

**Cu<sub>2</sub>O as active species in the steam reforming of methanol over CuO/ZrO<sub>2</sub>**

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**Introduction**

Hydrogen is much in demand for the fuel cell. CuO/CeO<sub>2</sub> and CuO/ZrO<sub>2</sub> catalysts were very active for the steam reforming of methanol (SRM)[1,2]. XRD diagrams showed that the starting coppers were CuO, and coppers in most catalysts were reduced to metallic Cu during SRM. However, the post-reacted coppers of 80 or 90 wt% CuO/ZrO<sub>2</sub> were Cu<sub>2</sub>O, while those of CuO/ZrO<sub>2</sub> having less than 40 wt% loading were metallic Cu. The oxidation states of Cu in the post-reacted catalysts depended upon CuO loading and water/MeOH ratio in SRM. The catalytic active copper species in CuO/CeO<sub>2</sub> and CuO/ZrO<sub>2</sub> have been elucidated from their XANES spectra.

**Experimental**

An aqueous solution containing known amounts of copper(II) nitrate, cerium(III) nitrate or zirconium(IV) oxynitrate was stirred at 80 °C for 20 min and 3 N NaOH was added until the pH of the solution was 11. The precipitate obtained was filtered and washed with deionized water three times. After drying at 353K overnight, it was calcined at 573K for 3 h. The steam reforming reactions (MeOH : H<sub>2</sub>O : He = 4.5 : 6.8 : 16) were carried out with a fixed bed reactor at 523K under atmospheric pressure. X-ray absorption measurements for K-edge of Cu were done at the Beam Line 10B.

**Results and discussion**

The summary of XRD data on CuO/CeO<sub>2</sub> and CuO/ZrO<sub>2</sub> catalysts is as follows: (1) the starting coppers were CuO, (2) the coppers of the post-reacted CuO/CeO<sub>2</sub> with 15-80 wt% loading were metallic Cu, (3) the coppers of post-reacted CuO/ZrO<sub>2</sub> with 15-40 wt% loading were metallic Cu, (4) those with 80-90 wt% loading were Cu<sub>2</sub>O. The structures of typical catalysts, 80 wt% CuO/CeO<sub>2</sub> and CuO/ZrO<sub>2</sub>, were analyzed. Their XANES spectra were different in the pre-edge region (Fig. 1). The XANES spectrum of CuO/CeO<sub>2</sub> is almost the same as that of metallic Cu. However, the spectrum of CuO/ZrO<sub>2</sub> resembles that of Cu<sub>2</sub>O. The second derivative of the XANES (Fig. 2) indicates that all of copper species in the post-reacted 80 wt% CuO/ZrO<sub>2</sub> are Cu<sub>2</sub>O. The catalyst gave no XRD patterns of ZrO<sub>2</sub>, resulting in highly dispersed in abundant copper species. Highly dispersed ZrO<sub>2</sub>, which is monoclinic from its FT spectrum, exerts all of copper species kept as Cu<sub>2</sub>O irrespective of the reducing conditions. The XANES spectrum of post-reacted CuO/CeO<sub>2</sub>/ZrO<sub>2</sub>(8: 1: 1) was the mixed spectrum of metallic Cu and Cu<sub>2</sub>O, their catalytic activity was higher than those of CuO/CeO<sub>2</sub> and CuO/ZrO<sub>2</sub>.

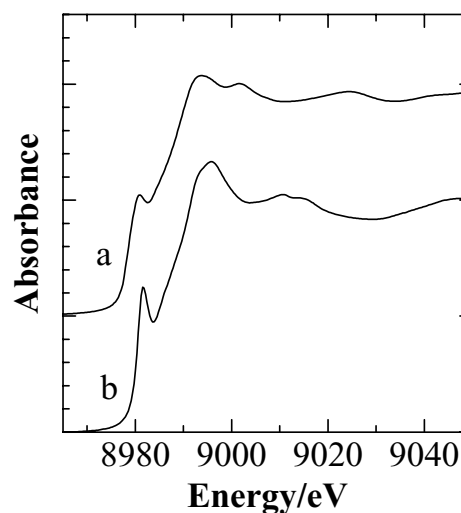


Fig. 1 XANES spectra of post-reacted 80 wt% CuO/CeO<sub>2</sub> and CuO/ZrO<sub>2</sub> catalysts

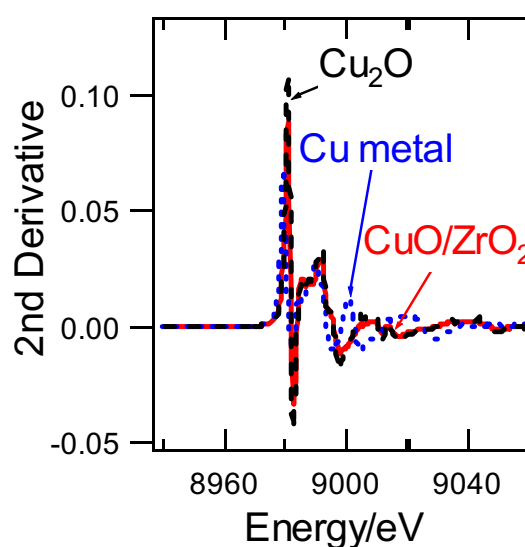


Fig. 2 The second derivatives of the XANES spectra of post-reacted 80 wt% CuO/ZrO<sub>2</sub>, metallic Cu, and Cu<sub>2</sub>O.

**References**

- [1] H. Oguchi, T. Nishiguchi, T. Matsumoto, H. Kanai, K. Utani, Y. Matsumura, S. Imamura, *Appl. Catal. A*, 281(2005) 69.
- [2] H. Oguchi, H. Kanai, K. Utani, Y. Matsumura, S. Imamura, submitted for publication in *Appl. Catal. A*.

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