XAFS analysis of the three-body interaction among Pd, CeO_2 and Al_2O_3 in methanol synthesis catalysts

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Introduction

The C1 chemistry based on synthesis gas has been extensively exploited. We have found that co-impregnation of CeO_2 with Pd/Al_2O_3 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 CeO_2.

Experimentals

$Pd\text{-}CeO_2/Al_2O_3$ catalysts(Pd: 5 wt%, Ce/Pd=1) were prepared by a co-impregnation of $Pd(NO_3)_2$ and $Ce(NO_3)_4$ on $\gamma\text{-}Al_2O_3$, followed by calcinations at 823K for 3 h. They were reduced with H_2(6.5 kPa) at 593-873K for 1 h. All samples were pressed to pellets and sealed into Q-pack pouches under N_2. X-ray absorption spectra were obtained with the 7C and 10B beam lines by a transmission mode.

Results and discussion

Ce L_3-edge XANES spectra are shown in Fig. 1. Reduction of CeO_2 to Ce_2O_3 requires as high as 1673K[1]. CeO_2 in $Pd\text{-}CeO_2/Al_2O_3$ was reduced with H_2 at higher than 873K. Less amounts of CeO_2 were reduced without Pd. The behavior was contrasted with that none of CeO_2 in $Pd\text{-}CeO_2/MgO$ and on MgO was reduced even at 873K [2]. Ce_2O_3 itself is sensitive to air, but no change was observed for reduced cerium oxide on Al_2O_3 when exposed to air. CeO_2 strongly interacts with Al_2O_3, but less with MgO.

Edge energies of Pd K edge in $Pd\text{-}CeO_2/Al_2O_3$ which are between those of Pd metal and PdO are almost the same for $Pd\text{-}CeO_2/Al_2O_3$ 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 A 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, CeO_2 and Al_2O_3 led to a mixture of Pd(0) and Pd(II) for selective production of methanol.

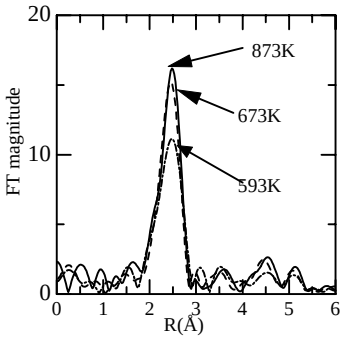

Fig. 2 Pd FT specta of 5 wt%Pd-8.1 wt%CeO_2/Al_2O_3. Effect of reduction temperature.

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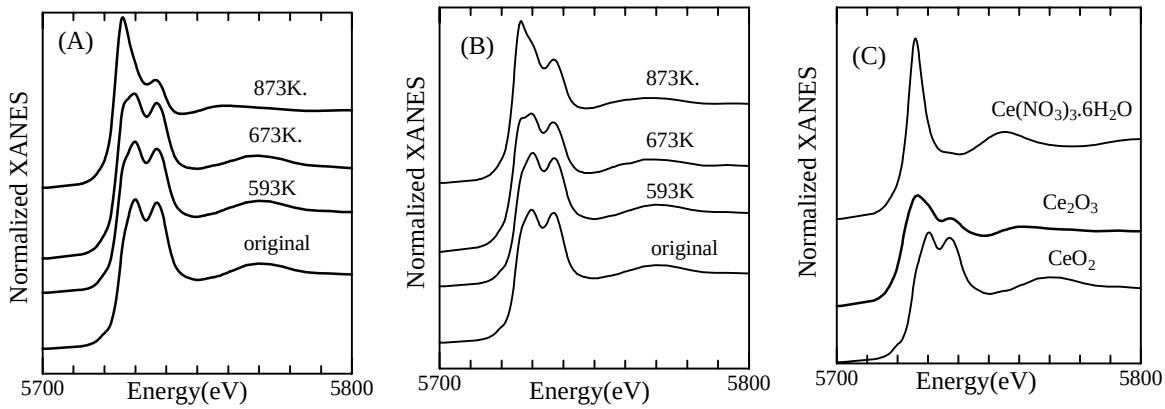

Fig.1 Ce L_3-edge XANES spectra. Effect of reduction temperature: (A) 5 wt%Pd-8.1 wt% CeO_2/Al_2O_3, (B) 8.1 wt% CeO_2/Al_2O_3, (C) Standard compounds.