Synthesis and redox properties of MCM-48 containing copper and zinc

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MCM-48 materials, synthesized for the first time in the presence of copper and zinc salts, show remarkable redox properties in contrast to materials prepared by ion-exchange or impregnation.

Since their rediscovery (as we learned recently[1] these materials were discovered more than 25 years ago) by researchers of the Mobil Oil Company in 1992[2,3] ordered mesoporous materials (denoted as M41S) have initiated intensive research resulting in an overwhelming number of publications. However, most studies have dealt with the hexagonal form, MCM-41.[4,5] MCM-48, the cubic member (space group $Ia\bar{3}d$) of the M41S family was investigated only in a limited number of studies.[6–9] The third member of the M41S family, MCM-50, is an unstable lamellar phase.[2,3]

The incorporation of transition metal ions into micro- or meso-porous molecular sieves is of considerable interest for catalytic applications. For MCM-48 to be useful with respect to catalytic applications, metal ions have to be incorporated into the amorphous walls. Attempts on the incorporation of Al, Mn, V, Ti and Cr have been reported so far.[11–14] Temperature programmed reduction (TPR) is a useful tool for collecting information on the redox properties of transition metal ions in zeolites and other porous supports.

The present work describes the first redox-type MCM-48 material containing copper and zinc introduced during the synthesis of the material. Temperature programmed reduction experiments of the calcined material show the availability of copper for redox reactions.

The MCM-48 materials were synthesized using cetyltrimethylammonium bromide (CTAB), tetraethylorthosilicate (TEOS) and NaOH. A gel with a molar composition of 0.61 CTAB : 1 SiO_2 : 0.25 Na_2O : 61 H_2O was prepared and different amounts of $Cu(MeCO_2)_2 \cdot H_2O$ and $ZnSO_4 \cdot 2H_2O$ were added. The resultant gel was loaded into autoclaves and heated to 373 K for 72 h. After synthesis the materials were recovered by filtration, washed with water and ethanol and finally calcined in flowing nitrogen up to 200 °C and in flowing air up to 540 °C for 18 h. For comparison, copper containing MCM-48 samples have been prepared by ion-exchange and impregnation, using standard procedures. The resulting materials were characterized by powder X-ray diffraction (XRD), atomic absorption spectroscopy, nitrogen adsorption and desorption (at 77 K) and temperature programmed reduction (TPR). The TPR measurements were performed in an Altamira AM1 instrument with a flow of 10 vol.% H_2 in Ar. A heating rate of 3 K min^{-1} was chosen to enhance resolution and avoid 'hot spots'. Prior to the first reduction experiment, the samples were activated in a helium flow containing 10 vol.% O_2 up to a maximum temperature of 400 °C at a rate of 5 K min^{-1}.

The powder X-ray diffraction patterns of the calcined CuMCM-48, CuZnMCM-48 and ZnMCM-48 materials are presented in Fig. 1 and correspond well with those reported for pure siliceous MCM-48. XRD studies reveal that MCM-48 materials can be synthesized in the presence of copper and zinc salts. While the addition of copper acetate to the synthesis gel up a ratio $n_{Si}/n_{Cu} = 15$ has no influence on the quality of the XRD pattern, the ZnMCM-48 materials show XRD patterns with somewhat lower intensity. Assuming cubic symmetry, the unit cell size of the calcined materials was calculated to be 9.36 nm for CuMCM-48, 9.31 nm for CuZnMCM-48 and 8.45 nm for ZnMCM-48 (Table 1).

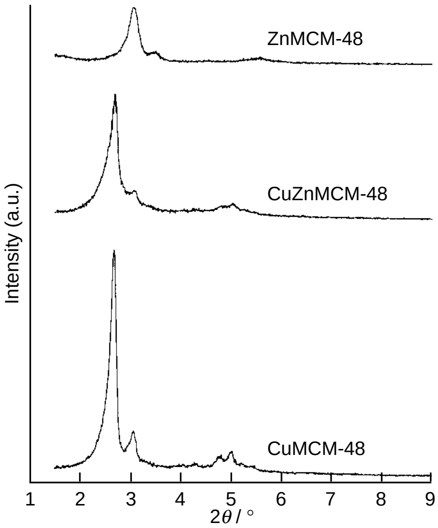

Fig. 1 X-Ray diffraction pattern of as-synthesized CuMCM-48, CuZnMCM-48 and ZnMCM-48

The N_2 isotherms (Fig. 2) show no hysteresis in all samples under investigation. The surface area of the transition metal ion containing materials is reduced in comparison to the pure siliceous material. The surface areas and pore diameters were calculated from the nitrogen adsorption–desorption isotherms using BET and BJH analysis. The results of these calculations and the chemical analysis are collected in Table 1. The molar silicon/metal ratios of the starting gel were $n_{Si}/n_{Me} = 80$ leading to a reduced ratio in the calcined materials.

In agreement with the XRD powder pattern the nitrogen adsorption is largely reduced in ZnMCM-48 with $n_{Si}/n_{Zn} = 80$, while copper introduction does not affect the adsorption capacity. Similar findings were reported on AlMCM-41 materials,[15] showing that the mechanism of copper and zinc introduction might be significantly different. While co-precipitation of $Cu(OH)_2$ or complexation of Cu^{2+} by the surfactant under the basic conditions of the synthesis prevent encapsulation of copper into the amorphous walls, Zn can be expected to be in the walls of MCM-48 as claimed in the Mobil patent.[16] The copper species can be removed by washing of the as-

Table 1 Properties of the samples under investigation

Sample	$n_{Si}/$ $n_{(Cu+Zn)}$	n_{Cu}/n_{Zn}	a_0/nm	A_{BET}/ $m^2\ g^{-1}$	$d_p{}^a$/nm
MCM-48	—	—	8.33	1400	2.4
CuMCM-48	35.8	—	9.36	1136	2.3
CuZnMCM-48	48.5	1.4	9.31	1059	2.3
ZnMCM-48	53.2	—	8.45	925	1.9

[a] The pore diameters were calculated from the desorption branch of the adsorption isotherm using the BJH model.

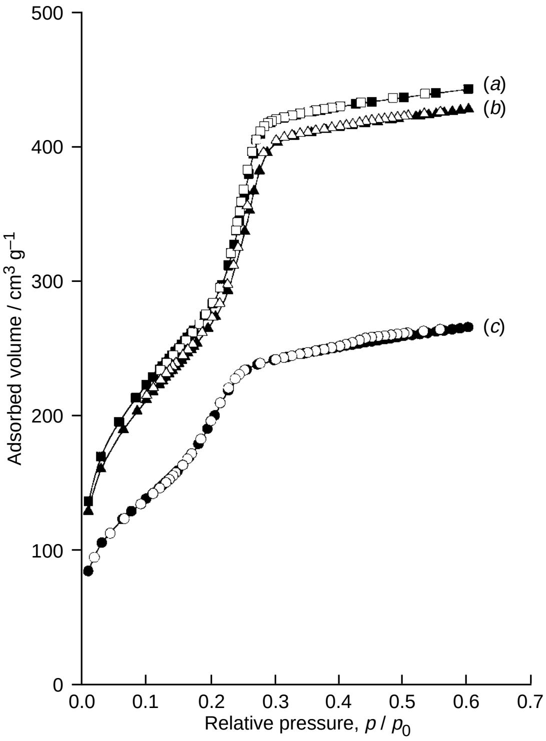

Fig. 2 Nitrogen adsorption (closed symbols) and desorption (open symbols) at 77.3 K of (*a*) CuMCM-48, (*b*) CuZnMCM-48 and (*c*) ZnMCM-48

synthesized samples with 0.1 M HCl solution at 80 °C and are therefore most likely located within the channels. Complexation of copper by the surfactant has been established by EPR spectroscopy.[17]

The TPR profiles of CuMCM-48 and CuZnMCM-48 are displayed in Fig. 3. The sharp maximum of hydrogen consumption at 164 °C is accompanied by a shoulder at 184 °C (CuMCM-48). Temperatures in this range can be associated with the reduction of finely dispersed CuO to copper metal in the channels of MCM-48. The copper oxide is formed during calcination and/or sample pretreatment along with a color change from blue to brown. After the TPR experiment the sample exhibits a gray–red color, which is typical for copper metal clusters. The structural integrity of the sample has been checked by XRD and N_2 adsorption. The complete reduction of CuO dispersed on MCM-48 can be achieved at a substantial lower temperature than on γ-Al_2O_3 (210 °C)[18] or SiO_2 (350 °C).[19] Copper impregnated (Fig. 3) or ion-exchanged MCM-48 (not shown) do not exhibit a sharp signal in this temperature range. The reduction of CuO diluted with SiO_2 can be observed at 220 °C.

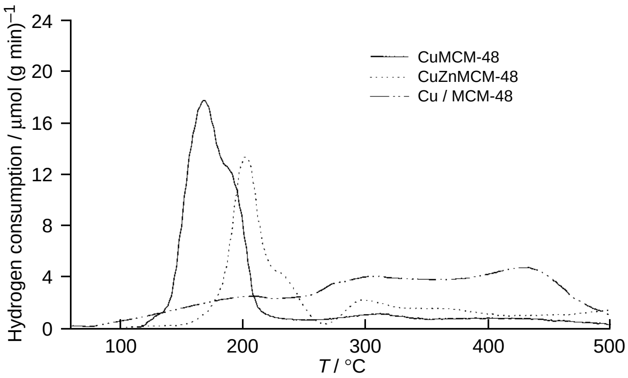

Fig. 3 TPR profiles of CuMCM-48, CuZnMCM-48 and Cu/MCM-48

CuZnMCM-48 exhibits a somewhat different TPR profile. In comparison with the TPR profile of CuMCM-48 the reduction occurs at a significantly higher temperature (197 °C), but the halfwidth of the peak and the degree of reduction are remarkably reduced. The delay in copper reduction owing to the presence of zinc has been well observed in zeolites and CuO/ZnO catalysts.[20] The synergistic effect of zinc in reduction of copper is exploited for the commercial methanol catalyst (CuO/ZnO/Al_2O_3)[21] and has been shown for the first time to be effective in the M41S class of materials, with copper and zinc introduced *via* synthesis. The low reduction temperatures in the MCM-48 materials compared to silica might be associated with the size of the copper oxide particles. Smaller CuO particles are expected to be reduced at lower temperatures. This finding is further substantiated by an increase in reduction temperature with repeated redox cycles leading to agglomeration of smaller particles.[22]

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Footnote and References

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