In-situ XAS Study of CuO/CeO_2 Catalysts for CO Preferential Oxidation under Hydrogen-rich Atmosphere

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In-situ X-ray absorption spectroscopy (XAS) was used to investigate the change of valence states of Cu in CuO/CeO_2 catalysts for CO preferential oxidation under hydrogen-rich atmosphere. CuO/CeO_2 catalysts were prepared by physical mixing with $Ce(NO_3)_3$ and $Cu(NO_3)_2$ and calcinations at 400-600°C. These CuO/CeO_2 catalysts were noted with the abbreviation of $Pmx\text{-}20CuCeO_2$, where x represents the calcination temperature in the unit of 100°C, and "20" was the molar percentage of Cu loading. In general, for catalytic activity of CO preferential oxidation reaction, the selectivity was decreased with increasing reaction temperature and declined dramatically as the reaction temperature was higher than 120°C. Among them, the best catalytic activity of the lowest T_{95} at 130°C with the highest S_{95} of 92% was obtained by $Pm4\text{-}20CuCeO_2$ catalyst. (T_{95}: at the temperatureat with 95% CO conversion; S_{95}: the selectivity with 95% CO conversion).

Before reaction, the oxidation state of Cu in CuO/CeO_2 catalysts was 2+ in form of CuO. As the reaction temperature raised from 110°C to 160°C, the valence state of Cu changed to metallic Cu from Cu^{2+} (Fig. 1(a)). The edge energy of Cu shifted to lower energy of 8979.409 eV from 8990.992 eV at 150°C. Up to 160°C, the XANES of Cu species in CuO/CeO_2 catalyst was almost similar to that of metallic Cu. As to the Fourie transformation profile without phase correction shown (Fig. 1(b)), the only peak of first shell was determined since the particle size of Cu was much smaller than that of Cu foil, Cu_2O and CuO standards. When the reaction temperature was higher than 140°C, the peak shifted to R value of 2.12Å at 150°C and 2.16Å at 160°C from 1.47Å at 110-140°C. These results implied that the Cu species in CuO/CeO_2 catalyst started to be reduced at temperature higher than 140°C. The ratio of Cu species in different valence state was calculated by linear combination, and was listed in Table 1. Below the temperature at 150°C, all the Cu species were in valence state of 2+. As the temperature was raised to 150°C, the Cu species were in mixed oxidation states of metallic Cu, 1+ and 2+ with ratio of 0.575/0.259/0.165. The content of Cu species in 1+ and 2+ was reduced with increasing temperature, while that of metallic Cu increased. This was consistent with the selectivity. Thus, the active site for CO oxidation would be Cu^{2+}, however, that for hydrogen oxidation is metallic Cu.

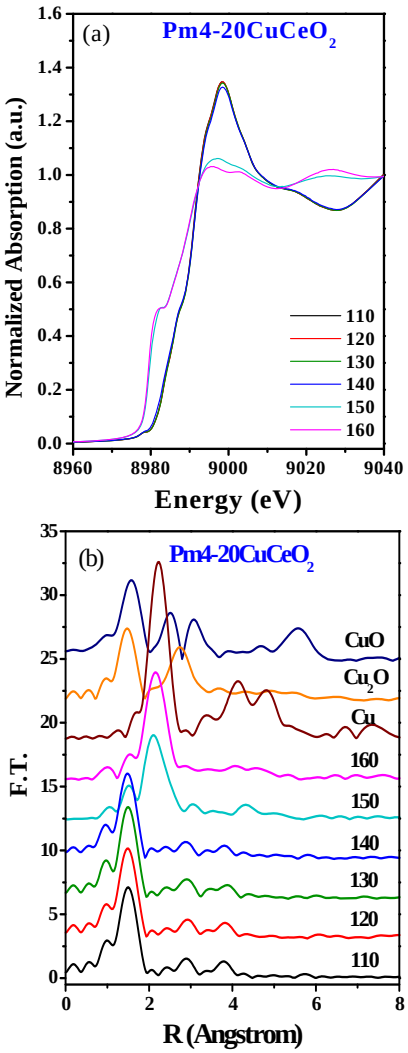

Fig. 1: (a) In-situ XANES of Cu K-edge and (b) Fourie transformation profiles of $Pm4\text{-}20CuCeO_2$ at varying temperatures under the condition of CO Preferential oxidation reaction in hydrogen-rich atmosphere.

Table 1: Linear combination analysis of Cu *K*-edge XANES

Catalyst	Rxn. Temp./°C	Content (%) Cu	Cu_2O	CuO
$Pm4\text{-}20CuCeO_2$	120	0	0	1
	130	0	0	1
	140	0	0	1
	150	0.575	0.259	0.165
	160	0.696	0.252	0.052