

Control and monitoring of the valence of Ce-doped Y-zeolites for CO₂ conversion

Gaku Mikami and Yasuo Izumi*

Graduate School of Science, Chiba University, Yayoi 1-33 Inage-ku, Chiba 263-8522, Japan

1 Introduction

Carbon dioxide is one of the major greenhouse gases. Catalysts for converting CO₂ to CO have been widely investigated [1]. We reported that the synthesis rates of dimethyl carbonate (DMC) from CO₂ and methanol was dependent on the ratio of Ce³⁺/Ce⁴⁺ sites in Ce-based catalysts [2]. CO₂ adsorbed at the surface defect sites, and the neighboring Ce³⁺ sites to the defects were oxidized to Ce⁴⁺.

In this study, we synthesized Ce³⁺ catalysts supported on HY-zeolite by changing the Ce amount and synthesis method. The local structure and valence of Ce were investigated using Ce L₃-edge XANES.

2 Experiments

Ce-doped HY zeolites were prepared by impregnation method (0.3, 4.3, 16 wt% of Ce; imp Ce-HY) and ion-exchange method (11 wt% of Ce; IE Ce-HY) using Ce(NO₃)₃·H₂O. CO₂ adsorption and CO desorption reaction were investigated using an online gas chromatograph. The samples were evacuated at 290 K for 1 h as pretreatment. 3.3 kPa of CO₂ was introduced and circulated for 1 h. Then it was evacuated for 30 s. Then, the samples was heated up to 573 K at a ramping rate of 2 K min⁻¹.

Ce L₃-edge XAFS spectra were measured on a beamline 7C and 9C in a transmission mode.

3 Results and Discussion

Ce L₃-edge XANES spectra taken for Ce-doped HY zeolites and standard Ce compounds are shown in Fig. 1. Twin peaks appeared at 5731 and 5738 eV in the XANES spectrum for CeO₂ (a), indicating that valence state of Ce⁴⁺. An intense whiteline peak was appeared at 5727 eV in the spectrum for Ce(NO₃)₃·H₂O (b). This peak is specific for the Ce³⁺ valence state. Spectra a and b were used as models of Ce⁴⁺ and Ce³⁺ sites, respectively. As the result of spectrum fit by changing the mixing ratio of the two spectra, IE Ce-HY 11 wt% and imp Ce-HY 0.3 wt% (spectra c and d) were found to contain more than 95% of Ce³⁺. The valence composition for imp Ce-HY 4.3 wt% and 16 wt% (spectra e and f) were also investigated based on the fits with spectra a and b. The best fits were with the mixing ratio were Ce³⁺/Ce⁴⁺ = 30/70 (e) and 5/95 (f).

The CO₂ desorption was monitored up to 573 K (Table 1). The amount of CO desorbed was 7.90 μmol g⁻¹ in IE Ce-HY 11 wt%. The Ce³⁺ sites for imp Ce-HY 0.3 wt%, 4.3 wt%, and 16 wt% were 2.6%, 11.7%, and 7.3% of that for IE Ce-HY 11 wt%. The CO amounts desorbed were 4.4%, 10.1%, and <0.4%, respectively. Bulk CeO₂ negligibly desorbed CO (Table 1). Thus, Ce³⁺ sites and CO₂ reduction to CO were closely correlated.

The photocatalytic reduction of CO₂ and CO₂ reaction with methanol into DMC are reported elsewhere.

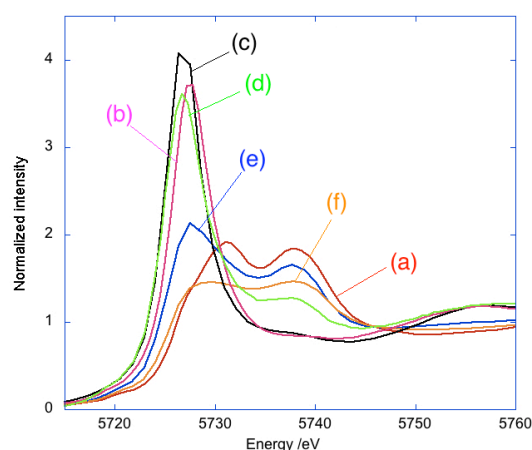


Fig. 1: Ce L₃-edge XANES spectra for CeO₂ (a), Ce(NO₃)₃·H₂O (b), Ce-HY IE 11 wt% (c), imp 0.3 wt% (d), imp 4.3 wt% (e), and imp 16 wt% (f).

Table 1: Amount of CO desorption

Samples	Molar ratio Ce ³⁺ /Ce ⁴⁺	Ce ³⁺ amount (μmol/g _{cat})	CO desorption (μmol _{CO} /g _{cat})
IE Ce-HY 11 wt%	~ 100 / ~ 0	785	7.90
imp Ce-HY 0.3 wt%	95 / 5	20.3	0.349
imp Ce-HY 4.3 wt%	30 / 70	92	0.08
imp Ce-HY 16 wt%	5 / 95	57	<0.030
Bulk CeO ₂	~ 0 / ~ 100	<291	0.04

References

- [1] Y. Izumi, *Coordination Chemistry Reviews*, **257**, 171–186 (2013).
 [2] S. Wada *et al.*, *Frontiers in Chemistry*, **1**, Article 8 (2013).

* yizumi@faculty.chiba-u.jp