

Characterization of Pd/ γ -Al₂O₃ Catalysts Prepared from β -Diketonate Precursors

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Introduction

Supported Pd catalysts are used in a variety of applications including selective hydrogenation, catalytic combustion, and vinyl acetate synthesis. Commercial Pd/ γ -Al₂O₃ catalysts typically are prepared by aqueous impregnation using inorganic salt precursors. The most common technique, incipient wetness impregnation, often results in non-uniform Pd distributions, poor Pd dispersions, and unwanted modification of the surface chemistry of the support. In this work, Pd/ γ -Al₂O₃ catalysts were prepared from the β -diketonate precursors, [Pd(acac)₂] acac = acetylacetonate and [Pd(hfac)₂] hfac = hexafluoroacetylacetonate. The [Pd(hfac)₂] precursor was chosen for its high solubility in liquid carbon dioxide (L-CO₂), an environmentally benign solvent with excellent wetting characteristics. The reduced catalysts were characterized by extended x-ray absorption fine structure (EXAFS) spectroscopy, x-ray photoelectron spectroscopy (XPS), pulsed CO chemisorption, diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS), and transmission electron microscopy (TEM).

Materials and Methods

[Pd(acac)₂] and [Pd(hfac)₂] were adsorbed on pretreated γ -Al₂O₃ powders (250 m²/g) from toluene and L-CO₂ solutions, respectively. The [Pd(acac)₂]/ γ -Al₂O₃ sample (0.5 wt.% Pd) was stored and manipulated under dry nitrogen and reduced *in situ* at 350°C prior to EXAFS, CO chemisorption, and DRIFTS measurements. A series of catalysts was prepared from [Pd(hfac)₂], and samples were reduced initially in the high-pressure CO₂ reaction cell using H₂ at 75°C [1]. The samples were removed, stored in a desiccator, re-reduced *in situ* at 250°C prior to EXAFS, CO chemisorption, and DRIFTS measurements. A commercial 1 wt.% Pd/Al₂O₃ catalyst (Johnson Mathey) was examined for comparison and underwent the same pretreatment as the catalysts prepared from [Pd(hfac)₂]. *In situ* x-ray absorption spectroscopy measurements were performed on beam line X-10C of the National Synchrotron Light Source. Selected catalysts derived from [Pd(hfac)₂] were characterized by *ex situ* XPS.

Results and Discussion

EXAFS spectroscopy of the 0.5 wt.% sample prepared from [Pd(acac)₂] gave an average Pd-Pd coordination number and distance of 6.3 and 2.73 Å, respectively, values indicative of highly dispersed supported Pd particles. This inference was confirmed by pulsed CO chemisorption measurements that gave a Pd dispersion of 70% and DRIFTS that evidenced an unusually large fraction of linear CO.

EXAFS spectroscopy of the 0.58 wt.% sample prepared from [Pd(hfac)₂] indicated that the initially oxidized Pd species were converted after re-reduction to supported Pd(0) particles. Pulsed CO chemisorption evidenced that the Pd dispersion of this sample was 55% and that the dispersion decreased linearly as the Pd loading was increased incrementally from 1.8 (51%

dispersion) to 3.9 wt.% (5% dispersion). TEM images of the 0.58 wt.% Pd sample evidenced 2-3 nm supported Pd particles consistent with the estimated dispersion. For samples with higher Pd loadings, larger particles with highly faceted surfaces are seen in the TEM images. DRIFTS of CO adsorbed on the samples prepared from [Pd(hfac)₂] evidenced a preponderance of linearly adsorbed CO species. In contrast, CO chemisorption on a commercial 1 wt.% Pd/Al₂O₃ catalyst (with 30% dispersion) gave predominantly 2-fold bridging CO species. XPS reveals a residual fluorine concentration of 16.8 at.% for the 3.9 wt.% catalyst prepared from the fluorinated β -diketonate precursor.

Significance

Supported Pd catalysts derived by impregnating γ -Al₂O₃ with [Pd(hfac)₂] using L-CO₂ can have higher dispersions than commercial catalysts with equivalent loadings. The supported Pd particles possess a more highly faceted morphology than either a commercial Pd/Al₂O₃ catalyst or a catalyst prepared from a non-fluorinated β -diketonate precursor. A higher fraction of edge- and corner-sites is inferred from CO DRIFTS experiments. This unusual site distribution may be useful for some catalytic reactions; however, XPS reveals that these catalysts contain significant amounts of residual fluorine that is likely bound to the γ -Al₂O₃ support.

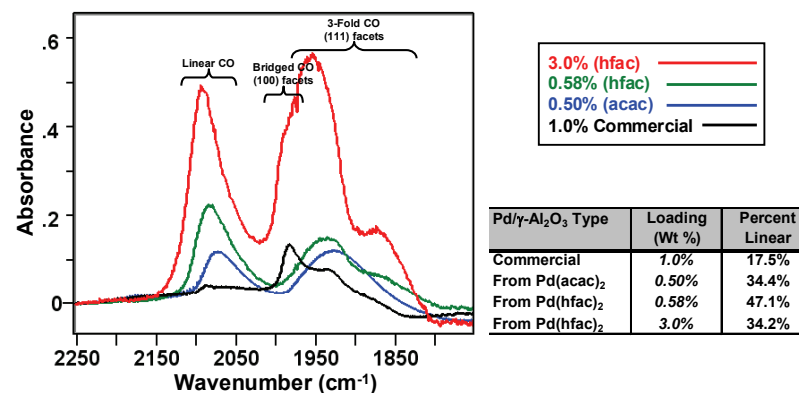


Figure 1. DRIFT spectra of CO adsorbed on four catalyst samples reveal differences in the site distributions. In the commercial catalyst, CO bonds primarily at bridging sites. The catalysts prepared from β -diketonate precursors, especially those produced by the L-CO₂ process, exhibit a larger area percentage of linear CO.

References

- Kim, J., Roberts, G.W., and Kiserow, D.J. *Chem. Mater.* 18, 4710 (2006).