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Characterization of PdCuCr Ternary Nanoparticles Constructed within a Basic Resin

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1 Introduction

Hydrogen has received increasing attention as a candidate for clean energy, and efficient energy conversion can be realized by combining with fuel cell technology. However, the widespread application of hydrogen as a transportation fuel is limited, mainly because of controllable storage and delivery problems. A considerable amount of research effort is currently devoted to exploring new storage methods.[1-5] Among investigated, formic acid (HCOOH), which is a liquid at room temperature and contains 4.4 wt% hydrogen, is one of the major products formed during biomass processing and is widely recognized as a convenient hydrogen carrier for fuel cells designed for portable use.

In the course of our ongoing studies to explore practical catalysts for targeted reactions, we found that PdCuCr ternary NPs within a macroreticular basic resin exhibit significant catalytic enhancement over that of bimetallic PdCu, PdCr, and monometallic Pd NPs. Here, we report the detail charactyerization of Cr species by in sutu XAFS measurements.

2 Experiment

Synthesis of PdCuCr/resin catalyst: Prior to the deposition, resins were crushed by a ball mill (600 rpm for 10 min). The resin (1.0 g) was mixed with 80 mL of aqueous solution containing 10 mL of $PdCl_2$ (29.7 mM), 5 mL of $CuCl_2{\cdot}2H_2O$ (29.7 mM), and 5 mL of $Cr(NO_3)_3{\cdot}9H_2O$ (29.7 mM) and stirred at room temperature for 1 h. The suspension was evaporated under vacuum and the obtained powder was dried overnight. Subsequently, the samples were pre-reduced with $NaBH_4$, giving PdCuCr/resin (Pd 3wt%; molar ratio of Pd : Cu : Cr = 1 : 0.5 : 0.5).

3 Results and Discussion

The Cr K-edge XANES spectrum for CrO_3 had an intense pre-edge peak at 5992 eV, which is characteristic of terminal Cr^{6+}=O species with a tetrahedral coordination (**Figure 1A**). The shape of the XANES spectrum for PdCuCr/resin is quite different from that of CrO_3 due to the absence of the characteristic pre-edge peak, but is similar to those of Cr^{3+}-type spectra, such as Cr_2O_3 and $Cr(NO_3)_3$. The edge energy for the PdCuCr sample is higher than that for Cr foil, which suggests that the Cr species is in a +3 oxidation state. In the FT-EXAFS spectra, the bond length of the first Cr−O bond in PdCuCr resembles those in Cr_2O_3 and $Cr(NO_3)_3$, but is longer than that in CrO_3, which reveals the lack of a Cr=O double bond in the PdCuCr/resin sample (**Figure 1B**). In comparison with the reference Cr_2O_3, the intensity of the second peak for PdCuCr/resin is significantly weakened. This peak in PdCuCr is attributable to the contiguous Cr−O−M (M: Cr, Cu, Pd) bonds. The reduced intensity in this region can be explained by the formation of structurally disordered and extremely small NPs. No metallic bonds, detectable at around 2.3 Å for Cr foil, were observed. Since the reduction potentials of Cr^{3+} ions ($E^{\circ}(Cr^{3+}/Cr^{2+}) = -0.42$ V, $E^{\circ}(Cr^{2+}/Cr^{0}) = -0.90$ V vs. NHE) are more negative than Pd^{2+} and Cu^{2+} ions ($E^{\circ}(Pd^{2+}/Pt^{0}) = +0.99$ V, $E^{\circ}(Cu^{2+}/Cu^{0}) = +0.34$ V vs. NHE), the reduction of Cr^{3+} ions is retarded more than those of Pd^{2+} and Cu^{2+} ions, and preferentially constitute extremely small clusters on the surface of NPs by interaction with Pd^0 and Cu^0.

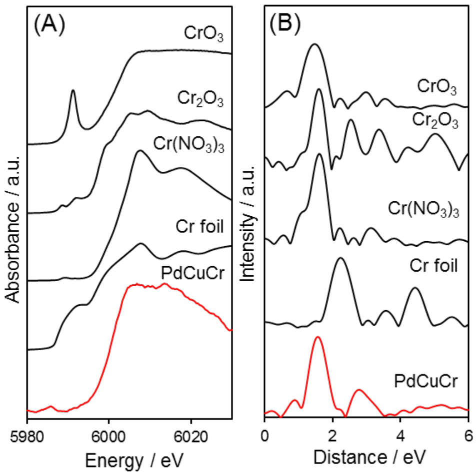

Figure 1. Cr K-edge (A) XANES and (B) FT-EXAFS spectra.

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