

XAFS characterization of Co-doped ZrO<sub>2</sub> catalyst.Abhijit Shrotri<sup>1,\*</sup>, Kiyotaka Asakura<sup>1,2</sup>, Nazmul Dostagir<sup>1,3</sup>, Jin Ota<sup>1,2</sup>, Atsushi Fukuoka<sup>1</sup><sup>1</sup>Institute for Catalysis, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan<sup>2</sup>Division of Quantum Science and Engineering, Graduate School of Engineering, Hokkaido University, Kita 21-Nishi 10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan<sup>3</sup>Graduate School of Chemical Sciences and Engineering, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan

### 1 Introduction

Recycling of CO<sub>2</sub> is an attractive approach to avoid the use of fossil fuels and produce value added chemical from a waste resource. Reduction of CO<sub>2</sub> via reverse water gas shift (RWGS) reaction produces CO, which is valuable for chemical synthesis. In RWGS reaction, achieving high CO selectivity at high conversion and low temperature is a challenge because of the formation of methanol and methane. Here we investigated the use of Co doped ZrO<sub>2</sub> catalyst for CO<sub>2</sub> hydrogenation.[1] XAFS analysis was used to determine the nature of Co and Zr atoms in Co doped ZrO<sub>2</sub> catalyst at increasing Co loading.

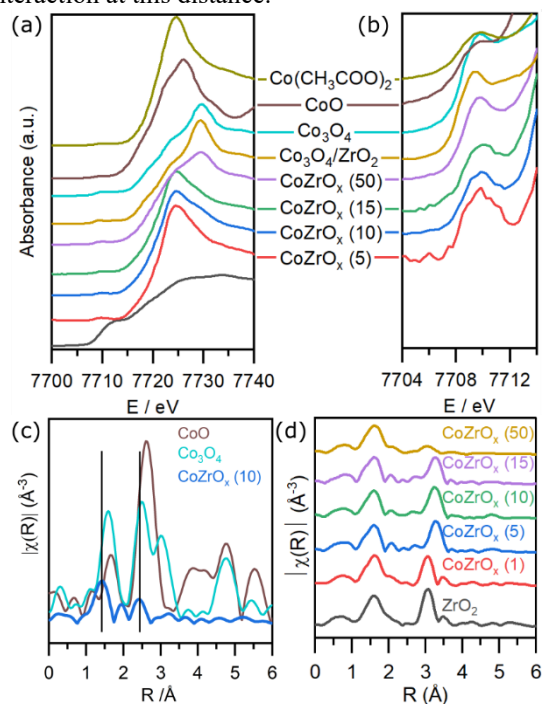
### 2 Experiment

Co doped ZrO<sub>2</sub> catalysts were prepared by coprecipitation method with Co loading of 1-15, and 50 atoms%. XAFS measurements were carried out at BL9C and NW10A beamlines of Photon Factory. For Co K-edge XAFS analysis, the X-rays emitted from 2.5 GeV Storage ring operating at 450mA were monochromatized by a Si(111) double crystal monochromator. X-ray beam was focused, and higher harmonics were rejected by a bent cylindrical mirror. The incident and transmitted X-rays were monitored by 17 cm and 34 cm long ionization chambers filled with N<sub>2</sub>. The samples were diluted with boron nitride and pressed into pellets. Data analysis was carried out using the REX package programs. Additional analysis was done using Athena software using standard parameters.

### 3 Results and Discussion

The presence of large amount of ZrO<sub>2</sub> caused severe absorption and limited the Co K-edge height to 0.1-0.2. In the X-ray absorption near-edge spectrum (XANES), the edge position for stable doped catalysts CoZrO<sub>x</sub> (X = 5, 10, and 15) was at 7722 eV, which was assigned to divalent Co<sup>2+</sup> species. CoZrO<sub>x</sub> (50) was the exception among doped catalysts and had a higher edge position of 7726 eV due to the presence of Co<sup>3+</sup> as found in Co<sub>3</sub>O<sub>4</sub> (Figure 1a). In the pre-edge region, the height of the pre-edge peak around 7710 eV was assigned to 1s to 3d transition, which was smaller when centrosymmetry was present, for example, in CoO and Co(CH<sub>3</sub>COO)<sub>2</sub> (Figure 1b). Larger peaks were observed for Co<sub>3</sub>O<sub>4</sub>/ZrO<sub>2</sub> and CoZrO<sub>x</sub> (50), containing Co<sub>3</sub>O<sub>4</sub> having a tetrahedral structure without

centrosymmetry. The pre-edge peaks for doped catalysts were larger than CoO and Co(CH<sub>3</sub>COO)<sub>2</sub>, indicating a loss of centrosymmetry in the Co<sup>2+</sup> local structure owing to its doping in the tetragonal ZrO<sub>2</sub>. The EXAFS region for the CoZrO<sub>x</sub> (10) catalyst is shown in Figure 1c. The noise in the EXAFS region was high due to the large background absorbance of ZrO<sub>2</sub>. Nevertheless, the Fourier transform of CoZrO<sub>x</sub> (10) differed from that of CoO and Co<sub>3</sub>O<sub>4</sub>. Curve fitting showed that the Co–O distance of 1.88 Å in CoZrO<sub>x</sub> (10) was shorter than that of CoO (Table 1). The small peak appearing at 2–3 Å was well fitted with Co–Zr interaction although with a short bond distance of 2.71 Å. Further studies are necessary to confirm the presence of Co–Zr interaction at this distance.



**Figure 1:** (a) XANES of doped and impregnated catalysts along with standard Co compounds. (b) Expanded spectra showing the pre-edge region for the Co XANES. (c) Fourier transform of EXAFS region for CoZrO<sub>x</sub> (10) and reference Co oxides. (d) Fourier transform of EXAFS region of Zr K-edge for CoZrO<sub>x</sub> (X) catalysts along with undoped ZrO<sub>2</sub>.

The phase transition in ZrO<sub>2</sub> with Co loading was also evident in the EXAFS analysis of Zr K-edge for doped

catalysts (Figure 1d). Undoped  $ZrO_2$  and  $CoZrO_x$  (1) exhibited a monoclinic structure with Zr–O and Zr–Zr distances of 2.12 and 3.45 Å, respectively. Tetragonal  $ZrO_2$  was observed for  $CoZrO_x$  (5),  $CoZrO_x$  (10), and  $CoZrO_x$  (15) catalysts as the Zr–O distance reduced to 2.08 Å and the Zr–Zr distance increased to 3.65 Å.  $CoZrO_x$  (50) showed features of monoclinic  $ZrO_2$  lacking long-range order in EXAFS.

**Table 1:** Co-ordination number and radial distance obtained for fitting of EXAFS data for  $CoZrO_x$  (10) in comparison to CoO and  $Co_3O_4$ .  $S^2 = 0.83$  for Co–O which was determined by using FEFF.

Sample	$CoZrO_x$ (10)	$Co_3O_4$	CoO
$N_{Co-O}$	2.3	6.0	6
$R_{Co-O}$ (Å)	1.88	1.94	2.12
$\sigma_{Co-O}$ (Å)	0.63	0.054	0.078
$\Delta E_{Co-O}$ (eV)	2.0	26.8	16.3
$N_{Co-Zr}$	0.50	-	-
$R_{Co-Zr}$ (Å)	2.71	-	-
$\sigma_{Co-Zr}$ (Å)	0.03	-	-
$\Delta E_{Co-Zr}$ (eV)	4.68	-	-
R (%)	6.38	1.3	4.3

Through the above analysis we could conclude that the Co atoms were divalent in the doped catalysts and did not resemble the crystal structure of CoO or  $Co_3O_4$ . The transformation of monoclinic to tetragonal  $ZrO_2$  happened at Co loading between 1 – 5 atom%.

#### References

- [1] N. H. MD Dostagir, R. Rattanawan, M. Gao, J. Ota, J. Hasegawa, K. Asakura, A. Fukouka, and A. Shrotri  
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#### Research Achievements

1. Abhijit Shrotri, Outstanding Discussion Award, 129<sup>th</sup> Catalysis Society Meeting, Catalysis society of Japan. 4 April 2022.

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