Investigation of the Role of Pd-Alloying in the Coarsening Behavior of Nano-Particulate Alumina-Supported Pt Catalysts for NO Oxidation

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Introduction

It is well known that highly-dispersed Pt loses surface area through particle coarsening, especially under lean-burn conditions [1,2]. Recent results have shown that alloying Pt with Pd in alumina-supported catalysts can suppress particle coarsening upon aging under such conditions, and that NO oxidation may be relatively insensitive to a Pd content approaching 50 mol% [3]. The mechanisms for this observed change in coarsening behavior are not fully understood. Moreover, multi-metallic alloy catalysts are generally expected to have different catalytic properties than their constituents. In the present work, various compositions of nano-particulate Pt-Pd catalysts were prepared from metal-organic precursors and exposed to various aging treatments. The chemical nature of these nanoparticles was characterized using both high angle annular dark field (HAADF) imaging and energy dispersive spectroscopy (EDS) in an analytical electron microscope (AEM). High resolution transmission electron microscopy (HRTEM) imaging was also performed.

Materials and Methods

Bimetallic catalysts were prepared by adsorption from solutions of mixtures of platinum(II) and palladium(II) bis-acetylacetonate precursors by methods described previously [4,5]. Catalyst samples were investigated in the 'as received' condition (no thermal aging) and after aging at 500°C, and 900°C. Aging took place in a quartz-tube furnace under a flowing (5 l/min) gas mixture of 5% O_2 and 10% H_2O in N_2 for 3 hours. The samples were then reduced for 1 h at 500°C under a flow of 1% H_2 in N_2. Following typical procedures [6], these samples were prepared for TEM examination by dispersing a small amount of powder on a 300 mesh carbon-coated copper grid.

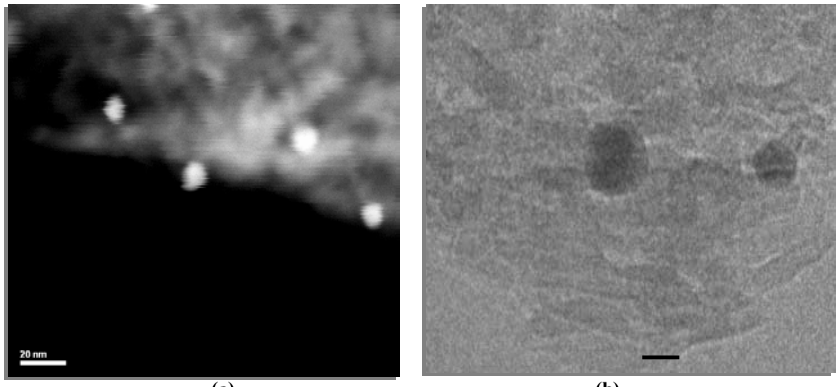
Two instruments were used for transmission electron microscopy analysis. HRTEM was performed with a JEOL 3011 high resolution microscope equipped with an integrated x-ray EDS detector. Point-to-point resolution was 0.17 nm. Z-contrast scanning transmission electron microscope (STEM) analysis and other AEM techniques were performed on a JEOL 2010F field emission microscope.

Results and Discussion

Typical images obtained from HRTEM and Z-contrast imaging of 90%Pt-10%Pd /Al_2O_3 samples are shown in Figure 1. EDS and other analytical techniques were used to measure the composition of individual particles in samples after various degrees of aging. Initial experiments indicate that extended-time (>100 minutes) EDS mapping could provide the means to check for alloy formation.

Significance

Dispersions determined from HRTEM measurements can be compared with CO chemisorption data, potentially providing CO adsorption stoichiometries as a function of alloy composition in the Pt-Pd system. Secondly, TEM combined with EDS mapping of selected samples should give a more complete picture of the role of Pd in the coarsening behavior of Pt catalysts than can be obtained from indirect techniques, such as XRD.



(a) (b)

Figure 1. (a) Z-contrast and (b) HRTEM of particles from (90%Pt-10%Pd)/Al_2O_3 catalysts aged at 500°C.

References

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