EXAFS Characterization of an Interface Model Nanocatalyst: Binary metal (Ti, Cu) Oxyhydroxy–Organic Framework

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1 Introduction

For heterogeneous catalysis, metal–support interfaces have frequently been considered as active sites. The interface between the nanoparticles and the metal oxide support is believed to play a crucial role in the catalysis. However, in nature, the interfaces have been difficult to characterize by spectroscopic or physicochemical methods. In this study, exact model composite consisting of $[Ti_8O_8(OH)_4]^{12+}$ clusters and $[Cu_2(OH)_6]^{2-}$ linkers was prepared as a molecular model of supported catalysts. $[Ti_8O_8(OH)_4]^{12+}$ cluster is tetragonally linked by bdc (1,4-benzene dicarboxylate) ligands (MIL125). The interface between $[Ti_8O_8(OH)_4]^{12+}$ and added Cu species during catalyst synthesis was characterized by XAFS.

2 Experimental Section

0.4 mL of Cu nitrate (0.5 mmol) aqueous solution was prepared and 200 mg of MIL125 was added. The mixture was magnetically stirred at 300 rpm and 290 K for 20 min and the water was evaporated at 353 K. The atomic ratio of Cu/Ti was 1/2 by incorporating 0.4 mL of Cu nitrate. The powder was calcined in air at 573 K for 2 h. The obtained green sample was denoted as Cu/MIL125.

Ti K and Cu K-edge XAFS spectra were measured at 290 K in a transmission mode on a beamline 9C in the Photon Factory and NW10A in the Photon Factory Advanced Ring at KEK. The storage ring energy was 2.5 GeV and the ring current was 450 mA for Ti K-edge. The values were 6.5 GeV and 37–54 mA for Cu K-edge. A Si(1 1 1) and Si(3 1 1) double-crystal monochromator was inserted in the X-ray beam path. The X-ray intensity was maintained at 65% of the maximum flux using a Piezo translator set on the crystal. The slit opening size in front of the I_0 ionization chamber was 1.0 mm (vertical) × 2.0 mm (horizontal). The Ti K and Cu K-edge absorption energy values were calibrated to 4964.5 and 8980.3 eV, respectively, for the spectra of Ti and Cu metal foils.

The XAFS data were analyzed using an XDAP package. Multiple shell curve fit (CF) analyses were performed for the Fourier-filtered k^3-weighted EXAFS data in k- and R-space using empirical amplitude and phase-shift parameters extracted from the EXAFS data of TiO_2 powder (JRC-TIO7) and CuO powder.

3 Results and Discussion

Based on the Cu–O and Ti–O interatomic distances determined by EXAFS for Cu/MIL125 (both 0.195 nm; Table 1) and assuming complete tetrahedral (T_d) or octahedral (O_h) coordination around Cu, three plausible Cu linker models were drawn (Chart 1).

The first model is $[Cu_2(OH)_6]^{2-}$, in which the Cu sites are T_d coordinated (Chart 1A). The second and third are $[Cu_2(OH)_6(OH_2)_4]^{2-}$ and $[Cu_4(OH)_{10}(OH_2)_6]^{2-}$, in which the Cu sites are O_h coordinated (Chart 1B and C, respectively).

In models A, B, and C, the nearest distances between Ti atoms in the neighboring $[Ti_8O_8(OH)_4(bdc)_2]^{8+}$ sheet were calculated as 0.838, 0.936, and 1.100 nm, respectively (Chart 1). Thus, model C was rejected as the linker in comparison to the experimental value: 0.874 nm based on XRD result [1]. If the O–Cu–O angles for central Cu_2O_2 core in model A were slightly distorted from 109.5° (T_d) to 96.1° (model A', Chart 1) or if the dihedral angle of two CuO_4 planes was distorted from 180° to 132° (model B'), the Cu linker length L became 0.874 nm, in agreement with XRD.
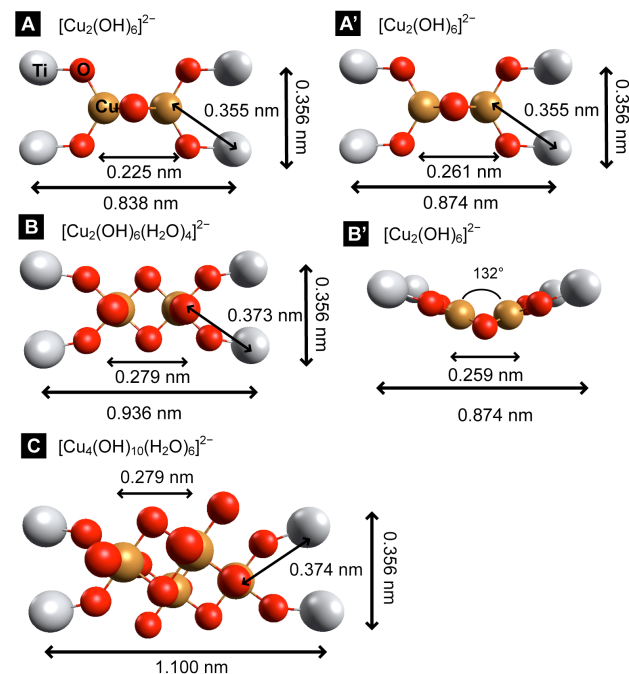

Chart 1. Plausible Cu hydroxide linker models. The Cu–O and Ti–O interatomic distances were fixed at 0.195 nm based on EXAFS. (A, A', B') $[Cu_2(OH)_6]^{2-}$, (B) $[Cu_2(OH)_6(OH_2)_4]^{2-}$, and (C) $[Cu_4(OH)_{10}(OH_2)_6]^{2-}$. The Cu site symmetry was T_d (A, A'), planar (B'), and O_h (B, C).

Table 1

Best-fit results of Ti and Cu K-edge EXAFS analyses for Cu/MIL125[*1]

Ti–O		Ti(–O–)Ti		Ti(–O–)Cu		Cu–O		Cu(–O–)M (M = Ti, Cu)	
N	R(nm)	N	R(nm)	N	R(nm)	N	R(nm)	N	R(nm)
5.2 (±1.2)	0.1945 (±0.0004)	3.8 (±0.3)	0.276 (±0.002)	2.6 (±0.6)	0.3797 (±0.0008)	3.6 (±0.6)	0.195 (±0.001)	2.8 (±2.2)	0.310 (±0.006)

[*1] The values in parenthesis are fit errors.

Based on the Ti K-edge EXAFS CF analyses for Cu/MIL125 (Table 1), the Ti(–O–)Ti interatomic distance changed from 0.305 nm (mean) for MIL125 to 0.276 nm. Its associated N value increased from 2.0 to 3.8. In addition, a new farther peak appeared at 0.33 nm (phase shift uncorrected) [1], that can be ascribed to a Ti(–O–)Cu interatomic pair fitted with the R value 0.380 nm and N value 2.6 (Table 1), strongly suggesting that new Ti(–O–)Cu interatomic links formed around the $[Ti_8O_8(OH)_4]^{12+}$ clusters. The N value was consistent with models A' or B' for Cu/MIL125 (Chart 1) within variation of ±0.6 (Table 1), because the models assumed that two-thirds of terephthalates coordinated to the Ti atoms in MIL125 were replaced by $[Cu_2(OH)_6]^{2-}$ linkers; thus, the N[Ti(–O–)Cu] value was two. The distance (0.380 nm; Table 1) was in agreement with the Ti···Cu interatomic distance in model B' (0.373 nm; Chart 1) rather than 0.355 nm in model A'. The formula would be $Ti_8O_8(OH)_4 \cdot (bdc)_2 \cdot [Cu_2(OH)_6]_4$ (Compound **1**) for Cu/MIL125.

The connection between $[Cu_2(OH)_6]^{2-}$ linkers and $[Ti_8O_8(OH)_4]^{12+}$ clusters was investigated by Cu K-edge EXAFS. The N value for Cu–O pairs (3.6; Table 1) supported the coordination of four O atoms both in models A' and B' (Chart 1) within the variation of ±0.6 (Table 1). The N value for Cu(–O–)M (M = Cu or Ti) was shown to be 2.8 (Table 1), consistent with coordination to one Cu and two Ti (Chart 1A', B'). The interatomic distance for Cu(–O–)M (0.310 nm; Table 1) was consistent with model A': $\frac{2}{3} \times 0.355 + \frac{1}{3} \times 0.261 = 0.324$ nm and model B': $\frac{2}{3} \times 0.373 + \frac{1}{3} \times 0.259 = 0.335$ nm.

The theoretical Ti and Cu K-edge XANES pattern generated using ab initio multiple scattering calculation code, FEFF8.4 and the greater Cu 1s-3d pre-edge peak intensity directly supported model B' as linkers for Cu/MIL125 [1]. However, model A' may be also acceptable.

Reference

[1] Y. Yoshida and Y. Izumi, *J. Catal.* **332**, 1–12 (2015).

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