

XAFS Study on Structure of Yttrium-Modified Cerium Oxide

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1 Introduction

The catalytic conversion of ethanol to propene (ETP reaction) has very recently been developed to use bio-ethanol as a starting material for chemicals and reduce the carbon dioxide emission. Among the active catalysts that have been developed, nickel ion-loaded mesoporous silica MCM-41 [1], scandium-modified indium oxides [2], and yttrium-modified cerium oxides (Y/CeO₂) [3], Y/CeO₂ resulted in good propene yield and remarkable durability. The propene yield showed a volcano-shaped dependence on the Y amount, being maximized at 20 atom % Y to that of Ce. The structural property of Y/CeO₂ was characterized using XAFS spectra to reveal the correlation between the catalytic activity and the property.

2 Experiment

Ceria-based catalysts were prepared using a conventional impregnation method or a co-precipitation method. In the former, the parent ceria, obtained from Catalysis Society of Japan (JRC-CEO-3), was impregnated using aqueous solution of yttrium nitrate. In the latter, Ce(NO₃)₃·6H₂O, Y(NO₃)₃·6H₂O, and ammonium hydrogen carbonate were used as precursors and a precipitant, respectively, and the solid solution was prepared according to the literature [4]. All samples were calcined at 873 K for 5 h in air. Catalysts prepared by the impregnation and the co-precipitation method are denoted by Y(x)/CeO₂ and Y(x)-CeO₂, respectively, where *x* represents the atomic % to that of Ce. The XAFS spectrum of Y K-edge was recorded on BL-9C of PF-KEK.

3 Results and Discussion

Fig. 1a shows the Y K-edge XANES spectra of the Y/ and Y-CeO₂. Two noticeable features were observed. First, all samples show no pre-edge peaks around 17030 eV, assignable to the 1s→4d transition of Y. This s→d transition is partially allowed for the distortion of octahedral environment, only when p-orbitals are mixed with d-orbitals. No appearance of this transition indicated little distortion of the octahedral symmetry. The second point was change in the white line shape with the sample. All samples exhibited two peaks at 17050 and 17058 eV attributable to two inequivalent Y sites in the C-type bixbyite structure, although the peak shapes were different. The Y(10)/, Y(20)/, and Y(67)-CeO₂ samples gave almost the same spectra, indicating the equivalent distributions of Y in the fluorite structure of CeO₂. On the other hand, the C-type sesquioxide Y₂O₃ and heavily

Y-doped Y(50)/CeO₂ exhibited the distinct increments in the 17058 eV. The change suggested the increase in the Y₂O₃ phase on these samples.

The FT-EXAFS spectra shown in Fig. 1b gave valuable information on the local structure. The Y(50)/CeO₂ and C-type Y₂O₃ samples showed three bands: the first peak at 1.8 Å was due to the Y-O shell, and the second and third peaks at 3.1 and 3.8 Å were due to two Y-Y shells distributed at different distance. In contrast, the Y(10)/, Y(20)/, and Y(67)-CeO₂ samples showed two significant signals at 1.8 and 3.6 Å which were attributed to the Y-O and Y-O-Ce shells, respectively. The Y(20)/CeO₂ sample also gave a small peak at 3.1 Å due to the Y-O-Y shell. The appearance of the 3.6 Å peaks for the Y(10)/, Y(20)/, and Y(67)-CeO₂ was interpreted as the evidence for formation of solid solution of CeO₂ and Y₂O₃ and no appearance of this peak for the Y(50)/CeO₂ was attributed to generation of thick Y₂O₃ phase on the surface.

From the above results, below 10 atom % Y, Y atoms were used for the formation of surface solid solution of CeO₂-Y₂O₃. At around 20 atom % Y, the surface and the inside of Y/CeO₂ were nearly covered with the solid solution. Too much Y loading (around 50 atom % Y) would cause the formation of thick Y₂O₃ layers. Taking the dependency of catalytic activity of Y/CeO₂ on Y loading into consideration, it was indicated that the solid solution phase of CeO₂ and Y₂O₃ is catalytically active for the ETP reaction.

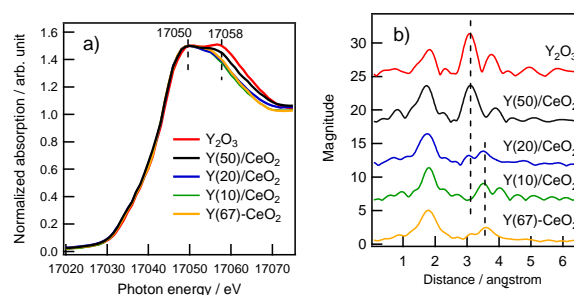


Fig. 1: Y K-edge XANES (a) and FT-EXAFS spectra (b) of Y/CeO₂, Y-CeO₂, and reference Y₂O₃.

References

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