

# Synthesis and characterization of mesoporic materials containing highly dispersed cobalt

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## Abstract

Highly dispersed Co particles in MCM-41 were prepared by direct addition of CoCl<sub>2</sub> to the synthesis gel. The small clusters of Co did not sinter during reduction and sulfidation. Incorporation of Co into the MCM-41 lattice was not observed. The addition of Co to the synthesis gel did not alter the structural characteristics of the MCM-41 samples.

*Keywords:* Cobalt; MCM-41; EXAFS; Sulfidation

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## 1. Introduction

Since the introduction of mesoporous materials with an uniform pore structure, designated as M41S by Mobil in 1992 [1,2] the material has received widespread interest because of its potential as catalyst, support, and as host lattice for advanced secondary organic structures like conducting filaments [3]. This high interest reflects the demand for treating heavier feedstocks in the refining industry and the need for large pore catalysts to convert bulky molecules in the production of fine chemicals [4,5].

Most of the work on mesopore molecular sieves has been carried out on the MCM-41 type [6,7]. This structure consists of uniform, hexagonal arrays of mesopores with pore openings between 2 and 10 nm, the size depending on the size of template molecules and the synthesis conditions

applied. All synthesis routes use surfactant molecules as structure directing templates for the meso-phase formation. The length of the hydrocarbon chain determines the diameter of the micellar rods and, thus, the diameter of the resulting mesopore material. Recently, syntheses of such materials with varying concentrations of non-siliceous framework cations like Al [8], Ti [9,10] and V [11] have been reported.

The goal of the present contribution is to describe the preparation of highly dispersed and stable Co clusters in MCM-41 for use as catalysts in hydrotreating reactions. We report a novel way of preparing highly dispersed Co in MCM-41 using a direct synthesis method and compare it to the material obtained by the more conventional solid-state ion exchange method. The characterization of the material by extended X-ray absorption fine structure (EXAFS), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area and benzene sorption, is reported.

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## 2. Experimental

### 2.1. Synthesis

Co/MCM-41 was prepared in analogy to the procedure of Chen et al. [6] and Schmidt et al. [12]. A solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  ( $1 \cdot 10^{-3}$  mol  $\text{l}^{-1}$ ) was added slowly to 20.84 g of waterglass (7.3% NaOH, 16.5%  $\text{SiO}_2$ ) under vigorous stirring. Subsequently, a solution of 0.6 g concentrated  $\text{H}_2\text{SO}_4$  in 8.5 g  $\text{H}_2\text{O}$  was added dropwise whilst continuously stirring. Finally a solution of 8.38 g  $\text{C}_{16}\text{TMABr}$  (hexadecyltrimethylammonium bromide) in 25 g  $\text{H}_2\text{O}$  was added to the synthesis mixture. The gel composition was 10  $\text{SiO}_2$ : 0.17 Co: 3  $\text{Na}_2\text{O}$ : 0.8  $\text{H}_2\text{SO}_4$ : 4  $\text{C}_{16}\text{TMABr}$ : 777  $\text{H}_2\text{O}$ .

The reaction mixture was loaded into a Teflon-lined autoclave with 150 ml volume and statically heated at 373 K for 6 days. The resulting solid products were separated by a centrifuge, washed with water until pH 8 was reached and dried in air at room temperature. The template was removed by heating in nitrogen with a rate of 1  $\text{K min}^{-1}$  to 813 K and maintaining that temperature for one hour. Subsequently, the gas stream was switched to dry air and the sample was kept for 8 h at 813 K.

A siliceous MCM-41 sample and an aluminum containing sample ( $\text{Si}/\text{Al}=100$ ) were prepared applying the same synthesis procedure without adding  $\text{CoCl}_2$ .

Co was incorporated into the Al containing MCM-41 sample by solid-state ion exchange, carried out by grinding the sample together with  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and heating the mixture in He to 811 K (heating rate 2  $\text{K min}^{-1}$ ) for 8 h. After the ion-exchange reaction the material was washed repeatedly with water until anions could no longer be detected in the solution and dried subsequently at 373 K.

### 2.2. Characterization

After synthesis, the structure of the materials was characterized by XRD. The surface area of the samples was calculated from a  $\text{N}_2$  isotherm applying the BET theory.

After activating the samples in vacuum at 773

K for 60 min, the sorption capacity of benzene was determined at 293 K using a CAHN microbalance.

X-Ray absorption spectra were measured at the ESRF in Grenoble at beamline D8 (GILDA) from the calcined sample, after reduction in  $\text{H}_2$  at 673 K for 45 min and after sulfidation in  $\text{H}_2\text{S}$  (5% in  $\text{H}_2$ ) at 673 K for 15 min. To optimize the signal-to-noise ratio, the weight of the samples was selected to achieve an absorption of less than  $\mu x = 2.0$  at the Co-K edge for the reduced catalyst [13]. The energy of the absorption edge was aligned to that of a bulk Co foil. The analysis was carried out using standard analysis procedures as described, e.g., in Ref. [13]. This included a polynomial baseline approximation, the isolation of the coordination shells by Fourier transformation and a determination of the structural parameters of the coordination shells under the assumption of single scattering and plane waves. The phase shift and amplitude functions for Co-Co and Co-O were obtained from experimental data of Co reference compounds, those of Co-S were calculated applying the FEFF theory [14] using the programs supplied in the 'Catalysis and Sorption Project' from Biosym Inc. [15]

## 3. Results and discussion

The XRD patterns of Co/MCM-41 and pure MCM-41 are shown in Fig. 1. Two reflexes were observed for both samples, which are similar to those reported previously for siliceous MCM-41 [2,16]. The BET surface area of the Co/MCM-41 sample was  $1010 \text{ m}^2 \text{ g}^{-1}$ , that of the MCM-41 sample  $1090 \text{ m}^2 \text{ g}^{-1}$ .

The benzene sorption capacities of Co/MCM-41 and of MCM-41 are presented in Fig. 2. The maximum benzene sorption capacity was  $575 \text{ mg g}^{-1}$  for MCM-41 and  $550 \text{ mg g}^{-1}$  for Co/MCM-41, respectively. The sorption capacity of the present samples is therefore slightly below the value of  $640 \text{ mg g}^{-1}$  reported in Ref. [2]. The Co-containing sample has a slightly smaller pore volume, which indicates that some extra-lattice material is present within the mesoporous structure of Co/MCM-41 after synthesis.

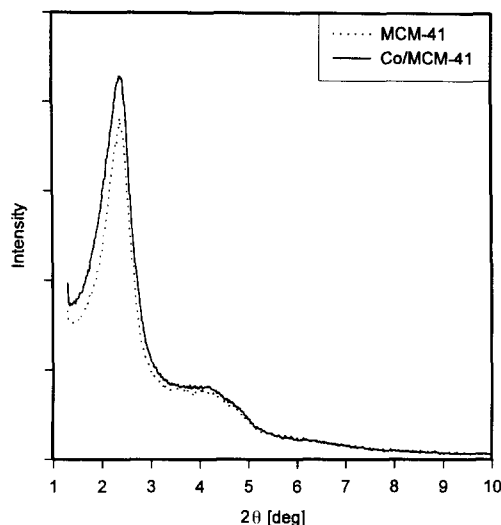


Fig. 1. XRD patterns of Co/MCM-41 and MCM-41.

To determine, if the Co atoms were located inside the walls of the mesopore structure or exist as a separate phase inside the mesopores, X-ray absorption spectra were collected from the Co/MCM-41 sample. To evaluate the efficiency of Co incorporation by synthesis, the distribution of Co in a sample prepared by solid-state ion exchange, was investigated in parallel. The results of the EXAFS analysis are given in Table 1, the Fourier transformed EXAFS of the oxidic and

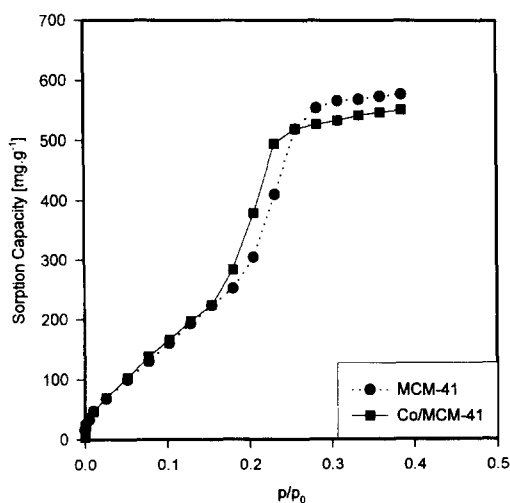


Fig. 2. Benzene sorption isotherms of Co/MCM-41 and MCM-41 at 298 K.

reduced samples are shown in Fig. 3 and Fig. 4, respectively.

In the calcined, directly synthesized Co/MCM-41 sample, the Co atoms were surrounded by oxygen atoms ( $N_{\text{Co-O}} = 3.6$ ) in the first and by Co atoms ( $N_{\text{Co-Co}} = 5.7$ ) in the second coordination shell. This indicates, that the Co atoms are not incorporated in tetrahedral lattice positions, as in this case only Co–O neighbors would have been observed. Due to the presence of a Co–Co coordination, we conclude that the main part of Co is present as small Co oxide particles. The size of these oxidic clusters is about 5 to 6 Co atoms, as determined from the Co–O and Co–Co coordination numbers by an atomistic simulation study [17]. After reduction in  $\text{H}_2$  at 673 K for 45 min, only Co neighbours ( $N_{\text{Co-Co}} = 4.5$ ) were observed. This coordination number corresponds to an average particle size of about 6 Co atoms, assuming cuboctahedral particle shape [18]. After sulfidation Co–S neighbors were observed ( $N_{\text{Co-S}} = 2.3$ ), while Co–Co neighbors were still present ( $N_{\text{Co-Co}} = 1.4$ ), but shifted to larger distances compared to the reduced material. Estimated from the Co–S and the Co–Co coordination numbers, the sulfided clusters consist in average of 4 to 5 Co atoms [17]. Although we obtained a smaller size for the CoS clusters, compared with the oxidic and the reduced ones, we do not attribute this to a redispersion of the particles, but rather to the limitations of the particle size determination of very small clusters from the EXAFS data [19,20]. However, these low coordination numbers indicate that by Co incorporation during synthesis small, uniform clusters were formed in MCM-41.

During the reduction and especially during the sulfidation, the particle size did not increase due to sintering or migration. The high dispersion and the structural stability during reduction and sulfidation indicate that the particles are spatially well separated and structurally stabilized within the mesoporous lattice.

For the sample prepared by solid-state ion exchange much higher Co–O and Co–Co coordination numbers were observed indicating that relatively large oxidic clusters were created during the postsynthetic Co incorporation. The reduction

Table 1  
Results of the EXAFS analysis

Sample	Co–O coordination			Co–S coordination			Co–Co coordination		
	<i>N</i>	<i>r</i> (Å)	$\Delta\sigma^2$ (Å <sup>2</sup> )	<i>N</i>	<i>r</i> (Å)	$\Delta\sigma^2$ (Å <sup>2</sup> )	<i>N</i>	<i>r</i> (Å)	$\Delta\sigma^2$ (Å <sup>2</sup> )
Co/MCM-41 (syn) precursor	3.6	1.97	$1 \cdot 10^{-4}$				5.7	3.33	$2 \cdot 10^{-4}$
Co/MCM-41 (syn) reduced							4.5	2.57	$1 \cdot 10^{-3}$
Co/MCM-41 (syn) sulfided				2.3	2.26	$5 \cdot 10^{-3}$	1.4	3.13	$3 \cdot 10^{-3}$
Co/MCM-41 (exch) precursor	6.0	1.95	$2 \cdot 10^{-3}$						
Co/MCM-41 (exch) reduced							8.4	2.55	$1 \cdot 10^{-3}$

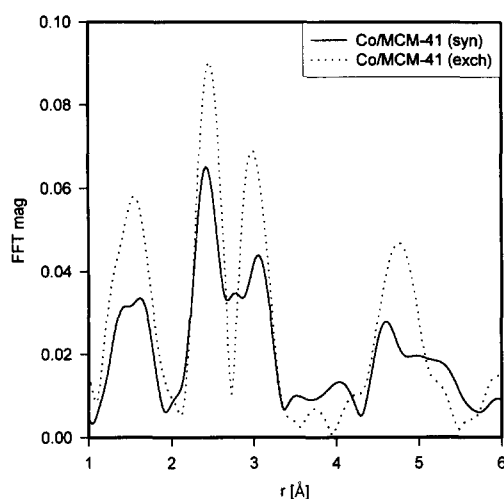


Fig. 3. Fourier transformed EXAFS of the oxidic Co/MCM-41 (syn) and Co/MCM-41 (exch) samples.

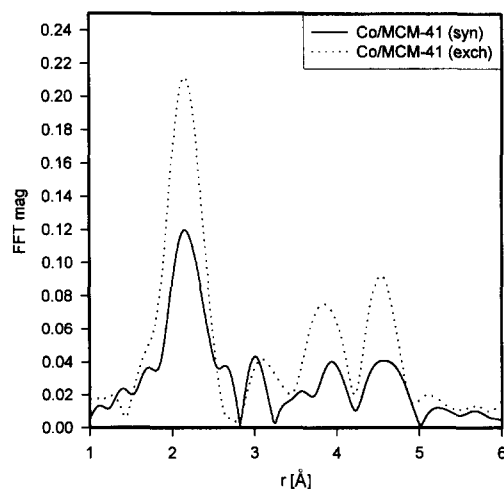


Fig. 4. Fourier transformed EXAFS of the reduced Co/MCM-41 (syn) and Co/MCM-41 (exch) samples.

leads to a Co/MCM-41 sample with significantly larger particles (ca. 50 atoms) than found with the directly synthesized material. Note, that for CoZSM-5 samples, prepared under identical conditions, we did not observe this difference between the solid-state ion exchange preparation and the direct synthesis route [21].

In Co/MCM-41, prepared by the new method, the interaction of Co with the lattice is much stronger than in solid-state ion exchanged samples. Furthermore, it seems that by ion exchange in mesoporous materials, large ionic clusters are easily formed inside the channel system of MCM-41. The formation of such large clusters is sterically restricted in microporous zeolites like ZSM-5 and the procedure leads to much smaller particle sizes in these materials.

#### 4. Conclusions

Co/MCM-41 synthesized by adding a Co salt to the synthesis gel, resulted in the formation of finely dispersed small Co oxide clusters within the pore structure. The pore volume and the surface area of this material were slightly smaller compared to MCM-41 indicating that indeed Co is placed inside the pores. During reduction in H<sub>2</sub> at 673 K and sulfidation in H<sub>2</sub>S/H<sub>2</sub> at 673 K the initial particle size of about 5 to 6 Co atoms did not increase. This indicates, that the Co clusters retain their size for a longer period of time on stream within the MCM-41 channels. The reason for this high stability of the Co clusters in MCM-41 lies in the strong interaction of Co with the lattice. We should like to speculate that this strong inter-

action is related to the formation of more covalent bonds between Co and the mesoporous material than it can be generated by ion exchange.

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