

XAFS Analysis for the Local Structures of Noble Metal-Ceria Catalysts

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The addition of cerium oxide to Pd/MgO enormously accelerated methanol production from CO and H₂ than that to Pd/Al₂O₃ and Pd/SiO₂. We have done XAFS analysis of Ce K edge to elucidate the role of cerium oxide.

Experimental

Catalysts were prepared by impregnation of MgO, Al₂O₃ and SiO₂ with an aqueous solution of palladium nitrate. An aqueous mixture of palladium nitrate and cerium(IV) nitrate was treated with MgO and Al₂O₃ followed by evaporation to dryness and calcination in air at 823K. Palladium catalysts were treated with hydrogen (100 Torr) at 593K for 2 hours. XAFS measurements were done at the BL01B1 station of JASRI for cerium K edge of H₂ treated samples in glass tubings.

Results and Discussion

XANES Since we didn't have a standard cerium metal, energy calibration was done for K edge of CeO₂ as 40.4560 keV.

The K edge of Ce₂O₃ was estimated as 40.4476 eV. The difference between K edges of Ce₂O₃ and CeO₂ is 8.4 eV as is similarly observed between their L edges.

XANES spectra of Pd-CeO₂/MgO, Pd-CeO₂/Al₂O₃ and their H₂-treated catalysts were shown in Fig. 1. No absorption energy shift was observed between H₂-treated and non-treated Pd-CeO₂/MgO. Their spectra are very similar to that of CeO₂. Cerium oxide was not reduced at all with hydrogen. The K edge XANES measured at the Photon Factory suggests that Pd of Pd/MgO is in a metallic state, but Pd of Pd-CeO₂/MgO is still in an oxidized state. Cerium oxide keeps Pd²⁺ resistant to reduction with hydrogen. Or Pd²⁺ makes cerium to stay Ce⁴⁺ since cerium on MgO was not susceptible to reduction.

A little lower shift (3.9 eV) was observed for the K edge absorption of H₂-treated Pd-CeO₂/Al₂O₃. The shift is less than the shift for Ce₂O₃. Since no shift was observed in H₂-treated CeO₂/Al₂O₃, the presence of palladium made cerium in a little reduced state.

Also a lower shift was observed for H₂-treated Pd-CeO₂/SiO₂.

EXAFS Fourier transforms of three samples

were shown in Fig. 2. When Pd-CeO₂/MgO was treated with hydrogen, the amplitude of nearest Ce-Ce bond decreased. New Ce-O bond assigned to reduced-Ce-O bond appears in the FT of Pd-CeO₂/Al₂O₃.

Strong interaction between Pd and cerium oxide on MgO keeps both species in oxidized states. However, such interaction can not be formed on SiO₂ and Al₂O₃.

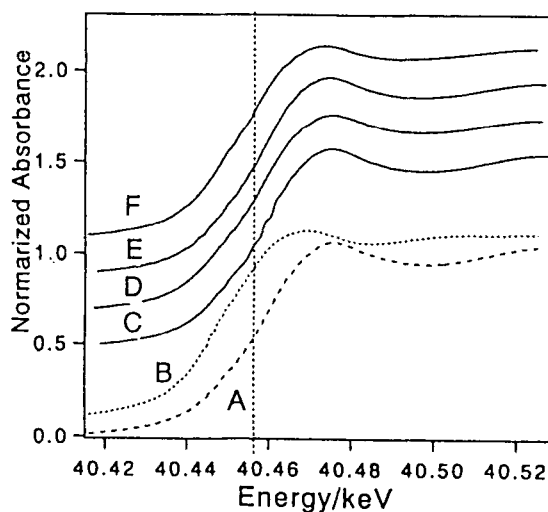


Fig. 1 XANES spectra. (A): CeO₂, (B): Ce₂O₃, (C): CeO₂/MgO, (D): H₂-treated Pd-CeO₂/MgO, (E): CeO₂/Al₂O₃, (F): H₂-treated Pd-CeO₂/Al₂O₃.

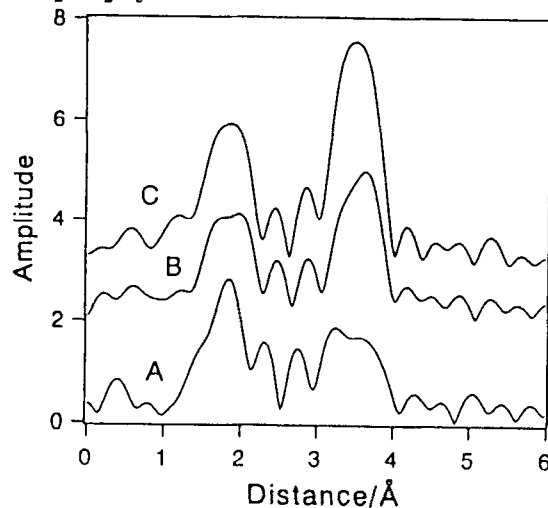


Fig. 2 Fourier transforms. (A): H₂-treated Pd-CeO₂/MgO, (B): H₂-treated Pd-CeO₂/Al₂O₃, (C): CeO₂/MgO.