Structure and Composition of Supported Palladium Catalysts During Hydrodeoxygenation of Phenol in Water

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Introduction

The conversion of biomass into energy carriers always involves reactions in the presence of water, either as a solvent or a product. For example, Chen et al.,1 have reported the quantitative conversion of aqueous mixtures of bio-derived phenolic compounds to saturated hydrocarbons and alcohols using combined metal and acid catalysts. This reaction sequence represents a prototypic chemical transformation of lignin-derived phenols to a component of a transportation fuel. Because this reaction is performed at elevated temperature (473 K) and pressure (up to 50 bar H2), the state of the Pd catalysts during reaction is not obvious, particularly in the case of Pd, which is susceptible to forming subsurface and bulk metal hydrides. We present here first results on the state of such Pd nanoparticles in aqueous phase during various stages of catalyst conditioning and catalytic action using X-ray Absorption Spectroscopy (XAS) with the aim of better defining its state under dynamic variations of the environment.

Materials and Methods

Commercial catalysts (Pd/C, Pd/Al2O3 and Pd/SiO2) and reagents were used as received. The near-edge structure (XANES) and fine-structure (XAFS) measurements were performed in transmission mode at the Pacific Northwest Consortium/X-ray Science Division (PNC/XSD) bending-magnet beamline at Sector 20 of the Advanced Photon Source (APS) at Argonne National Laboratory (ANL). The previously described high-pressure, high-temperature microreactor/cell and H2 delivery system [2] was modified for operation at 473 K using glassy carbon windows. Typically the cell was charged with 30-mg of catalyst and 1.1 mL of aqueous solution and pressurized with H2 (~35 bar) to give 50 bar total pressure at 473 K. The liquid contents of the cell were removed after reaction and analyzed by capillary gas chromatography. Ab initio molecular dynamics simulations were performed using spin-polarized dispersion corrected density functional theory implemented in the CP2K code (http://www.cp2k.org).

Results and Discussion

Figure 2 shows a Pd K-edge spectra we obtained during hydrodeoxygenation (HDO) of phenol catalyzed by 10 wt% Pd/C. The black spectrum was obtained at the start of reaction. Repeated measurements showed it to persist for up to a few hours before changing abruptly to the latter red spectrum. Analyses by gas chromatography of the recovered reaction solutions showed the phenol conversion to be ≥95% indicating the change to latter spectrum correlated with the ending of the HDO reaction. Quantitative analysis of the data showed that the Pd-Pd nearest neighbor distance increased from an initial value of ~277 pm to ~283 pm at the reaction’s end. The particle sizes estimated from the Pd-Pd first coordination number (10.1) averaged ~4 nm and remained about constant throughout the reaction. These results show that little change in structure of the particles occurs during the reaction other than the lattice expansion to accommodate filling of additional interstitial sites with hydrogen when the reduction of substrates is complete. Experiments with 5 wt% Pd nanoparticles on C, Al2O3 and SiO2 supports having average particles sizes of 3, 4 and 6 nm, respectively provided similar results. Furthermore, the reduction of Pd nanoparticles in either H2-saturated water or in H2 gas produced the same XAFS spectra. The results of ab initio molecular dynamic simulations support these experimental results by showing only weak interaction of water with surfaces of PdHx.

Significance

The state and structure of the supported PdHx nanoparticles under hydrogen are unaffected by water, acid, substrates or the supports (C, Al2O3, or SiO2). The particles undergo a slight increase in size with the conversion of reactants due to the absorption of hydrogen.

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