Journal of Catalysis 318 (2014) 75–84

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Modifying structure-sensitive reactions by addition of Zn to Pd

David J. Childers [a], Neil M. Schweitzer [b], Seyed Mehdi Kamali Shahari [c], Robert M. Rioux [c], Jeffrey T. Miller [d,*], Randall J. Meyer [a,*]

[a] *Department of Chemical Engineering, University of Illinois at Chicago, United States*
[b] *Center for Catalysis and Surface Science, Northwestern University, United States*
[c] *Department of Chemical Engineering, The Pennsylvania State University, United States*
[d] *Division of Chemical Sciences and Engineering, Argonne National Laboratory, United States*

ARTICLE INFO

Article history:
Received 9 May 2014
Revised 17 July 2014
Accepted 18 July 2014
Available online 17 August 2014

Keywords:
Structure-sensitive reaction
Intermetallic PdZn
Propane dehydrogenation
CleanCat
DRIFTS
CO calorimetry
EXAFS
Neopentane conversion

ABSTRACT

Silica-supported Pd and PdZn nanoparticles of a similar size were evaluated for neopentane hydrogenolysis/isomerization and propane hydrogenolysis/dehydrogenation. Monometallic Pd showed high neopentane hydrogenolysis selectivity. Addition of small amounts of Zn to Pd lead Pd–Zn scatters in the EXAFS spectrum and an increase in the linear bonded CO by IR. In addition, the neopentane turnover rate decreased by nearly 10 times with little change in the selectivity. Increasing amounts of Zn lead to greater Pd–Zn interactions, higher linear-to-bridging CO ratios by IR and complete loss of neopentane conversion. Pd NPs also had high selectivity for propane hydrogenolysis and thus were poorly selective for propylene. The PdZn bimetallic catalysts, however, were able to preferentially catalyze dehydrogenation, were not active for propane hydrogenolysis, and thus were highly selective for propylene formation. The decrease in hydrogenolysis selectivity was attributed to the isolation of active Pd atoms by inactive metallic Zn, demonstrating that hydrogenolysis requires a particular reactive ensemble whereas propane dehydrogenation does not.

1. Introduction

The catalytic performance of metal nanoparticles can be modified by changes in the surface geometry due to modification of the particle size or changes in the electronic properties by the addition of promoters or alloy formation. Boudart was the first to divide reactions into two groups based on sensitivity of the catalytic activity to particle size [1]. Structure-sensitive reactions are those for which the kinetics is dependent on the particle size (due to changes in the coordination of surface atoms with particle size), while structure-insensitive reactions are independent of the particle size. For structure-sensitive reactions, the turnover rate (TOR), or rate per surface atom, changes with size. This geometric effect results because the active site for structure-sensitive reactions requires an ensemble of active atoms and the number of these ensembles changes with particle size. For structure-insensitive reactions, every surface atom is an active site, and thus, the rate is directly proportional to the dispersion.

Electronic effects alter the chemical reactivity of the metal nanoparticle due to changes in the electronic structure. These two effects are often interrelated as changes in surface geometry often lead to changes in electronic properties. For example, as the size of a metal cluster is reduced, the cluster exhibits quantum confinement effects that perturb the electronic structure and in some cases, can even give rise to a band gap [2–4]. The reduced coordination of the cluster often results in changes in the energy of the valence orbitals that alter the bond strength of adsorbates [5–7].

Alloying with another metal can also affect the electronic properties of a catalyst [8]. Two effects appear simultaneously when metals are alloyed. First, charge transfer may occur between the alloying elements due to differences in the level of filling and relative energies of the valence orbitals. Second, changes in hybridization of the bonding between metals may result due to changes in the bond distances between metal atoms. At the same time, the orbital extent or the size of the valence orbitals of the alloying elements is different, resulting in changes in the overlap between the bonding orbitals. Therefore, alloying can result in both electronic effects (degree of charge transfer and hybridization) and geometric effects due to the creation of specific reaction ensembles. Although it is well known that these two aspects of the catalyst are important, it is often unknown whether one factor contributes more than another with respect to selectivity control for a particular reaction. However, understanding which factor is dominant for a particular reaction can be used to design improved catalysts.

---

* Corresponding authors.
E-mail addresses: millerjt@anl.gov (J.T. Miller), rjm@uic.edu (R.J. Meyer).

http://dx.doi.org/10.1016/j.jcat.2014.07.016

Previous work on Pt and Pd catalysts of different particle sizes yielded a correlation between neopentane isomerization selectivity and the initial CO heat of adsorption [9]. Isomerization selectivity increased with decreasing CO heat of adsorption and this correlation appears to be independent of metal, nanoparticle size, and the configuration of adsorbed CO. Large Pd particles have primarily bridge-bound CO, while small Pt particles have primarily linear-bound CO, but they have similar catalytic behavior. This provides strong evidence that the selectivity is dependent on electronic effects and the strength of adsorbate chemisorption. Extending this correlation, high selectivity to isomerization should be achieved by materials which bind CO even less strongly than Pt terrace sites. From previous DFT calculations, an intermetallic 1:1 PdZn (1 1 1) surface was shown to have a lower CO adsorption energy compared to Pt(1 1 1) [10]. Sarkrany et al. found experimentally that the CO heat of adsorption on a PdZn alloy was 67 kJ/mol lower than that of monometallic Pd [11,12]. Using our correlation between the heat of adsorption and the neopentane isomerization selectivity, it is anticipated that alloy formation between Pd and Zn would lead to a lower heat of adsorption and also improve neopentane isomerization selectivity [10].

PdZn alloys have been studied for a number of different reactions, including methanol steam reforming, water–gas shift, alkene hydrogenation and auto-thermal reforming [11,13–19]. Pd and Zn form a large number of bimetallic structures each with their own unique crystal structure and stoichiometry. At a 1:1 ratio of Pd:Zn, a face centered tetragonal structure forms, which is present for a wide range of Pd compositions (30–70%) [13,17,18,20]. Improved selectivity and stability were the main benefits that PdZn catalysts exhibited for these various reactions. These improvements were credited to both geometric changes caused by zinc altering the catalyst surface by expanding the palladium bond distance and electronic effects observed by the weakening of the Pd–CO bond [12,18]. Chen et al. performed DFT studies on the surface structure of PdZn alloys and found that the (1 1 1) surface was the most energetically favorable [21]. Calculations also suggested that the Pd d-band valence width was significantly reduced compared to pure Pd which was linked to improvements in methanol steam reforming performance. Many of these studies used ZnO as a support or supported ZnO, e.g., from a $Zn(NO_3)_2$ precursor, as a source of zinc for alloy formation. PdZn intermetallic structures are typically synthesized with excess zinc and not in nominal molar ratios close to 1:1. Iwasa et al. were unable to form the PdZn intermetallic structure on silica at temperatures up to 700 °C due to a lack of zinc reduction in ZnO [22]. Fottinger et al. performed methanol steam reforming over Pd/ZnO catalysts and found that reaction conditions caused PdZn intermetallic formation which resulted in improvements to selectivity [19]. Through *in situ* XAS it was also shown that the PdZn intermetallic structure was also reversible upon exposure to oxygen.

Here, we report on the synthesis, characterization, and testing of two PdZn nanoparticle catalysts supported on silica with different Pd:Zn molar ratios. The catalysts were characterized by electron microscopy, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of adsorbed CO, X-ray absorption spectroscopy (XAS), CO chemisorption, and isothermal calorimetry. Neopentane hydrogenolysis/isomerization and propane hydrogenolysis/dehydrogenation reactions were used to evaluate the influence of Zn on the hydrogenolysis selectivity of Pd.

2. Experimental methods

2.1. Catalyst synthesis

PdZn bimetallic catalysts supported on silica (Davisil 646 silica gel from Sigma–Aldrich, 300 m^2/g and 1.15 mL/g pore volume) were synthesized by two different synthesis methods – sequential and co-incipient wetness impregnation (co-IWI) under controlled pH conditions [23,24]. During IWI, the support is contacted with just enough metal precursor solution to fill the pore volume. All of the metal precursor solution contacts the surface due to the incipient amount of liquid used. Sequential impregnation requires the two metals be added in separate incipient wetness impregnation steps, while co-impregnation combines the metals into a single solution. The 2% Pd catalyst was synthesized using a procedure described in previous work [9].

2.1.1. 2%Pd–10%Zn

This catalyst was synthesized by sequential impregnation. Zinc was first added to silica using the IWI method. 18.1 g of $Zn(NO_3)_2\cdot 6H_2O$ was dissolved in 15 mL of H_2O. 15 M NH_4OH was then added to this solution to initially form a white precipitate which dissolved when additional NH_4OH was added bringing the total volume to 50 mL. This solution was added dropwise to 40 g of silica and stirred. The catalyst was dried overnight at 125 °C and then calcined at 300 °C for 3 h. Palladium was also added by the IWI method. 2.81 g of 10% $Pd(NH_3)_4(NO_3)_2$ solution from Aldrich was added dropwise to 5 g of the 10% Zn/SiO_2 catalyst. This catalyst was then dried overnight at 125 °C, calcined at 500 °C for 3 h and reduced at 550 °C in 4% H_2/He at 30 cc/min for 30 min.

2.1.2. 3%Pd–1.8%Zn

The catalyst was synthesized by co-IWI with both zinc and palladium precursors added simultaneously. 0.42 g of $Zn(NO_3)_2\cdot 6H_2O$ was dissolved in 1.5 mL of 15 M NH_4OH and this solution was added to 4.21 g of 10% $Pd(NH_3)_4(NO_3)_2$ solution in H_2O. This solution was then added dropwise to silica (5 g) and mixed between drops. The catalyst was dried overnight at 125 °C, calcined at 225 °C for 3 h and then reduced at 300 °C at 30 cc/min in 4%H_2/He for 30 min.

2.2. STEM

The STEM images were taken at UIC's Research Resources Center facility using the JEOL-ARM 200CF aberration-corrected microscope (70 pm spatial resolution and 300 meV energy resolution). Samples were dispersed in isopropyl alcohol and sonicated for 20 min. A drop of the solution was added to a holey-carbon copper grid and dried under a heat lamp for 20 min. Images were taken using the high angle angular dark field (HAADF) mode and particle size was counted using the Particule2 program. A minimum of 100 particles were counted to get an accurate representation of the particle size distribution for each catalyst.

2.3. X-ray absorption spectroscopy (XAS)

X-ray absorption spectroscopy (XAS) measurements for the Pd K (24350 eV) edge were made on the bending magnet beamline of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source (APS), Argonne National Laboratory. Measurements were taken in transmission mode. A palladium foil spectrum was acquired through a third ion chamber simultaneously with each measurement for energy calibration.

Samples were prepared by grinding the catalysts into a fine powder and pressing them into the sample holder. The sample holder is a metal cylinder capable of holding up to six individual samples. The sample holder is then placed in a quartz tube with ports containing Kapton windows on each end to flow gases or isolate the sample after treatment. The sample thickness was chosen to give a total absorbance at the Pd K-edge between 1 and 2 absorption lengths and edge steps around 0.3–0.5. The XAS spectra were obtained following reduction at 275 °C and 550 °C at