

Speciation and Distribution of Copper and Zinc in MCM-41

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A family of mesoporous silicate and aluminosilicate molecular sieves, designated as M41S was first synthesized by Mobil's scientists in 1992. M41S including MCM-41 (hexagonal), MCM-48 (cubic) and MCM-50 (laminar) synthesized with liquid crystal templates possesses a well-order array of structure. MCM-41 has attracted much attention due to its high thermal stability (up to 1300 K), high surface areas (500-1500 m²/g), and an array of tubular channels of a uniform diameter (adjustable at 15-200 Å). Functional groups such as thiol (-SH), amine (-NH₂), pyridine and imidazole are generally grafted to modify surface characteristics of MCM-41. For instance, trace toxic metals in wastewater can be adsorbed with a high selectivity and effectiveness on a SH-surface modified MCM-41. However, chemical structure of nanosized metals adsorbed on the surfaces of MCM-41 still lacks in the literature.

The XRD patterns of the calcined CuO-ZnO/MCM-41-SH at 573-1173 K are shown in Fig. 1. Mainly CuO was found in the channels of MCM-41-SH after calcination at 923 K. At 1173 K, CuO and Zn₂SiO₄ were observed. However, nanosize (<26 nm) CuO and ZnO as well as adsorbed copper or zinc may not be observed by XRD.

To further study chemical structural changes of copper and zinc in the channels of MCM-41-SH after calcination treatments, their XANES and EXAFS spectra were also determined. In Figs. 2(a)-(d), the pre-edge XANES spectra of copper in the MCM-41-SH exhibited 1s-to-4p_z and 1s-to-4p_{x,y} transitions at 8985-8988 and 8994-9002 eV, respectively, which indicated the existence of the CuO. The main copper compound in the channels of MCM-41-SH was Cu-O_(ads) (97%) prior calcination (see Fig. 2(a)). In Fig. 2(b), a small amount of Cu-Zn alloys was found in MCM-41-SH at the calcination temperature of 573 K. At higher temperatures (923-1173 K), nanosize CuO in MCM-41-SH was observed. Note that about 15% of nanosize CuO in the channels of MCM-41-SH was aggregated at 1173 K.

In Figs. 2(e)-(g), the white line feature at 9667 eV is normally attributed to electronic transition of 1s-to-4p. The major zinc compounds in the channels of the MCM-41-SH were Zn-O_(ads) (92%) and Zn-S_(ads) (8%). Note that fractions of copper and zinc in MCM-41-SH were 4.1 and 4.8%, respectively. At 573 K, Cu-Zn alloys in channels of MCM-41-SH are also observed (see Fig. 2(f)). Interactions between ZnO and amorphous SiO₂ (wall of MCM-41-SH) might occur in MCM-41-SH.

Although mainly ZnO and a small amount of Cu-Zn alloy are observed in MCM-41-SH at the calcination temperature of 573 K, as shown in Fig. 3, the Zn/Cu ratio is decreased. In Fig. 3, at the step I (T<573 K), about 23% of nanosize metallic zinc in MCM-41-SH may be formed and subsequently evaporated. At 573-923 K (step

II), mainly nanosize CuO is observed while 51% of zinc interact with the amorphous SiO₂ and form Zn₂SiO₄. At the step III (923-1173 K), nanosize metallic copper may be formed possibly via the self-reduction processes. Metallic copper may be evaporated at 1173 K.

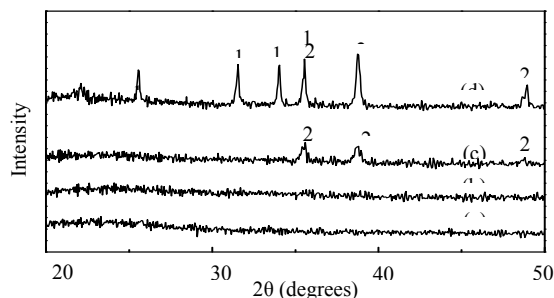


Fig. 1. XRD patterns of (a) dried (at 383 K for 16 hours) and calcined (at (b) 573, (c) 923, and (d) 1173 K for two hours) CuO-ZnO/MCM-41-SH. (1: Zn₂SiO₄; 2: CuO)

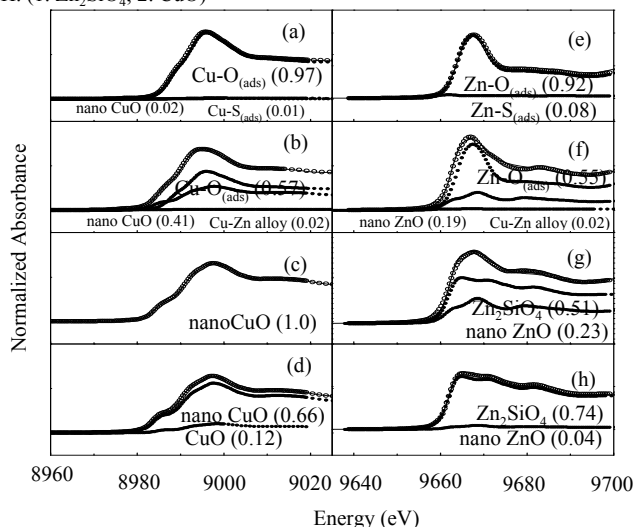


Fig. 2. Experimental data (solid line) and the least-squares fits (circles) of XANES spectra of copper in (a) dried and calcined (at (b) 573, (c) 923, and (d) 1173 K) CuO-ZnO/MCM-41-SH and zinc in (e) dried and calcined CuO-ZnO/MCM-41-SH at (f) 573, (g) 923, and (h) 1173 K.

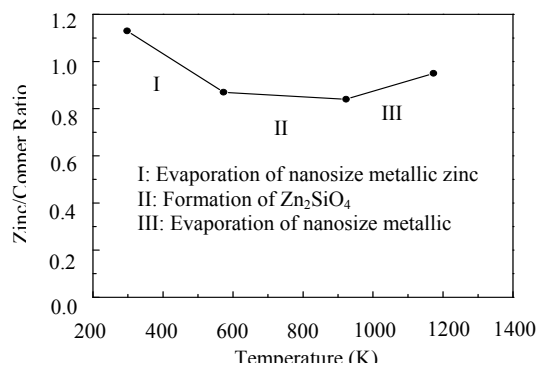


Fig. 3. Temperature dependence for the Zn/Cu ratio in the channels of MCM-41-SH and the possible reaction path during calcination at 573-1173 K for two hours.

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