

Spectroscopic Analysis of Supported Bimetallic Catalyst Surfaces

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Introduction

Supported bimetallic catalysts are of great interest due to their potential for favorable synergy between the metals resulting in catalysts that are superior to single metals. Combinations of Group 10 and Group 11 in particular have been investigated for a variety of industrial applications such as PdAu for vinyl acetate synthesis, PdCu for denitration of water, and PtCu for cleanup of chlorinated hydrocarbon streams. With all supported bimetallic catalysts, detailed characterization of the distribution of metals between the bulk and surface of the nanoparticles is challenging, especially with respect to time-on-stream response in various gas atmospheres, including under reaction conditions.

In this work we studied three bimetallic catalysts, PdAu, PdCu, and PtCu all supported on Al₂O₃, in an effort to develop reliable, quantitative methods of characterizing the surface composition in supported bimetallic nanoparticles. Using a combination of Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Absorption Spectroscopy (XAS), and analysis of the Pair Distribution Function (PDF) we tracked surface composition changes induced by treatment in CO, He, H₂, and their mixtures, and the reversibility of those changes.

Materials and Methods

PdCu/Al₂O₃ and PtCu/Al₂O₃ were prepared by incipient wetness impregnation and PdAu/Al₂O₃ was prepared by deposition precipitation of Au followed by incipient wetness impregnation of Pd, using high purity precursors from Aldrich. γ -Al₂O₃ was synthesized in-house from aluminum isopropoxide; its structure was confirmed by XRD, the BET surface area was 200 m²/g and the liquid pore volume was 1.2 mL/g. The FTIR, XAS, and PDF data were collected from samples in controlled gas and temperature environments.

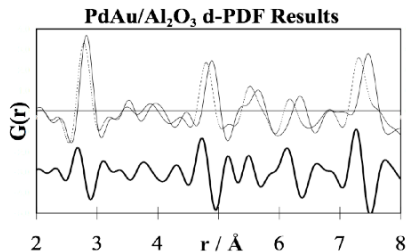


Figure 1. PDF results from a PdAu/Al₂O₃ sample revealed a significant difference (thick line) between the freshly reduced sample (thin line) and the CO treated sample (dashed line).

Results and Discussion

The surface compositions of all three catalysts were affected by treatment in the gas atmospheres. In CO, the metal that binds more strongly to the CO was pulled toward the surface. The changes induced by CO treatment of a PdAu/Al₂O₃ sample as measured by differential PDF analysis are depicted in Figure 1.

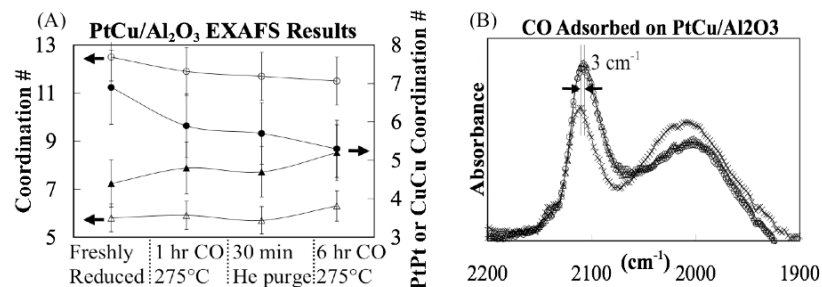


Figure 2. (A) For a PtCu/Al₂O₃ sample, treatment in CO caused total Pt coordination (○) and Pt-Pt coordination (●) to decrease, while total Cu coordination (△) and Cu-Cu coordination (▲) increased. (B) Compared to a fresh PtCu/Al₂O₃ sample (○), the CO adsorption band on a CO treated sample (×) was shifted, but further treatment in H₂ reversed the changes (△).

The EXAFS and FTIR results in Figure 2 show the effect of gas treatments on PtCu/Al₂O₃. EXAFS of the freshly reduced sample revealed that Pt was coordinated to 55% Pt and 45% Cu with a total coordination number of ~12, and Cu was coordinated to 75% Cu and only 25% Pt with a total coordination number of ~6. This indicated that the freshly reduced catalyst comprised a well-mixed Pt-Cu core encapsulated by a Cu shell. As is illustrated in Figure 2(A), CO treatment effected a decrease in total Pt coordination and an increase in total Cu coordination, suggesting that Pt moved from the core toward the surface. This reasoning is strengthened by the concurrent increase in Pt-Cu EXAFS correlation despite a decrease in Cu-Pt EXAFS correlation. Figure 2(B) shows the FTIR results from a similar CO treatment experiment. The initial peak position reflected CO adsorbed on Cu that was electronically modified by Pt.¹ The 3 cm⁻¹ shift after CO treatment indicated an increased interaction of Pt with Cu. Upon subsequent H₂ treatment the IR peaks shifted back to the original positions.

Significance

We have demonstrated methods for carrying out quantitative characterization of small changes in the bulk and surface distributions of metals in three supported bimetallic catalysts. More complete understanding of time-on-stream response to various gas atmospheres and under reaction conditions will aid in implementation of viable, long term, supported bimetallic industrial catalysts.

References

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