Speciation of CuO in MCM-41 during oxidation of naphthalene

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Accepted 11 October 2005

Abstract

By extended X-ray absorption fine structural (EXAFS) spectroscopy, copper oxide clusters with a square-plane structure are found in the channels of mesoporous molecular sieve MCM-41. Bond distances of Cu–O and Cu–Cu are 1.90 and 2.80 Å, respectively. Oxidation of naphthalene at 723 K for 4 h in MCM-41 leads to structural perturbation of the clusters (e.g., Cu–O: +0.02 Å and Cu–Cu: +0.02 Å) with little change in their coordination numbers.

Keywords: EXAFS; Copper oxide; Cluster; MCM-41

1. Introduction

In general, incineration of wastes can have a desired destruction and removal efficiency (DRE). However, trace carcinogenic by-products such as polycyclic aromatic hydrocarbons (PAHs), dioxins, and furans are frequently detected in the emission stream. Many PAHs (2–6 fused benzene rings) have been recognized as toxic and suspected carcinogens. From the viewpoint of the environment, it is essential to achieve complete destruction and removal of environmentally hazardous compounds with a minimal release of toxic by-products. Catalytic incineration has been considered as an effective method for emission controls of toxic species (Junges et al., 1995). Molecular sieves, mainly due to their unique pore structures, have produce excellent shape selectivities for the products or by-products in the catalytic reactions. MCM-41 is a silicate molecular sieve with a hexagonal array of two-dimensional mesoporous channels, which can be adjusted in the range of 16–100 Å (Kresge et al., 1992; Beck et al., 1992). The pore size of MCM-41 is relatively much larger than that of microporous materials (~5–7 Å) (e.g., ZSM-5, Zeolite Y). Thus, MCM-41 can be expected to allow larger molecules with two or more fused benzene rings such as PAHs to diffuse into the channels, where the hazardous compounds can be decomposed and by-products with high-molecular weight can be reduced. On the contrary, the diffusion of the larger molecules into channels of the microporous materials would be relatively restricted.

The by-product selectivity of catalytic incineration in the channels or cages of molecular sieves has not been extensively investigated (Derouane and Gabelica, 1980;
Chiang et al., 1993). Therefore, the main objective of the present work was to study speciation of CuO in MCM-41 during catalytic oxidation of naphthalene (Nap) by EXAFS spectroscopy.

2. Experimental methods

Fused silica (Sigma) or rice husk ash (oxidation at 873 K for 16 h) and sodium silicate solution (14% NaOH, 27% SiO₂) were used as silica sources. Aluminium isopropanoxide (Fluka) was used to control the Si/Al ratio of MCM-41. Tetramethylammonium hydroxide (25%), TMAOH and cetyltrimethylammonium bromide (CTMABr) were used as a mineralizer and a template, respectively, in synthesis of MCM-41. 9.6 g TMAOH and 23.4 g of CTMABr were dispersed in 100 g of water with stirring until the solution was clear. 5.67 g of sodium silicate and 4.52 g of silica or 4.7 g of rice husk ash and desired amount of aluminum isopropanoxide were added into the solution and stirred for 2 h. The molar composition of the mother solution was: 1SiO₂: 0.27TMAOH: 0.58CTMABr: 86H₂O: (0–0.3) Al₂O₃. The mother solution was heated at 423 K in a Teflon-lined autoclave for 48 h. MCM-41 was also synthesized by the microwave-enhanced method. The as-synthesis MCM-41 materials were filtered, washed with distilled water, dried at 343 K for 16 h, and calcined at 813 K for 10 h. Impregnation of 5 wt% of copper onto MCM-41 was conducted by dissolving Cu(NO₃)₂ in water using the amount equal to the pore volume of the MCM-41 support. The solution was dispersed uniformly on the support, which was dried at room temperature for 24 h. The catalysts were then calcined at 813 K for 16 h.

About 250 mg of Cu/MCM-41 (5 wt% Cu supported on MCM-41) catalysts were placed into a fixed-bed quartz tube reactor. Saturated vapor of Nap was fed into the fixed bed with 30 mL/min of nitrogen at 523–723 K, and a desired amount of oxygen was supplied simultaneously. Products were collected by a solvent of DCM + hexane (v/v = 1:1). Conversion of the catalytic oxidation was determined by gas chromatography (GC) equipped with a FID detector. A capillary column was used in separation constituents in the product at 423 K.

The EXAFS spectra were collected at a bending-magnet double-crystal monochromator (DCM) X-ray beamline at the National Synchrotron Radiation Research Center (NSRRC) of Taiwan. The electron storage ring was operated with an energy of 1.3 GeV and a current of 100–200 mA. A Si(1 1 1) DCM was used for providing highly monochromatized photon beams with energies of 1–9 keV and an energy resolution of 1.9 × 10⁻⁴ (eV/keV). Data were collected in fluorescence mode with a Lytle detector in the region of the Cu K edge (8978.9 eV) at room temperature. The absorption spectra were collected using ion chambers that were filled with helium gas. The photon energy was calibrated with characteristic pre-edge peaks in the absorption spectrum of a copper foil. The raw absorption data in the region of 50–200 eV below the edge position were fit to a straight line using the least-square algorithms. The fitted pre-edge background curves were extrapolated throughout all data range, and subtracted and normalized to minimize the effect of sample thickness. The near-edge structure in an absorption spectrum covers the range between the threshold and the point at which the EXAFS begins. The XANES extend to an energy of the order of 50 eV above the edge. The k²-weighted and EXAFS spectra were Fourier transformed to R space over the range between 2.3 and 10.5 Å⁻¹. The EXAFS data were analyzed using the UWXAFS 3.0 and FEFF 7.0 programs (Yasuda and Takahashi, 1998; Bjoerst, 1983; Kaune et al., 1998; Breck, 1974; Rehr and Stern, 1976; Zabinsky et al., 1995).

3. Results and discussion

Experimental results revealed that CuO/MCM-41 presented a high conversion rate (> 99.9%) for the catalytic oxidation of Nap at 723 K. The amount of carcinogenic polycyclic aromatic hydrocarbons (PAHs) was dramatically reduced.

In general, XANES spectroscopy can provide the information of electronic configuration, stereochemistry and oxidation state of catalytic active species. Fig. 1 shows the XANES spectra of the fresh and used CuO/MCM-41 in oxidation of Nap at 723 K for 4 h. The pre-edge XANES spectrum of the fresh CuO/MCM-41 (Fig. 1(a)) presented a very weak absorbance feature for 1s–3d transition, which is forbidden by the selection rule in the case of perfect octahedral symmetry. The sharp feature at 8982–8983 eV, which is attributed to the dipole-allowed 1s–4pₓᵧ electron transition, indicated the existence of Cu(I) in MCM-41. Moreover, the shoulder at 8984–8986 eV and the intense feature at 8995–8997 eV can be attributed to the 1s–4pₓᵧ transition, suggesting the existence of Cu(II) species on MCM-41. The upshift of the edge energy and the very weak absorbance for 1s–3d forbidden transition near the pre-edge also confirmed these observations. For the used CuO/MCM-41 catalyst, Cu(I) was not observed (in Fig. 1(b)) during oxidation of Nap at 723 K.

In addition, EXAFS spectra of copper can provide the information on the atomic arrangement including bond distance, number of near-neighbors, thermal and static disorder. The EXAFS spectra were recorded and analyzed in the k range between 2.7 and 10.5 Å⁻¹. An over 99% reliability of the EXAFS data fitting for copper species in MCM-41 was obtained. For all the analyzed EXAFS data, the Debye–Waller factors (Δσ²)
were less than 0.02 Å. Table 1 summarizes structural parameters of copper extracted from the best-fitted EXAFS data. In a parallel experiment, we found that the Cu(II) species has a square-plane structure in the channels of MCM-41. By combination of EXAFS and XANES spectroscopic observations, copper oxide clusters might form in the channels of MCM-41, which also involved in the catalytic oxidation of Nap at 723 K. Moreover, we found that the copper oxide clusters possessed Cu–O and Cu–Cu bond distances of 1.90 and 2.80 Å, respectively with coordination number (CN) of 2.2 and 4.5. However, oxidation of Nap at 723 K for 4 h on CuO/MCM-41 led to structural perturbation of the copper oxide clusters. A decrease of Cu–O bond distance (1.88 Å) and increase of Cu–Cu bond distance (2.82 Å) were observed.

4. Conclusions

CuO/MCM-41 presented a high conversion rate (>99.9%) for catalytic oxidation of naphthalene (Nap) at 723 K. Copper oxide clusters with a square-plane structure were found in the channels of the mesoporous molecular sieve MCM-41. Bond distances of Cu–O and Cu–Cu in MCM-41 were 1.90 and 2.80 Å, respectively. The oxidation of Nap at 723 K for 4 h led to structural perturbation of the copper oxide clusters in MCM-41.

Acknowledgments

The financial support of the National Science Council, Taiwan is gratefully acknowledged. We also thank Prof. Y.W. Yang and Dr. Jyh-Fu Lee of the NSRRC for their XAS experimental assistance.

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