized Cu-Kα radiation $(\lambda = 1.5406$ Å) in the angle range of 0.5–10°2Θ with the steps of 0.04° and a step time of 8 s.

Scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) was employed to study the morphology of mesoporous silica. HRTEM measurements were carried out on a Philips CM300UT FEG with 300 kV field emission gun. SEM images were recorded using a JEOL JSM-6300F electron microscope operating at a voltage of 5 kV.

3. Results and discussion

The yield of 54% was achieved in the synthesis of MCM-41. The selectivity of the coating, defined

as the mass of MCM-41 coated the grid referred to the total mass of MCM-41 formed (attached to the grid and in the solution), was about 24%. The grid coverage was found to be ~100 g_{MCM-41}/m^2_{grid}. In our previous work devoted to the ZSM-5 deposition on metal grid [9,12], it was possible to attain this coverage only after a three-step synthesis.

Fig. 1 shows the XRD patterns of the coated MCM-41 and of the mesoporous formed in the solution. The powder sample was used as a reference and considered to have a random orientation. Both samples exhibit a single broad d_{100} reflection in the 2Θ range of 1.8–2.4°, characteristic for the MCM-41 phase [15]. The higher order reflections are barely resolved in the X-ray patterns of coated material and non-coated sample. Weak reflections observed in the 2Θ range from 4° to 6° confirm a long-range hexagonal order. It is important to note the shift of the reflection maximum in the patterns of these two samples. In other words, the coated MCM-41 has a spacing between two reticular plans of 37 Å, which is less than in the bulk MCM-41, being 49 Å. So, the MCM-41 structure appears more compact when formed on the grid than in the bulk solution. Five times less intensity of the (1 0 0) reflection of the MCM-41 coatings as compared to the powder, indicates a lower semi-crystallinity. These results clearly indicate an influence of metal grid on the morphology of a mesoporous layer.

Previous studies on zeolite coatings on metals have demonstrated an influence of the support on the crystals morphology and on the density of the coating film [16,17]. The zeolite coatings had much higher density as compared to the grains formed in the bulk volume due to the preferential growth of crystals from the surface nucleation sites [17]. Mesoporous materials are formed through complementary electrostatic interactions between charged surfactant and inorganic Si-containing species. Under highly basic conditions (pH = 11) used during the MCM-41 synthesis, the metallic support together with the negatively charged OH-groups form a double electric layer in the vicinity of the support. The self-arrangement of the micelles in a two-dimensional scale is affected by this induced electric field reducing the critical diameter of the surfactant micelles. The effect of the electric field on the morphology and orientation of zeolite crystals was already reported in the scientific literature [18]. Therefore, a more compact mesoporous structure with a lower d-spacing between each element and a lower semi-crystallinity is formed on the metallic support as compared to its formation in the bulk solution.

The nitrogen adsorption–desorption isotherms with the PSD calculated on the base of Dollimore/Heal model (inset) are presented in Fig. 2. They are typical for well-defined mesoporous materials. The inflection point in the region of $P/P_0 =$ 0.30–0.45 and the maximum in PSD indicate a uniform pore framework with a diameter of ~30 Å, characteristics of MCM-41.

Fig. 3(a) presents a SEM micrograph of a grid after synthesis of MCM-41 without impregnation
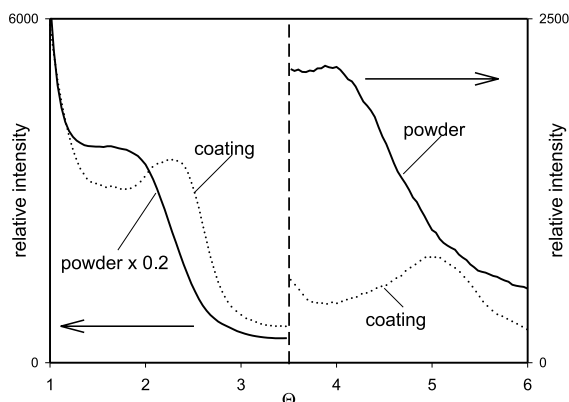

Fig. 1. Powder XRD pattern of coated and unsupported MCM-41 synthesized under the same conditions.
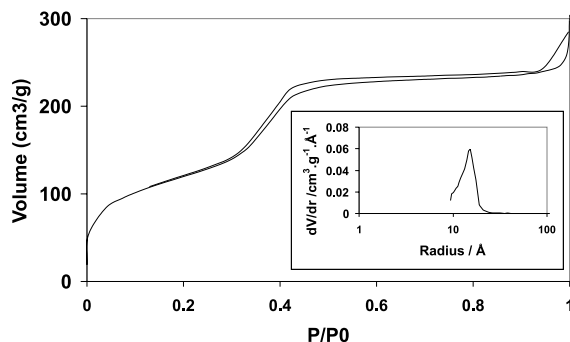

Fig. 2. N$_2$ adsorption–desorption isotherms and pore-size distribution.

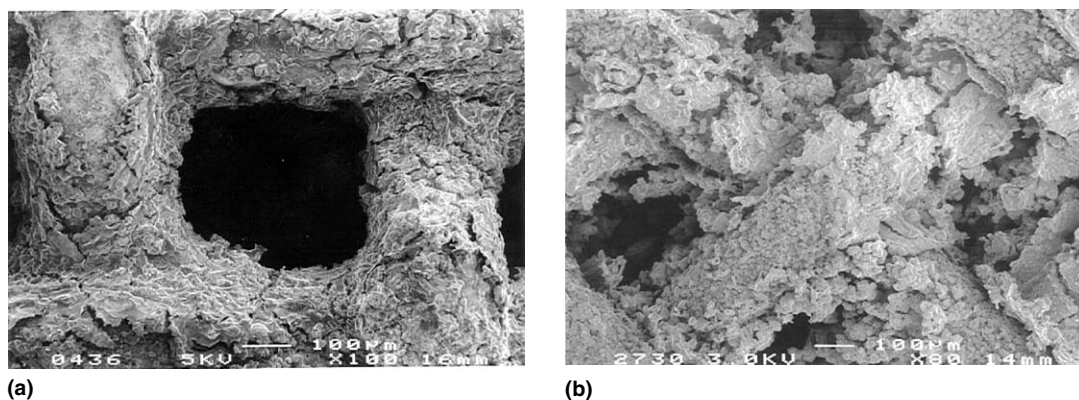**(a)**   **(b)**

Fig. 3. SEM images of Si-MCM-41/grid packings: (a) non treated; (b) pre-impregnated with CTABr.

by CTABr. It is seen that some regions of the support are not covered. On the contrary, a complete coverage by the MCM-41 is seen after the CTABr treatment (Fig. 3(b)) with a layer thickness of 80 μm. Therefore, it can be concluded that such a treatment directs the formation of the mesoporous material on the metal grid. Surfactant molecules contain hydrophilic head and hydrophobic tail. They seem to provide spatial distribution minimizing the interaction with incompatible substrates. Relatively high selectivity (24%) of the coating synthesis suggests an increased affinity of the support for the micelle formation, probably due

to creation of "sticking sites" by the template adsorption on the metal surface.

Fig. 4(a) shows the layer morphology and the uniform size of grains ∼4–5 μm. The ordered structure is clearly seen on HRTEM image presented in Fig. 4(b). The *d*-spacing value is about 37 Å, confirming the value obtained by XRD (Fig. 1). The hexagonal structure, known to be the main characteristic of MCM-41 [1–5], is observed in a suitable orientation of the sample in the electron beam.

Studies are in progress involving the tests of catalytic activity of MCM-41 modified by Al and

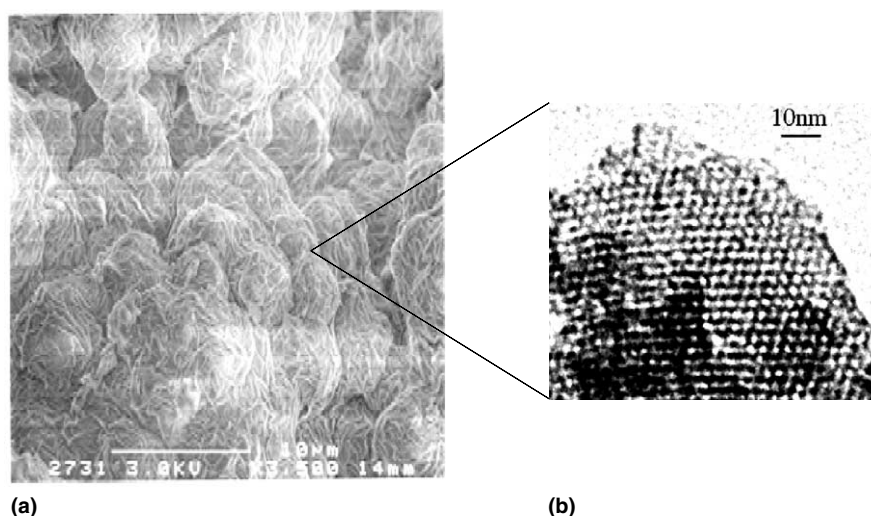**(a)**   **(b)**

Fig. 4. Morphology of the coatings: (a) SEM micrograph and (b) high-resolution TEM image of MCM-41 structure.

transition-metal cations, aiming on active sites modulation.

4. Conclusions

The MCM-41 mesoporous sieves were supported on metal grids via in situ hydrothermal synthesis. After a one-step synthesis, the support is completely covered by a dense layer with a thickness of ∼80 μm. This method opens the route for applications of mesoporous materials in the form of structured catalytic packings.

Acknowledgements

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