

Introduction

Many monometallic catalysts used in industrial chemical processes have been replaced by bimetallic catalysts to give enhanced performance [1]. These bimetallic catalysts are often prepared by either co-impregnation or successive impregnation [2]. In both methods, it is very difficult to ensure formation of truly bimetallic particles; instead, formation of separate monometallic particles and bimetallic particles with varying compositions occurs. The resulting complex mixture of bimetallic and monometallic particles results in poor control over the final catalyst performance, complicates catalyst characterization, and makes it very difficult to directly correlate the relationship between catalyst composition, characterization, and performance. An alternate method for the preparation of bimetallic catalysts is electroless deposition (ED) of reducible metal salts onto other metals [3]. ED is a liquid phase, kinetic process for the selective deposition of metallic components onto catalytically active sites by a controlled chemical reaction that is catalyzed by the activation of a suitable reducing agent on a pre-existing metal (catalysis) or the metal which is being deposited (auto-catalysis). Whether or not catalytic or auto-catalytic deposition predominates is a function of the organic reducing agent (formaldehyde, borohydride, amine boranes, hydrazine, etc.), the reducible metal salt in solution, and/or the pre-existing catalytic metal surface. In principle, ED should result in the targeted deposition of the secondary metal onto a metallic surface with no formation of isolated crystallites of the secondary metal on the catalyst support. Thus, it is possible to systematically vary the coverage of M on a catalytic surface, making it possible to examine potential ensemble, electronic, and/or bifunctional catalysis effects.

We present data for the characterization and catalytic evaluation of a series of bimetallic Ag-Pt catalysts prepared by the ED of variable amounts of Ag on Pt/SiO₂ [2]. Similarly, preparation and characterization data will be presented for Cu deposition on Pd/SiO₂ [4] and Au deposition on Pd/SiO₂ to contrast differences in the kinetics of ED and the sites for Cu, Ag, and Au deposition on the Pt and Pd surfaces. Finally, preparation and characterization data will be presented for bimetallic Pt-Co particles prepared by the ED of variable levels of Pt on Co/C to form Co core-Pt shell bimetallic particles that have applications as improved PEM fuel cell electrocatalysts.

Results and Discussion

Chemisorption results and FTIR of adsorbed CO are shown in **Figures 1 and 2** for a series of Ag-Pt/SiO₂ catalysts. The results show that Ag is systematically deposited on the Pt surface until approximately 0.50 ML coverage. Higher coverages of Ag result in autocatalytic deposition of Ag on Ag sites, consistent with the activation trend of formaldehyde on Ag and Pt surfaces (Ag > Pt for HCHO activation). The FTIR data indicate that Ag is preferentially deposited on the Pt(111) sites, rather than the coordinatively unsaturated corner and edge Pt sites. For the case of Cu deposition on Pd/SiO₂, CO chemisorption results show that Cu is preferentially deposited on Pd until approximately 0.3 ML of Cu coverage. Deposition of higher concentrations of Cu results in autocatalytic deposition of Cu. FTIR results show that initial Cu deposition is slightly preferred on corner/edge Pd sites, although Cu deposition does occur on all Pd sites; the specificity of Cu deposition on Pd is not as pronounced as Ag on Pt.

Electroless deposition of Pt onto Pd-seeded carbon supports has also been used to improve Pt dispersion and distribution of Pt particles sizes [5] for PEM fuel cell catalysts. Platinum particles prepared by ED of Pt onto Pd-seeded carbon supports produce smaller particles with a more narrow distribution than a commercial PEM fuel cell catalyst because of the controlled deposition rate of Pt during ED. Finally, ED has been used to deposit Pt on a

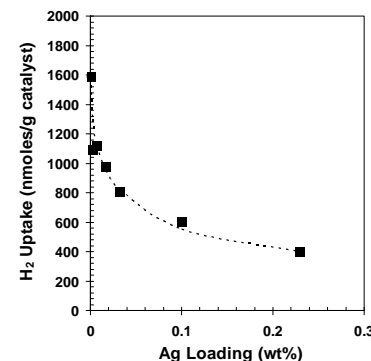


Figure 1. Effect of Ag coverage of Pt on H₂ uptake.

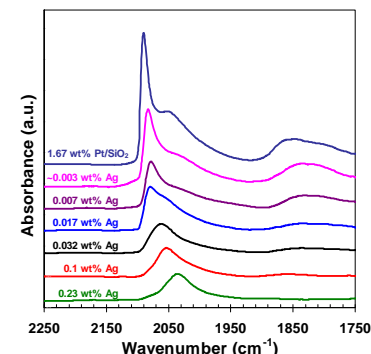


Figure 2. FTIR of CO on Ag-modified Pt catalyst.

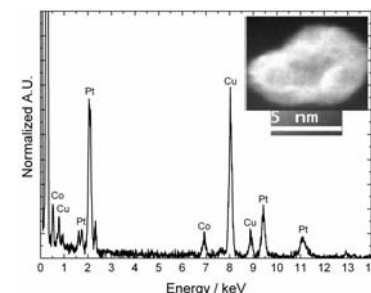


Figure 3. EDX spectra and HRTEM image of Pt-Co/C

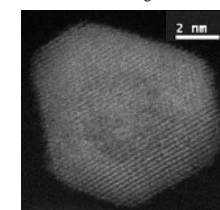


Figure 4. STEM image of Pt-Co.

Co/C catalyst. By using dimethylamine borane (DMAB) as the reducing agent, the catalytic deposition of Pt on Co is favored until the Co surface is essentially covered by Pt. Autocatalytic deposition of Pt on Pt then occurs to form increasingly thicker Pt shells; the thickness of the Pt shell is controlled by the concentration of PtCl₆⁴⁻ and DMAB. Typical HRTEM micrographs of Co-Pt core shell particles are shown in Figures 3 and 4. The darker interior of the particles correspond to the Co core, while the Pt shell appears brighter. The EDX in Figure 4 indicated the particle contains both Co and Pt, consistent with the core-shell model.

Significance

Electroless deposition is an industrially-relevant method of catalyst preparation that provides a pathway for the controlled modification of multi-metallic catalyst compositions. Applications range from chemical and environmental catalysis to PEM fuel cells and biomass conversion.

References

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