

Speciation of Raney Copper Oxide during High-Temperature Desulfurization

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Abstract. Speciation of copper in the Raney copper oxides (R-CuO) during high-temperature desulfurization has been studied by X-ray absorption spectroscopy. The preedge XANES spectra (8975–8979 eV) of R-CuO exhibit a very weak 1s-to-3d transition forbidden by the selection rule in the case of the perfect octahedral symmetry. A shoulder at 8985–8988 eV and an intense band at 8994–9002 eV can be attributed to the 1s-to-4p transition that indicates the existence of the Cu(II) species. The preedge band at 8981–8984 eV can be attributed to the dipole-allowed 1s-to-4p transition of Cu(I), suggesting an existence of Cu₂S during sulfurization. An enhanced absorbance at 9003 eV shows that Cu(0) species may be formed in the sulfurized R-CuO. The main copper species in regenerated R-CuO are CuO (96%) and Cu₂S (4%).

Keywords: Desulfurization, Raney, CuO, XANES

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INTRODUCTION

Integrated gasification combined cycle (IGCC) is gaining momentum as a commercially viable source of clean energy. IGCC based power generation is cleaner and more efficient than conventional coal-fired boilers. Sulfur must be reduced in the hydrocarbon derived synthesis gas (syngas) before fed to the combustion turbine. Sulfur (composed primarily of H₂S and COS) can be separated traditionally by wet chemical absorption. Although IGCC with cold syngas clean-up is more efficient than the traditional coal fired power process, further gains in efficiency are possible if the syngas can be cleaned up at high temperatures. Economic studies show that a 3% reduction in the heat rate, a 6% decrease in capital cost, and 6% decrease in the levelized cost of electricity are possible if hot gas cleanup with high-temperature desulfurization is used [1]. ZnO is an effective desulfurization absorbent. However, in the reducing atmospheres (gasification), ZnO might be reduced to form metallic Zn and volatilized at T > 923 K [2, 3].

Raney metals oxides generally have high catalytic activities in dehydrogenation processes simply due to relative enrichments of surface active species. In

addition, Raney catalysts have a low initial cost per unit mass of metal and therefore provide the lowest ultimate cost per unit mass in catalysis applications. A better resistance to catalytic poisoning for the Raney catalysts has been found. Raney metals such as nickel, iron, cobalt, copper, platinum, ruthenium, palladium, zinc, chromium, and molybdenum have shown enhanced catalytic activities, for instance. Raney copper is usually used in selective hydrogenation of aldehydes or esters to alcohol and dehydrogenation of alcohols to aldehydes or ketones [4-6]. Raney copper has also been found an effective desulfurization absorbent [6]. However, speciation of raney copper oxide is still lacking in the literature. Thus, the main objective of this work was to study chemical structure of copper in the R-CuO for high-temperature desulfurization.

EXPERIMENTAL

The Raney CuO (R-CuO) was prepared by the oxalate gel coprecipitation method. The R-CuO absorbent were calcined at 873 K for 2 h. A vertical fixed bed steel reactor (1 inch in diameter) was used in the desulfurization and regeneration (oxidization)

experiments. 1% H₂S gas, balanced with N₂, entered from the top of the reactor (873–1073 K), and the flow rate (50 mL/min) was measured by digital flow rate meters. After desulfurization, regeneration was performed with air (50 mL/min) at 873–1073 K. The volume space velocity (STP) for the desulfurization and regeneration reactions was 6000 mL/hg.

XANES spectra of copper were collected on the Wiggler beamline at the Taiwan National Synchrotron Radiation Center (NSRRC). A Si(111) double-crystal monochromator (DCM) was used for providing highly monochromatized photon beams with energies of 1–9 keV. The electron storage ring was operated with energy of 1.5 GeV (current = 100–200 mA). Data were collected in the transmission and fluorescence mode in the region of the Cu (8979 eV) K edge at 298 K. The XANES spectra extend to energy of 50 eV above the edge. XANES spectroscopy can combine with principal component analysis (PCA) and least-squares fitting (LSF) as a quantitatively analytical tool for speciation of dilute and/or amorphous multi-components, which is not easily attainable with conventional methods. Semi-quantitative analyses of the XANES spectra were conducted by the least-square fitting of linear combinations of standard spectra to the spectrum of the sample. XANES spectra of copper model compounds such as CuO and Cu₂S were also measured on the Wiggler beamline.

RESULTS AND DISCUSSIONS

Figure 1 shows the XANES spectra of copper for calcined, sulfurized and regenerated R-CuO. The preedge XANES spectra (8975–8979 eV) of R-CuO exhibit a very weak 1s-to-3d transition forbidden by the selection rule in the case of the perfect octahedral symmetry. A shoulder at 8985–8988 eV and an intense band at 8994–9002 eV can be attributed to the 1s-to-4p transition that indicates the existence of the Cu(II) species.

The preedge band at 8981–8984 eV was attributed to the dipole-allowed 1s-to-4p transition of Cu(I), suggesting an existence of Cu₂S during sulfurization. An enhanced absorbance at 9003 eV shows that Cu(0) species might be formed during sulfurization.

XANES spectra of copper and component fits for the regenerated R-CuO are shown in Fig. 2. The XANES spectra were also expressed mathematically in a LC XANES fit vectors, using the absorption data within the energy range 9639–9699 eV (zinc) and 8959–9019 eV (copper). XANES spectra of copper model compounds such as CuO and Cu₂S were also measured on the SRRC Wiggler beamline. The XANES features at 8985–8988 eV and 8994–9002 eV for the 1s-to-4p transition Cu(II) was found in the

regenerated ZnO/R-CuO. The main copper species in regenerated R-CuO were CuO (96%) and Cu₂S (4%).

CONCLUSION

The preedge XANES spectra (8975–8979 eV) of R-CuO show the existence of the Cu(II) species. The preedge band at 8981–8984 eV was attributed to the dipole-allowed 1s-to-4p transition of Cu(I), suggesting an existence of Cu₂S during sulfurization. An enhanced absorbance at 9003 eV shows that Cu(0) species may be formed during sulfurization. The XANES features at 8985–8988 and 8994–9002 eV for the 1s-to-4p transition Cu(II) was found in the regenerated ZnO/R-CuO. The main copper species in regenerated R-CuO were CuO (96%) and Cu₂S (4%).

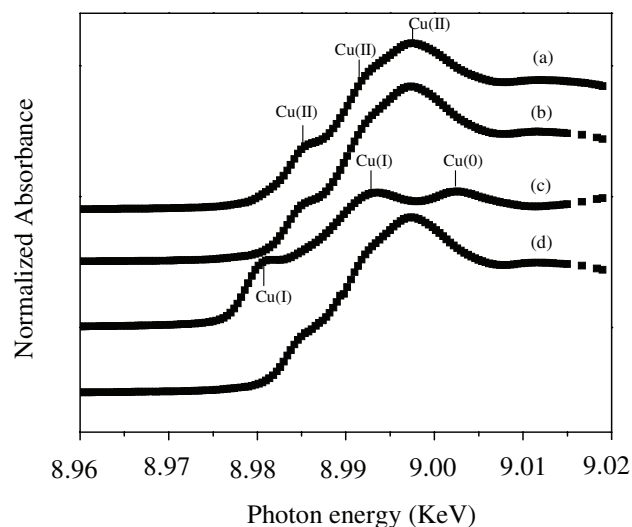


FIGURE 1. XANES spectra of copper in (a) nano CuO and (b) calcined (at 1073 K), (c) sulfurized (at 873 K) and (d) regenerated R-CuO (at 873 K).

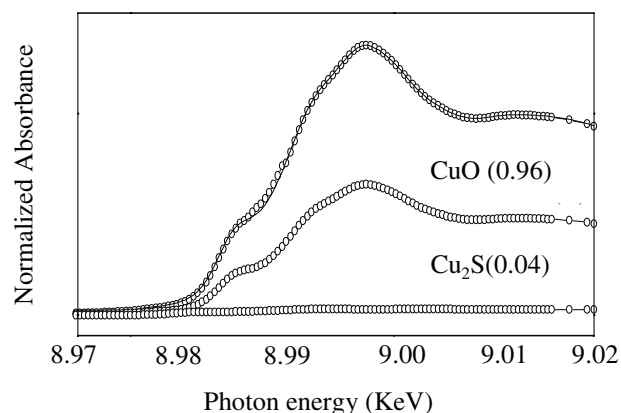


FIGURE 2. XANES spectra of copper and component fits of regenerated R-CuO.

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