

EXAFS analysis for Low-temperature CO-PROX over CuO<sub>x</sub>-CeO<sub>2</sub> CatalystRajaram Bal<sup>1,\*</sup> and Takehiko Sasaki<sup>2</sup><sup>1</sup> Light Stock Processing Division, CSIR-Indian Institute of Petroleum, Dehradun-248005, India<sup>2</sup> Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa, Chiba, 277-8561, Japan

### 1 Introduction

Substantial effort has been made in recent years to combat the global climatic challenges by exploiting various green alternatives to fossil fuels. Modern society considers hydrogen as a clean fuel due to its high calorific value with water as the only by-product. Fuel cell (FC) technology has become popular due to its significant efficacy, availability, and performance. Compared to conventional technologies, FC uses hydrogen, which generates electricity in an environmentally benign way (electrochemically). For this purpose removal of CO is necessary to protect the Pt-anode, on which hydrogen is oxidized. Therefore, preferential catalytic carbon monoxide oxidation (PROX) in presence of excess hydrogen is the most crucial strategy for purification of H<sub>2</sub> to be used in PEMFC. In this study Cu/CeO<sub>2</sub> catalysts were developed for the efficient PROX catalysts and XAFS characterization was achieved.

### 2 Experiment

Cu/CeO<sub>2</sub> catalysts were prepared by a surfactant assisted hydrothermal method by adapting our own synthesis method [1]. Extended X-ray absorption fine structure (EXAFS) measurements at the Cu-K edge were carried out in transmission mode at room temperature at the BL9C station of the Photon Factory at the Institute of Materials Structure Science, High Energy Accelerator Research Organization in Japan (KEK-IMSS-PF). The electron storage ring was operated at 2.5 GeV. A Si(111) channel-cut crystal was used as a monochromator. Ionization chambers for incident X-rays (I<sub>0</sub>) and transmitted X-rays (I) were filled with N<sub>2</sub>(100%) and 25%Ar/N<sub>2</sub> gas, respectively. EXAFS data were analyzed and fitted using Athena and Artemis package based on IFFEFFIT program Backscattering amplitude, and phase shift were obtained by FEFF calculation..

### 3 Results and Discussion

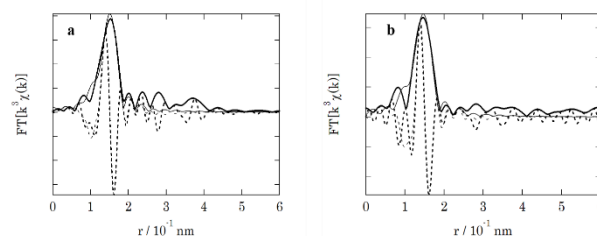
Cu K-edge EXAFS spectra of the spent and fresh 5% Cu-CeO<sub>2</sub><sup>HT</sup> catalysts (Fig. 1 a and b) show the first shell corresponding to Cu-O coordination of ca. 1.946 Å and 1.936 Å (Table 1), which is different from the crystalline CuO (1.959 Å) or Cu<sub>2</sub>O (1.858 Å). The corresponding coordination numbers are 3.4±0.6 and 3.2±0.9 for fresh and spent 5% Cu-CeO<sub>2</sub><sup>HT</sup>, respectively, instead of 4 in CuO. Moreover, there is no indication for a Cu-Cu shell-like in the Cu oxide and metallic Cu compounds. This is a strong indication for the high dispersion of Cu within the CeO<sub>2</sub>

lattice of sample 5% Cu-CeO<sub>2</sub><sup>HT</sup>, i.e., the generation of a Cu-O-Ce solid-state solution in the form of Ce<sub>1-x</sub>Cu<sub>x</sub>O<sub>2-δ</sub>, where one Cu<sup>2+</sup> replaces a Ce<sup>4+</sup> ion and creates an oxygen vacancy [2]. Furthermore, the lower Cu-O coordination number in the 5% Cu-CeO<sub>2</sub><sup>HT</sup> samples agrees with the fact that the incorporation of Cu<sup>2+</sup> in a Ce<sup>4+</sup> lattice site creates an oxygen vacancy [2].

Table 1: Summary of the EXAFS fitting results for the 5% Cu/CeO<sub>2</sub> catalysts<sup>a</sup>

	Path	R (10 <sup>-1</sup> nm)	CN	DW (10 <sup>-5</sup> nm <sup>2</sup> )	ΔE <sub>0</sub> (eV)	R <sub>f</sub> (%)
Fresh	Cu-O	1.946±0.014	3.4±0.6	4.8±1.7	0.12±2.2	0.78
Spent	Cu-O	1.936±0.013	3.2±0.9	5.2±2.5	-2.8±2.5	1.30

<sup>a</sup> Fitting was conducted in the range Δk: 2–12 (10<sup>-1</sup> nm) and ΔR: 1.2–2.2 (10<sup>-1</sup> nm). Amplitude reducing factor S<sub>0</sub><sup>2</sup> = 0.95



**Fig. 1.** Cu K-edge EXAFS spectra of a) the fresh and b) the spent 5% Cu-CeO<sub>2</sub><sup>HT</sup> catalyst after 120 hours. K<sup>3</sup>-weighted Fourier transform (amplitude (solid curve) and imaginary part (dotted curve)). Observed data: thick curves, fitting data: thin curves.

In summary, Cu K-edge EXAFS measurements confirmed the well dispersed Cu states in the 5% Cu/CeO<sub>2</sub> catalyst which showed 100% conversion of CO at 65 °C and 100% selectivity of O<sub>2</sub> towards CO in presence of excess hydrogen, without the latter's partial burning.

### References

- [1] R. Bal, C. Pendem, A. Bordoloi, Catalyst for carbon monoxide oxidation and process for the preparation thereof. (U.S. Patent 10322407B2), 2019. <https://patents.google.com/patent/US10322407>.
- [2] P. Bera, K. R. Priolkar, P. R. Sarode, M. S. Hegde, S. Emura, R. Kumashiro, N. P. Lalla, Chem. Mater. 14 (2002) 3591–3601.

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