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Structure of Co and Co oxide clusters in MCM-41

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Abstract

The structural properties of Co/MCM-41 with pore diameters between 2.9 and 3.6 nm prepared by direct synthesis and impregnation were investigated. For both preparation methods, the size of the metal particles decreased with the pore diameter. For Co/MCM-41 with the same pore diameter we observed that the direct synthesis method led to significantly smaller metal clusters compared to the impregnation method. For all Co/MCM-41 samples constraints of the metal cluster sizes were observed, which are speculated to result from influences of the micro structure during the formation of the catalyst precursor. © 1998 Elsevier Science B.V.

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1. Introduction

Mesoporous molecular sieves of the MCM-41 type received widespread attention because of their potential use as catalysts and support for small, catalytically active metal and metal oxide clusters [1,2]. MCM-41 consists of well-defined hexagonal arrays of uniform mesopores with a diameter between 2 and 10 nm, which can be controlled by varying the alkane chain of the template molecules during synthesis [3,4].

The incorporation of small metal (oxide) clusters into molecular sieves may lead to catalysts, in which the properties of metals are synergetically linked to the shape selectivity of molecular sieves. The use of mesoporous molecular sieves extends the range of applicable shape selective supports from that of microporous molecular sieves (0.4–1.5 nm) to about 10 nm. Purely siliceous MCM-41 catalysts did not show any considerable activity, however, the incorporation of non-siliceous elements, such as Al [5,6], Ti [7,8], V [9], Pt [10] and Co [11], allows the application of MCM-41 based catalysts in alkylation [12,13], oxidation [10,14] and hydrotreating reactions [15,16].

The goal of this communication is to describe the structural properties of highly dispersed Co and Co oxide clusters in MCM-41 as a function of the pore diameter of the support and of the preparation method.

2. Experimental

2.1. Materials

Co/MCM-41 samples were prepared in analogy to the procedure described by Chen et al. [17] and Schmidt et al. [18] by adding $CoCl_2 \cdot 6H_2O$ to the synthesis gel. Hexadecyltrimethylammoniumbromide (C_{16}TMABr) and dodecyltrimethylammoniumbro-

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mide (C_{12}TMABr) were used as templates. The template was removed by heating the sample in nitrogen to 813 K (heating rate 1 K min^{-1}) and maintaining it at that temperature during 1 h in nitrogen and subsequently during 8 h in dry air. Details on the preparation and the structural properties of Co/MCM-41(C_{16}) prepared by the direct synthesis method were previously described in [11].

Siliceous MCM-41 samples were prepared following the procedure for synthesis and template removal as described above. Cobalt was incorporated into these samples by impregnation with $Co(NO_3)_2 \cdot 6H_2O$ using the incipient wetness technique.

In order to evaluate the role of the mesoporous support, an amorphous Co/SiO_2 sample was prepared by incipient wetness impregnation of Aerosil 200. The metal concentration of the Co/MCM-41 and Co/SiO_2 samples were 1 and 2.3 wt%, respectively.

2.2. *Characterization*

After synthesis, the structure and pore size of the mesoporous molecular sieves were verified by XRD. The BET surface area was determined from N_2 adsorption isotherms.

X-ray absorption spectra were measured at the SRS (Synchrotron Radiation Source, Daresbury, UK) at station 8.1. The samples were prepared as self-supporting wavers and placed inside a cell which allows X-ray absorption spectra to be measured in situ during the sample pretreatment. The weight of the samples was selected to achieve a total absorption of $\mu x \approx 2.0$ [19]. The samples were reduced in flowing H_2 at 673 K for 30 min using a temperature increment of 20 K min^{-1} and measured at liquid nitrogen temperature.

EXAFS analysis was carried out using standard analysis procedures as described, e.g. in [19]. The background was removed using a polynomial baseline and the contributions of the first coordination shell were isolated by a Fourier transformation of the k^2-weighted oscillations in the range k=3–18 Å^{-1}. The structural parameters were determined under the assumption of single scattering and plane waves applying phaseshift and amplitude functions obtained from experimental data of Co reference compounds, i.e. bulk Co foil, CoO and Co_3O_4.

3. Results and discussion

X-ray diffraction patterns of the MCM-41 samples showed the reflections usually observed for siliceous MCM-41 [2,3]. The pore diameters, calculated from the (1 0 0) reflection of the XRD, were 3.7 and 2.8 nm for MCM-41 synthesized with C_{16}TMABr and C_{12}TMABr, respectively. The BET surface areas were 1300 $m^2 g^{-1}$ for MCM-41(C_{16}) and 1560 $m^2 g^{-1}$ for MCM-41(C_{12}).

The results of the EXAFS analysis of the samples after calcination in He at 673 K and after reduction in H_2 at 673 K are given in Tables 1 and Table 2, the Fourier transformed EXAFS of the precursors and the reduced Co/MCM-41 samples are shown in Figs. 1 and 2. The average number of Co atoms per cluster and its diameter were estimated from the average coordination number of the first Co-Co coordination shell ($N_{\text{Co-Co}}$) using the assumption of a cuboctahedral particle shape [20].

Reduction, independent of the preparation method, led to a lower average coordination number for the nearest neighbors of Co/MCM-41(C_{12}) compared to Co/MCM-41(C_{16}). The average coordination number $N_{\text{Co-Co}}$ increased from 3.4 to 4.5 and from 4.0 to 7.9 for the samples prepared by direct synthesis and impregnation, respectively. This clearly indicates the formation of larger Co clusters on the MCM-41 samples with the bigger pore diameter. For Co/MCM-41 with the same pore diameter, incorporation during synthesis led to smaller metal clusters compared to the incipient wetness impregnation. Significantly larger Co clusters were present on the Co/SiO_2 sample compared to all Co/MCM-41 samples investigated. After reduction, mainly Co-Co contributions were observed for the Co/MCM-41 samples, which indicated the reduction of the metal. However, the appearance of a shoulder in the Fourier transformed EXAFS

Table 1
Results of the EXAFS analysis after preparation and removal of the template

Sample (Co-O contributions)	$N_{\text{Co-O}}$	$r_{\text{Co-O}}$ (Å)	$\Delta\sigma^2_{\text{Co-O}}$ (Å^2)
CoMCM41(C_{12})$_{\text{synthesis}}$	4.1	1.98	1×10^{-3}
CoMCM41(C_{16})$_{\text{synthesis}}$	3.6	1.97	4×10^{-4}
CoMCM41(C_{12})$_{\text{impregnation}}$	4.2	1.99	3×10^{-3}
CoMCM41(C_{16})$_{\text{impregnation}}$	6.0	1.96	1×10^{-3}

Table 2
Results of the EXAFS analysis of the reduced Co/MCM-41 samples

Sample (Co-Co contributions)	$N_{Co\text{-}Co}$	$r_{Co\text{-}Co}$ (Å)	$\Delta\sigma^2_{Co\text{-}Co}$ (Å^2)	Average number of Co atoms per particle
CoMCM41$(C_{12})_{synthesis}$	3.4	2.56	6×10^{-4}	4
CoMCM41$(C_{16})_{synthesis}$	4.5	2.57	1×10^{-3}	7
CoMCM41$(C_{12})_{impregnation}$	4.0	2.57	2×10^{-3}	6
CoMCM41$(C_{16})_{impregnation}$	7.9	2.55	1×10^{-3}	45
Co/SiO$_2$ $_{impregnation}$	10.6	2.57	2×10^{-3}	~2000

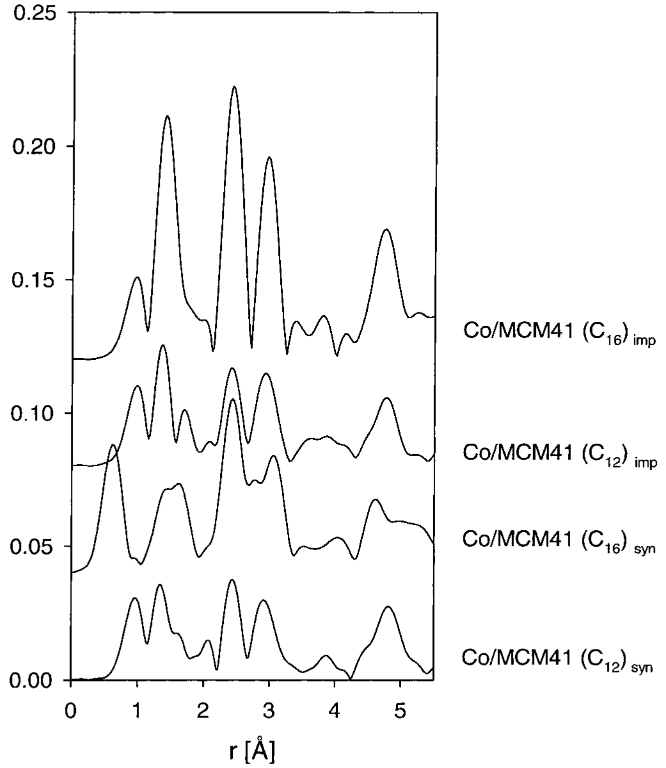

Fig. 1. Fourier transformed EXAFS after preparation and removal of the template of Co/MCM-41.

at distances below $r_{Co\text{-}Co}$ implied the presence of Co-O neighbors, which might result from oxygen atoms of the mesoporous support or from the presence of residual unreduced species. Note that these contributions were more pronounced on the synthesized samples, which can be an indication that the Co species were located inside the amorphous walls and therefore, were more difficult to reduce compared to the Co oxide clusters present after impregnation.

It can be clearly observed that all metal clusters incorporated into MCM-41 were significantly smaller than the pore diameter of the support. Even the largest Co clusters, i.e. those prepared by impregnation on MCM-41(C_{16}) with a diameter around 1.3 nm, were much smaller than the pore diameter of the enclosing molecular sieve (3.7 nm). Note that the assumption of a cuboctahedral particle shape underestimates the number of atoms per cluster for small, strongly

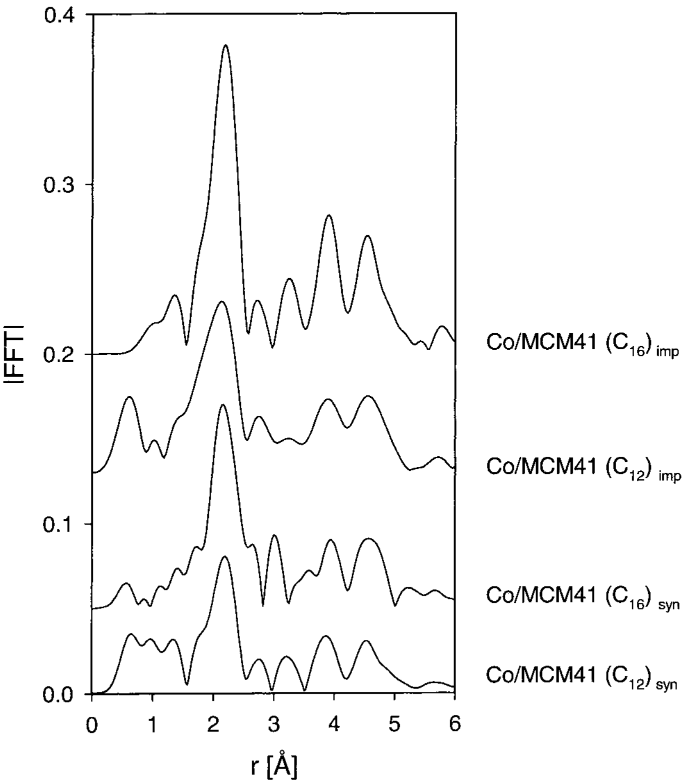

Fig. 2. Fourier transformed EXAFS after reduction of Co/MCM-41.

deformed supported clusters by approximately 15% [21].

The question arises, if the particle size is largely predetermined by limitations of the size of the precursor of the final material. Indeed, unreduced Co/MCM-41(C_{16}) samples prepared by impregnation exhibited higher average coordination numbers for the first neighbors ($N_{\mathrm{Co\text{-}O}}$) compared to Co/MCM-41(C_{12}), indicating the presence of larger Co oxide clusters. Note that coordination numbers between Co and the nearest oxygen neighbors close to 4 could alternatively indicate a partial incorporation of single Co atoms into the walls of MCM-41. However, the additionally observed Co-Co and Co-O contributions at larger distances (see Fig. 1) clearly reveal that mainly small Co oxide clusters were present after preparation and removal of the template.

The smaller size of the reduced Co clusters in Co/MCM-41(C_{12}) compared to Co/MCM-41(C_{16}) and the formation of significantly larger Co clusters on SiO_2 indicate that the structural properties of MCM-41 strongly influence the formation of the Co clusters. We speculate that these structural restrictions already occur during the precursor formation, because the diameters of the reduced metal clusters were always smaller than the pore diameter of the support. For samples prepared by impregnation we expect that the larger amount of $Co(NO_3)_2$ solution, retained after the impregnation inside the pores of MCM-41(C_{16}), led to a higher concentration of the precursor complexes which resulted in the increased particle size. Additionally, the high surface area of the MCM-41 samples, compared with other supports, will further favor the formation of highly dispersed metal particles.

For the samples prepared by adding the Co source during synthesis we observed that the effect of the pore diameter on the particle size was less pronounced. We would like to speculate that during synthesis small Co oxide clusters were formed on the interface between the template and the silicate precursor of MCM-41. Note that their presence was confirmed by the occurrence of well-defined Co-O and Co-Co contributions in the EXAFS of the catalyst precursors, which would be absent if Co would have been finely dispersed in the synthesis gel. After removal of the template small Co oxide domains remained which might be partially incorporated into the amorphous walls of MCM-41. However, the reduction of Co indicates that all Co oxide species were accessible for H_2.

The reason for the stabilization of highly dispersed Co clusters in MCM-41 during calcination and reduction might lie in the strong interaction between the metallic particles and the molecular sieve. The metallic clusters might be able to form spatially restricted domains within the amorphous walls which will further enhance the interaction between cluster and support. Note that simulation studies of the structural and energetic properties of Co oxide clusters in molecular sieves showed that such interactions are always energetically favorable [22].

4. Conclusions

The size of the MCM-41 pores strongly influences the structural properties of the incorporated Co clusters. For Co/MCM-41 samples prepared with the same method, the Co particles were larger on the support with the bigger pores. For Co/MCM-41 samples with the same pore diameter, the preparation by adding $CoCl_2$ into the synthesis gel resulted in the formation of finely dispersed small Co oxide clusters, while impregnation methods led to somewhat larger metallic particles. Structural restrictions of the mesoporous molecular sieve on the particle morphology occur and we expect them to be already present after the precursor formation. The reason for the stabilization of the small Co clusters in MCM-41 might lie in the strong interaction of the Co clusters with the amorphous lattice. For samples prepared by direct synthesis we would like to speculate that small Co oxide domains within the amorphous walls were present after the synthesis and that after reduction the metallic clusters form local domains within the walls of MCM-41.

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