XAFS analysis of the three-body interaction among Pd, CeO₂ and Al₂O₃ in methanol synthesis catalysts

Hiroyoshi KANAI¹, Hideyuki YAMANE², Seiichiro IMAMURA²

¹Department of Environmental Information, Kyoto Prefectural University, Sakyō-ku, Kyoto 606-8522, Japan
²Department of Chemistry, Kyoto Institute of Technology, Sakyō-ku, Kyoto, 606-8585, Japan

Introduction

The C1 chemistry based on synthesis gas has been extensively exploited. We have found that co-impregnation of CeO₂ with Pd/Al₂O₃ catalyst selectively produced dimethyl ether which is formed from methanol once-produced. XAFS analyses of Ce L and Pd K edges were done to elucidate the role of CeO₂.

Experimental

Pd-CeO₂/Al₂O₃ catalysts (Pd: 5 wt%, Ce/Pd=1) were prepared by a co-impregnation of Pd(NO₃)₂ and Ce(NO₃)₃ on γ-Al₂O₃, followed by calcinations at 823K for 3 h. They were reduced with H₂ (6.5 kPa) at 593-873K for 1 h. All samples were pressed to pellets and sealed into Q-pack pouches under N₂. X-ray absorption spectra were obtained with the 7C and 10B beam lines by a transmission mode.

Results and discussion

Ce L₃-edge XANES spectra are shown in Fig. 1. Reduction of CeO₂ to Ce₂O₃ requires as high as 1673K[1]. CeO₂ in Pd-CeO₂/Al₂O₃ was reduced with H₂ at higher than 873K. Less amounts of CeO₂ were reduced without Pd. The behavior was contrasted with that none of CeO₂ in Pd-CeO₂/MgO and on MgO was reduced even at 873K[2]. Ce₂O₃ itself is sensitive to air, but no change was observed for reduced cerium oxide on Al₂O₃ when exposed to air. CeO₂ strongly interacts with Al₂O₃, but less with MgO.

Edge energies of Pd K edge in Pd-CeO₂/Al₂O₃ which are between those of Pd metal and PdO are almost the same for Pd-CeO₂/Al₂O₃ reduced at 593-873K. The isosbestic points indicate the coexistence of Pd(0) and Pd(II). Reducing at as high as 873K never gave all Pd species into metallic Pd.

FT spectra of Pd K edge EXAFS were shown in Fig. 2. Gradual increase in the height of a peak assigned to Pd-Pd bond is observed. Signals corresponding to Pd-O bonds in the range of 1-2 Å are very small. Most of Pd are metallic. The increase of reduction temperature led to the increase of peak heights of Pd-Pd bond.

It can be concluded that the strong three-body interaction among Pd, CeO₂ and Al₂O₃ led to a mixture of Pd(0) and Pd(II) for selective production of methanol.

Fig.1 Ce L₃-edge XANES spectra. Effect of reduction temperature: (A) 5 wt% Pd-8.1 wt% CeO₂/Al₂O₃, (B) 8.1 wt% CeO₂/Al₂O₃, (C) Standard compounds.

*Imamura@ipc.kit.ac.jp