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Modifying structure-sensitive reactions by addition of Zn to Pd

ABSTRACT

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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

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

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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.



Silica-supported Pd and PdZn nanoparticles of a similar size were evaluated for neopentane hydrogenol-

vsis/isomerization and propane hydrogenolysis/dehydrogenation. Monometallic Pd showed high neopen-

tane 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 dehydroge-



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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 (111) surface was shown to have a lower CO adsorption energy compared to Pt(111) [10]. Sarkrany et al. found experimentally that the CO heat of adsorption on a PdZn alloy was 67 kI/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 (111) surface was the most energetically favorable [21]. Calculations also suggested that the Pd dband 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 m²/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. $18.1 \text{ g of } Zn(NO_3)_2$ · $6H_2O$ was dissolved in 15 mL of H_2O . 15 M NH₄OH was then added to this solution to initially form a white precipitate which dissolved when additional NH₄OH 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(NH₃)₄(NO₃)₂ solution from Aldrich was added dropwise to 5 g of the 10% Zn/SiO₂ catalyst. This catalyst was then dried overnight at 125 °C, calcined at 500 °C for 3 h and reduced at 550 °C in 4% H₂/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 NH₄OH and this solution was added to 4.21 g of 10% Pd(NH₃)₄(NO₃)₂ solution in H₂O. 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%H₂/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 atmospheric pressure in a 4% H_2/He mixture at 50 cm³/min flow rate. After reduction, the samples were purged with He at 100 cm³/min at the reduction temperature and cooled to room temperature in He flow. Trace oxidants in He were removed by passing through a Matheson PUR-Gas Triple Purifier Cartridge containing a Cu trap. All spectra were obtained at room temperature in He.

WINXAS 3.1 software was used to fit the XAS data. The EXAFS coordination parameters were obtained by a least-squares fit in k-space of the k^2 -weighted Fourier transform data from 2.6 to 12.1 $Å^{-1}$, and the first shell fit of the magnitude and imaginary parts were performed between 1.6 and 3.0 Å. Because of the limited data range and number of allowed fit parameters of the twoshell fit in the bimetallic nanoparticles, the error in the fits was determined by fixing $\Delta \sigma^2$ at values typical of 2.5–3 nm nanoparticles, that is, 0.001-0.002 greater than metallic foils. The error in N was $\pm 10\%$ and in *R* was ± 0.02 Å, within the typical fitting errors of EXAFS. Fits were performed by altering the coordination number (CN), bond distance (*R*), σ^2 , and energy shift (*E*₀). The σ^2 value was kept constant through all sample fits, and CN and R were allowed to vary in turn to determine the correct fit. Although CN is determined for each catalyst, they used only to determine the coordination environment of the Pd. Although coordination numbers can be used to determine the particle size [25] and morphology in monometallic NPs [26], the complex structure, i.e., Pd–Zn alloy and multiple phases, e.g., Pd core with Pd-Zn alloy shell, makes determination of the particle size, for example, unreliable.

2.4. Neopentane hydrogenolysis and isomerization

Neopentane hydrogenolysis and isomerization kinetics and selectivity were determined using 0.05-0.15 g of catalyst diluted with 0.9 g of silica and loaded into a 0.5" O.D. quartz plug-flow reactor. Glass wool was used for the bottom 2 cm of the bed. A 0.5-cm silica layer was placed on top of the glass wool before the catalyst and silica mixture was added to the reactor resulting in a catalyst bed height of 3 cm. The reactor was purged with He for 5 min before each run, and the catalyst was reduced in $4\% H_2/$ He as the temperature was increased to the reaction temperature. 273 ± 2 °C. This temperature allowed for all the catalysts to be tested at differential conversion. A K-type thermocouple was inserted from the bottom of the reactor into the lower portion of the catalyst bed. Once the reaction temperature stabilized, the pre-mixed reactant feed gas consisting of 0.35% neopentane and 3.5% H₂ balanced in He was passed through the reactor. The flow rate of the feed gas was varied from 25 to 100 cm³/min to obtain differential conversions (0.5-6%). Each flow rate was run for at least 1 h to ensure steady-state conversion had been reached. An Agilent 6890N gas chromatograph (J&W Scientific GS-Alumina column) with an FID detector was used to analyze the products and was equipped with a back pressure regulator at the outlet to hold the system at a constant pressure of 9 psig. Each experimental run was completed within 6 h for consistency, and multiple runs for each catalyst were performed. No appreciable deactivation during neopentane hydrogenolysis was observed in any of the catalysts over this period of time. The maximum relative error of any selectivity measurements was 6%, with most of the data being reproducible within 2%. Turnover rates were calculated based upon the moles of neopentane converted divided by the number of active sites determined by the dispersion calculated from CO chemisorption.

2.5. Propane dehydrogenation

Propane dehydrogenation selectivity and rate were determined using 0.2-0.5 g of catalyst diluted with 0.9 g of silica and loaded into the same 0.5'' O.D. quartz plug-flow reactor used for neopen-

tane hydrogenolysis. The reactor was purged with He for 5 min before each run, and the catalyst was reduced in 4% H₂/He as the temperature was increased to the reaction temperature, 550 ± 2 °C. Once the reaction temperature stabilized, the premixed reactant feed gas consisting of 2% propane and balance Ar was passed through the reactor. The flow rate of the feed gas was set to 50 cm³/min and held constant throughout the test so that the deactivation of each catalyst could be determined. The test was run until a steady-state conversion was reached. Each experimental run was completed within 6 h for consistency and multiple runs for each catalyst were performed. The maximum relative error of any selectivity measurements was 6%, with most of the data being reproducible within 2%.

2.6. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

Infrared spectra were obtained using a Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with a Harrick Scientific Praying Mantis diffuse reflectance in situ cell at the Northwestern Clean Catalysis (CleanCat) Core Facility. Samples were ground to a fine powder using a mortar and pestle and packed into the sample chamber to create a uniform surface. The chamber was purged with Ar, then the gas was switched to $10\% H_2/N_2$ and the temperature was raised to 250 °C and held for 15 min. After reduction of the catalyst, the gas was switched back to Ar and the temperature was reduced to 25 °C. A background scan was then recorded, which was averaged over 100 scans (2-min observation time) with 4 cm^{-1} resolution. The sample was then exposed to 1.02% CO/N₂ and another scan was taken once equilibrium was reached, at which point the flow was changed back to Ar and a final scan was taken once the intensity of the adsorbed CO peak was invariant with time. The linear-to-bridge-bound ratios reported here do not take into account the differences in extinction coefficients between the adsorption sites and therefore do not represent quantitative coverages, but rather reflect qualitative differences between catalysts [27].

2.7. CO heats of adsorption

Determination of the initial heat of adsorption of carbon monoxide on the two Pd-Zn catalysts (60-70 mg) reduced at two different temperatures (300 and 550 °C) was conducted utilizing a Setaram Sensys EVO differential scanning calorimetry interfaced with a plug-flow reactor. The plug-flow reactor was connected to a mass spectrometer. After reduction at the specified temperature in 5.11% H₂/Ar (both gases 99.999%) for 2 h, the catalyst was cooled down to 35 °C in the same gas, and the catalyst was exposed to a mixture of 1% CO (99.999% research grade) in He (99.9999%, research grade) pulsed into the 5% H₂/Ar stream from a ten-way switching value with a 1000 µL sample loop. The number of moles of CO per pulse calculated from the ideal gas law was $\sim 4 \times 10^{-4}$ mmol. Twenty pulses of carbon monoxide were employed; the initial heat of adsorption was determined by only considering injections in which the entire pulse of carbon monoxide was consumed. The 3Pd-1.8Zn/SiO₂ adsorbed entirely 5-6 pulses depending on the reduction temperature, while the 2Pd-10Zn/SiO₂ adsorbed entirely \sim 1 pulse of carbon monoxide.

2.8. CO chemisorption

The CO chemisorption measurements were conducted at the Northwestern University Clean Catalysis (CleanCat) Core Facility using an Altamira Instruments AMI-200. Catalysts (0.05–0.2 g) were loaded into a U-shaped quartz reactor tube, which was weighed before and after sample addition to ensure an accurate

weight measurement. The loaded tube was then loaded into the furnace, and the catalysts were reduced in H₂/Ar at 300 °C or 550 °C for 2 h (10 °C/min ramp rate) and then flushed for 30 min in He. Using a six-way valve, 5% CO/He was then pulsed (595 μ L loop volume) into the system 15 times at 30 °C to ensure the surface was saturated. Each pulse peak was integrated to find the volume of CO remaining following adsorption. Surface saturation was typically reached within 10 pulses. The dispersion determined by CO chemisorption also included average stoichiometric factor determined from the uncorrected DRIFTS linear-to-bridging ratios for each catalyst. CO bound linearly account for one CO molecule per surface atom while bridge-bound CO implies there is one CO molecule per two surface atoms. The equation used to get the dispersion is given below.

$$\begin{aligned} \text{Dispersion} &= \frac{\text{mol CO adsorbed}}{\text{mol metal}} \times ((\text{linear CO fraction} \times 1) \\ &+ (\text{bridge CO fraction} \times 2)) \end{aligned}$$

3. Results

3.1. Particle size analysis

STEM imaging was used to determine metal nanoparticle size. A representative STEM image for the 3%Pd–1.8%Zn catalyst and corresponding size distribution are shown in Fig. 1. The particle sizes for the three catalysts tested are reported in Table 1 and show that the average particle sizes are similar. The 3%Pd–1.8%Zn catalyst was also reduced at the propane dehydrogenation reaction temperature (550 °C) to determine if any sintering occurred. The particle size did not appreciably change, between the two temperatures. Having similar particle sizes between catalysts enables the changes caused by alloying to be studied without having to account for changes in particle size which are known to alter the kinetics of structure-sensitive reactions. From our previous studies, there are results for similar sized monometallic Pd catalysts for comparison with these PdZn bimetallic catalysts [9].

3.2. X-ray absorption spectroscopy (XAS)

Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge (XANES) spectra were gathered for each catalyst following reduction at 275 °C and fitting done to determine bond distances and coordination numbers (CN). The XANES spectra are shown in Fig. 2a and an expanded view to the leading edge is

Table 1

Sample	Particle size by STEM (nm)
2%Pd 2%Pd-10%Zn 300 °C 3%Pd-1.8%Zn 300 °C	$2.5 \pm 1.1 \\ 2.2 \pm 0.8 \\ 2.7 \pm 0.8 \\ 2.6 \pm 0.7 \\ $
5%Pu-1.8%ZII 550 °C	2.0 ± 0.7

shown in Fig. 2b. XANES were analyzed to determine the Pd K-edge position of each catalyst and evaluate the oxidation state of palladium. The edge energy is defined as the inflection point of the leading edge and is determined by taking the maximum of first derivative of the spectra in Fig. 2a. The edge energy for all three catalysts is summarized in Table 2. A K-edge energy of 24.350 keV corresponds to metallic Pd and the PdZn catalysts are slightly shifted as seen in Fig. 2b (to 24.349 keV) from Pd which is consistent with the presence of bimetallic nanoparticles [8]. The intensity of the first absorption peaks is similar indicating that the palladium is metallic rather than oxidized which would cause the peak intensity to increase. The small differences in the spectra following the first peak, changes in intensities and peak shifts, also indicate that non-Pd neighbors are near to Pd.

Fig. 3 shows the EXAFS spectra for the Pd foil reference and all three catalysts reduced at 275 °C, and Table 2 summarizes the parameters calculated from the fitting of the spectra. Coordination numbers and bond distances were determined by fitting the magnitude and imaginary parts of the Fourier transform of the k^2 weighted first shell spectra. Although the total coordination numbers for each of the samples are identical, the identity of the neighbors and their distances change between the three catalysts. The monometallic Pd catalyst shows two prominent peaks at 2.05 and 2.50 Å (phase uncorrected distances) at a ratio of 2:1, typical of metallic Pd and also observed for the Pd foil spectra seen in Fig. 3a [18]. The Pd–Pd bond distance of 2.75 Å in Table 2 also corresponds to metallic Pd. Fig. 3b shows both bimetallic PdZn catalysts; the 3%Pd-1.8%Zn spectra look similar to metallic Pd; however, a change in the peak ratio to 1.45:1 is consistent with a small number of non-Pd scattering atoms. The fit confirms there are Pd-Zn bonds with a coordination number of 2.3 and a bond distance of 2.56 Å. The coordination number for the Pd–Pd scatters is 5.3 with a bond distance of 2.73 Å (similar to metallic Pd). The differences in the coordination numbers between the Pd-Pd and Pd-Zn scatterers indicate that the majority of the palladium atoms in this catalyst are still surrounded by other palladium atoms with a



Fig. 1. 3%Pd-1.8%Zn sample image and particle size distribution determined by STEM.



Fig. 2. Pd XANES K-edge spectra for catalysts reduced at 275 °C. (a) Full edge and (b) expanded view of the leading edge of the XANES near the inflection point.

Table 2 XANES and EXAFS fitting parameters following 275 $^\circ\!C$ reduction.

Catalyst	Edge energy (keV)		Coordination number	Bond distance (Å)
2Pd	24.3500	Pd-Pd Pd-Zn	7.5 -	2.75 -
3Pd-1.8Zn	24.3496	Pd-Pd Pd-Zn	5.3 2.3	2.73 2.56
2Pd-10Zn	24.3494	Pd-Pd Pd-Zn	2.7 5.2	2.72 2.56

few Zn neighbors. The 2%Pd–10%Zn catalyst also has two prominent peaks, but these peaks deviate from the pure Pd spectra significantly. Although the peak positions are similar, the ratio of the peaks has changed, suggesting that the bonding environment of Pd has changed with the addition of zinc. The fits in Table 2 confirm this shift from Pd-rich particles to a catalyst with significant interaction between Pd and Zn as the Pd–Zn coordination number increases to 5.3 and the Pd–Pd coordination number decreases to 2.7. The bond distances have not changed significantly in the two Pd–Zn catalysts and these bond distances are also similar to those found in the literature [18]. Although the average coordination environment in these catalysts is different, EXAFS is a bulk characterization; therefore, the surface composition and structure, which is responsible for the catalytic activity, is uncertain. 3.3. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

DRIFTS of CO adsorption was used to evaluate changes in surface composition and structure of the catalysts. Fig. 4 shows the DRIFTS spectra for the PdZn catalysts as well as the monometallic Pd catalyst with a similar particle size. Bridge-bound CO has previously been assigned to the peaks in the range of 1800–2000 cm⁻¹. Within this range, peaks between 1800 and 1900 cm⁻¹ are attributed to CO bridge-bound on terrace and hollow sites, while peaks between 1900 and 2000 cm⁻¹ are assigned to CO bridge-bound to corner and edge sites [28,29]. Linear bound CO is characterized by two peaks typically appearing around 2080 and 2050 cm⁻¹ in which Lennon et al. have assigned to corner and edge adsorption sites respectively [28].

The 2%Pd catalyst, with an average particle size of 2.5 nm, has one very prominent bridge-bound CO peak at 1936 cm⁻¹, a shoulder centered around 1835 cm⁻¹, and one linear CO peak at 2084 cm⁻¹. The presence of two bridge-bound CO peaks is typical of pure Pd catalysts [28,29]. The 3%Pd–1.8%Zn catalyst has one bridge-bound CO peak located at 1975 cm⁻¹. The loss of the bridge-bound CO peak around 1835 cm⁻¹ peak suggests zinc breaks up palladium terraces on the surface typically responsible for bridge-bound CO. Since the tail of the peak extends into the terrace site range, there may be a small percentage of Pd ensembles remaining. The shift of the linear peak to 2075 cm⁻¹ from 2084 cm⁻¹ indicates there is a small fraction of CO linearly bound to edge sites since most is still bound to corner sites. These shifts



Fig. 3. Pd K-edge spectra and fitting parameters following 275 °C reduction. (a) 2%Pd (black) and Pd foil (red) and (b) 3%Pd-1.8%Zn (red) and 2%Pd-10%Zn (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. Normalized DRIFTS spectra of CO adsorption on: 2%Pd (black), 2%Pd-10%Zn (blue) and 3%Pd-1.8%Zn (red) reduced at 250 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

have also been reported for other PdZn catalysts [18,30]. The 2%Pd-10%Zn catalyst has a small bridge-bound CO peak at 1960 cm⁻¹ corresponding to corner and edge sites. The peak position has shifted from the other PdZn catalyst; however, it is still in the range of bridge-bound CO on corner and edge sites and there are no longer peaks for CO in the terrace region. The linear region has two distinct peaks at 2080 cm⁻¹ and 2050 cm⁻¹, which indicates that CO is linearly bound to edge sites as well as corner sites suggesting further zinc addition continues to reduce the number of surface palladium ensemble sites. Two peaks in the linear region have also been observed for PdZn catalysts [18].

The linear-to-bridge-bound ratio calculated by comparing the raw areas of the different peaks is presented in Table 3. The addition of zinc causes a dramatic shift in the CO adsorption resulting in greatly reduced concentration of bridge-bound CO. While the monometallic Pd catalyst has mostly bridge-bound CO, the addition of zinc causes a significant increase in linear-bound CO. The addition of excess zinc in the 2%Pd–10%Zn catalyst leads to a minor increase in the overall ratio of linear-to-bridge-bound CO (2.5:1) compared to the lower Zn sample (2.1:1), but there are differences in the peak positions as discussed above. The shift in the linear-to-bridge ratio indicates that zinc breaks up palladium ensembles on the surface and decreases the number of Pd ensemble sites capable of adsorbing bridge-bound CO. Weilach et al. used DFT to study CO adsorption on PdZn surfaces and found that adsorption on top sites

Table 3

Initial heat of CO adsorption values (±5 kJ/mol) in the presence of chemisorbed hydrogen and linear-to-bridge ratios from DRIFTS.

Sample ^a	Reduction temperature (°C)	CO (initial) heat of adsorption with chemisorbed H (kJ/mol CO) ^b	Linear-to- bridge ratio
2Pd/SiO2 ^c 2Pd-10Zn/SiO2 3Pd-1.8Zn/SiO2	225 300 300 550	92 102 99 93	0.2:1 2.5:1 2.1:1 1.8:1

 $^{\rm a}$ Catalysts were initially reduced under 5.11% H₂/Ar (both gases, 99.999% UHP) for 2 h at the specified reduction temperature, followed by subsequent cooling in H₂.

H₂. ^b Initial heat of CO adsorption determined by microcalorimetry on a reduced Pd or PdZn surface containing chemisorbed hydrogen.

^c Monometallic Pd catalyst from previous work studied using the modified procedure.

was preferred on the intermetallic surface past ½ ML CO coverage [31].

3.4. Heat of adsorption of CO determined by isothermal calorimetry

The initial heat of adsorption determined previously for a pair of Pd/SiO₂ catalysts with a mean TEM particle size of 2.5–3 nm was \sim 130 kJ mol⁻¹ [9]. The heat of CO adsorption on Pd was previously determined for the catalysts reduced in H₂, evacuated at the reduction temperature, followed by cooling in an inert gas to the adsorption temperature (35 °C). In the previous work, the differential (initial) heat of adsorption was determined using a volumetric adsorption instrument (Micromeritics ASAP 2020C) interfaced with a Setaram Sensys EVO differential scanning calorimeter. For the Pd-Zn catalysts studied in this work. calorimetric measurements of CO adsorption led to abnormally large heat flow which was associated with the oxidation of CO by small quantities of oxygen in He (99.999% UHP) led to the oxidation of CO. Enthalpy measurements in He were unreliable since the oxidation reaction is highly exothermic and contributed significantly to the measured heat. All attempts to eliminate the CO oxidation reaction were unsuccessful including utilizing a CO/He mixture containing research grade He (99.9999%). As a result, the PdZn bimetallic catalysts were cooled in a 5% H₂/Ar mixture to the adsorption temperature of 35 °C. Due to the small particle size and alloy formation with Zn, the formation of a hydride is not expected, but there will be an adsorbed layer of hydrogen on the surface of these PdZn catalysts [32-35]. Chemisorbed hydrogen will lower the heat of adsorption compared to an adsorbate-free surface of Pd [36]. The results in Table 3 also show that increasing reduction temperature slightly lowered the heat of adsorption. For comparison the heat of CO adsorption of monometallic Pd catalyst was obtained using the same procedure.

3.5. Neopentane isomerization and hydrogenolysis

Neopentane conversion was conducted at 273 ± 2 °C. 9 psig and varving flow rates in order to varv conversion within range of differential conversion (<10%). There are two possible reaction pathways: hydrogenolysis and isomerization. Isomerization products include isopentane produced from an initial isomerization reaction and *n*-pentane if isopentane undergoes a second isomerization reaction before desorption from the surface. A single hydrogenolysis reaction will produce isobutane and methane, and any subsequent steps will produce additional methane and lighter hydrocarbons (propane and ethane). All selectivities given in Table 4 are extrapolated to 0% conversion. Calculated turnover rates (TOR) using the same method described previously are also given in Table 4 [9]. Products with non-zero selectivity at 0% conversion are considered primary products while products that have 0% selectivity are considered to be secondary products [37]. The isomerization selectivity is defined as the selectivity to isopentane and hydrogenolysis products are any molecule lower than C₅ shown in Table 4. The 2%Pd catalyst has an isomerization and hydrogenolysis selectivity of 9% and 91%, respectively. The 3%Pd-1.8%Zn catalyst has a similar isomerization selectivity (13%) and hydrogenolysis selectivity (87%). The product distributions are also similar for the various hydrogenolysis products. If a single hydrogenolysis event occurs per converted neopentane molecule, equal amounts of methane and isobutane should be identified in the product distribution. An excess of methane can be seen for both catalysts in Table 4 which indicates that further hydrogenolysis is occurring, as evidenced by the presence of small amounts of ethane and propane at 0% conversion.

Since zinc does not adsorb CO, the amount of surface palladium was determined by chemisorption and used to calculate the TOR

Catalyst	Dispersion	TOR (mol conv/metal site/s)	Initial product distribution (%)					
(by CO chemisorption)			CH ₄	C_2H_6	C_3H_8	n-C4H10	i-C4H10	i-C ₅ H ₁₂
2%Pd	0.23	$1.0 imes 10^{-3}$	49	1	5	2	33	9
3%Pd-1.8%Zn	0.35	$1.3 imes 10^{-4}$	46	1	5	2	32	13
2%Pd-10%Zn	0.12	0	No mea	surable prod	ucts			

Table 4 Neopentane hydrogenolysis TOR and product selectivity.

Table 5

Propane dehydrogenation product selectivity data.

Catalyst	Dispersion ^a	Steady-state TOR (s^{-1})	Product distribution at 15% conversion (%)			
			CH ₄	C_2H_6	C_2H_4	C ₃ H ₆
2Pd	0.23	Rapid deactivation	75	6.3	8.1	10.7
3Pd-1.8Zn	0.27	$8.8 imes 10^{-3}$	0.3	0	1.7	98.3
2Pd-10Zn	0.08	$1.9 imes 10^{-2}$	1.2	0	0.7	98.4

^a Determined by CO chemisorption.

values in Table 4 [38–40]. Despite the similar selectivity distribution and particle size, the TOR of 3%Pd–1.8%Zn is an order of magnitude lower than that of the 2%Pd catalyst. The 2%Pd–10%Zn catalyst had negligible activity for neopentane conversion despite reduced palladium on the nanoparticle surface as observed by DRIFTS, CO chemisorption and calorimetry.

3.6. Propane dehydrogenation

The catalysts were also evaluated for propane dehydrogenation at 550 °C. In addition to propane dehydrogenation to form propylene, hydrogenolysis may also occur under these conditions producing methane and ethylene. The latter hydrogenolysis product can also be hydrogenated to ethane. In order determine differences in catalyst performance, all catalysts are compared at a similar level of conversion. The product selectivities in Table 5 are all reported at a propane conversion of 15%. The 2%Pd catalyst has a propylene selectivity of 11% and an overall hydrogenolysis selectivity of 88%. Within the hydrogenolysis product distribution, the selectivity to methane is 75%, 8% to ethylene and the remainder (6%) to ethane. The high hydrogenolysis selectivity is consistent with the results for neopentane.

The two PdZn catalysts have a similar dehydrogenation selectivity of 98%. The very low propane hydrogenolysis selectivity of 2%Pd-10%Zn is consistent with the low selectivity for hydrogenolysis of neopentane; however, the low hydrogenolysis selectivity of 3%Pd-1.8%Zn differs from the selectivity measured during neopentane conversion on the same catalyst. The selectivity for dehydrogenation over both PdZn catalysts is comparable to those reported for PtSn and chromia, the two industry standard catalysts [41-45].

Although both PdZn catalysts have similar selectivity, there are some differences in their time-on-stream performance (Fig. 5a). The 2%Pd catalyst begins with an initial conversion of 54%, but deactivates to 2% conversion within 1 h. Due to the rapid catalyst deactivation and large loss in conversion, TORs were not determined for the Pd catalyst. The 2%Pd-10%Zn (35%) and 3%Pd-1.8%Zn (31%) catalysts start with lower initial conversions and deactivate to a steady-state conversion of 7% and 15%, respectively. The TORs of the PdZn catalysts calculated at steady state are given in Table 5. These have not been corrected for deactivation and thus are only approximate values.

Propane dehydrogenation is an endothermic reaction and equilibrium-limited to a conversion of 40% at 550 °C [45]. The high conversion observed initially for Pd and 3%Pd-1.8%Zn is a result of the hydrogenolysis pathway; while the steady-state conversion for dehydrogenation is below the equilibrium conversion.

Fig. 5b shows the change in propylene selectivity vs. conversion. At high conversion, which also corresponds to early time-onstream, the 2%Pd catalyst has low selectivity to propylene (0%) and methane is the most abundant product. The selectivity improves as the catalyst deactivates; although the 2%Pd catalyst does not begin to improve until about 10% conversion. The



2%Pd-10%Zn catalyst had a stable propylene selectivity at 98%, while the 3%Pd-1.8%Zn catalyst increases in propylene selectivity from 79% as the conversion decreases.

The 3%Pd-1.8%Zn catalyst has a low selectivity toward propane hydrogenolysis at 550 °C, which is in contrast to the high selectivity to hydrogenolysis for neopentane at 275 °C. This difference in selectivity suggests a change in the surface composition may be occurring between these two reaction temperatures. Additional characterization was done after reduction at this elevated temperature in order to evaluate these changes. The XANES spectra (not shown) do not indicate any change in Pd K-edge energy position, but there are small changes in the peaks following the edge, consistent with a change in the nearest neighbors to Pd.

Fig. 6 shows the differences in the magnitude of the Fourier transform of the EXAFS region of the XAS spectra taken at both reaction temperatures (275 and 550 °C) for the two PdZn catalysts. The EXAFS of the 3%Pd-1.8%Zn catalyst shown in Fig. 6a undergoes a change in the EXAFS from a Pd-rich PdZn bimetallic catalyst to one that looks similar to the 2%Pd-10%Zn catalyst reduced at 275 °C, i.e., a structure with an increased number of Pd–Zn bonds. The fits in Table 6 confirm the number of Pd–Pd scatters decreases form 5.3 to 2.7 and the number of Pd-Zn increases from 2.3 to 4.9 with increasing reduction temperature. After high-temperature reduction, the structure of the metallic nanoparticles on the 3%Pd-1.8%Zn catalyst has very similar composition to those on the 2%Pd-10%Zn catalyst reduced at 275 °C. Fig. 6b also shows a change in the composition of the 2%Pd-10%Zn nanoparticles reduced at 550 °C with the appearance of a single peak centered at 2.19 Å (phase uncorrected distance). This single peak spectrum is characteristic of a PdZn intermetallic alloy [18,20]. The coordination numbers and bond distances given in Table 6 show a majority of Pd-M scatterers in the catalyst are now Pd-Zn interactions and the Pd–Pd bond increases from 2.75 Å to 2.84 Å. A similar change in EXAFS has been observed in the literature which used increasing amounts of Zn to form the intermetallic structure [18.46]. After high-temperature reduction, the structure of the 2%Pd-10%Zn nanoparticles is similar to that of a 1:1 PdZn intermetallic alloy [18].

DRIFTS of the 3%Pd–1.8%Zn catalyst pre-reduced at 300 and 550 °C is shown in Fig. 7. The linear CO peak shifts from 2075 cm⁻¹ to 2070 cm⁻¹ at the higher reduction temperature, which indicates a slight increase in linear-bound CO at edge sites. The bridge-bound CO peak also shifts when the reduction temperature is increased from 1975 cm⁻¹ to 1965 cm⁻¹ and the peak broadens. There is also a shift in the linear CO peak which brings the peak position in line with the linear CO peak of the 2%Pd–10%Zn spectra seen in Fig. 4. The overall linear-to-bridge ratio cal-

Table 6

EXAFS fitting parameters after reduction 550 °C for both PdZn catalysts.

Catalyst	Edge energy (keV)		Coordination number	Bond distance (Å)
3Pd-1.8Zn	24.3495	Pd–Pd Pd–Zn	2.7 4.9	2.72 2.56
2Pd-10Zn	24.3492	Pd–Pd Pd–Zn	2.6 8.0	2.84 2.57



Fig. 7. Normalized DRIFTS spectra taken of the 3%Pd–1.8%Zn catalyst pre-reduced at 300 °C (red) and 550 °C (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

culated from the areas of each peak did not change significantly at the higher reduction temperature, from 2.1:1 at 275 °C to 1.8:1 at 550 °C.

4. Discussion

The 2%Pd catalyst had a high hydrogenolysis selectivity during neopentane (91%) and propane (89%) conversion. Results for both reactions were expected as palladium is well known to have high hydrogenolysis selectivity [9,47–52]. For propane, the initial conversion of a 2%Pd catalyst is high, but deactivates quickly due to coking (Fig. 5) with high selectivity to methane during this period. Pd ensemble sites, as evidenced by bridge-bound CO, promote



Fig. 6. EXAFS spectra following reduction at both reaction temperatures 275 °C (red) and 550 °C (blue) of (a) 3%Pd-1.8%Zn and (b) 2%Pd-10%Zn (right plot). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

hydrogenolysis and coking reactions, rather than dehydrogenation of propane.

While the Pd catalyst performed as expected, the 2%Pd–10%Zn PdZn catalyst exhibited behavior not characteristic of monometallic Pd. It proved to be unreactive toward neopentane despite evidence for the presence of surface (metallic) Pd. Although the PdZn intermetallic alloy was inactive for neopentane conversion, it was highly active for propane dehydrogenation with high propylene selectivity and stability. From Table 5, propane dehydrogenation is a structure-insensitive reaction and the high selectivity results from the ability to catalyze dehydrogenation but not the structure-sensitive propane hydrogenolysis reaction.

The EXAFS and DRIFTS spectra are consistent with the formation of a PdZn intermetallic alloy. The changes in performance are likely related to differences in the surface structure of Pd and PdZn, i.e., geometric effects. Hydrogenolysis is a well-known example of a structure-sensitive reaction, where a certain ensemble size or geometry is required for the reaction to occur [48,53–55]. From previous literature, it has been proposed that the hydrogenolysis pathway requires a minimum of two active sites [53,55,56]. Fig. 8 shows the structure and bond distances for the bulk PdZn intermetallic alloy. In this intermetallic composition, Pd has only Zn neighbors and the Pd–Pd bond distance is 0.15 Å larger than in monometallic Pd nanoparticles. In the ideal structure there are no Pd ensemble sites since Pd atoms are at a non-bonding distance. The lack of adjacent Pd atoms results in no catalytic activity for neopentane conversion. While hydrogenolysis is a well-known structure-sensitive reaction, the lack of neopentane isomerization suggests this is also a structure-sensitive reaction. This conclusion is consistent with the mechanism postulated by Anderson and Avery where neopentane isomerization requires ensembles with more than one attachment point for the neopentane molecule [57].



Fig. 8. Structure of PdZn intermetallic alloy, coordination numbers and bond distances of the bulk alloy. Pd atoms are blue and Zn atoms are purple. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

For the 3%Pd–1.8%Zn catalyst reduced at low temperature, the selectivity during neopentane conversion is very similar to monometallic Pd nanoparticles. The lack of significant change in neopentane selectivity suggests there are active Pd ensembles similar to those in the Pd nanoparticles. While the selectivity is similar, the TOR of 3%Pd–1.8% Zn is 10 times lower than that of Pd. If the surface of the 3%Pd–1.8% Zn is high fraction of (unreactive) ordered PdZn intermetallic alloy and a small fraction of the surface covered with Pd ensemble sites, then the IR would look very similar to the 2%Pd–10%Zn catalyst, and the selectivity would look similar to that of Pd, but with a reduced TOR. This also implies that even when there is a small amount of reduced Zn, i.e., at low temperature, the surface layer forms an ordered PdZn intermetallic alloy leading to isolation of the active Pd atoms. This geometric effect is primarily responsible for the changes in catalytic performance.

For propane dehydrogenation, it might be expected that the Pd and 3%Pd-1.8%Zn catalysts would have similar catalytic performance; however, the latter has high propylene selectivity with little hydrogenolysis selectivity similar to that of the 2%Pd-10%Zn catalyst. The EXAFS shows there is an increase in the number of PdZn neighbors, while there is only a small increase in the linear-to-bridge ratio of adsorbed CO, which indicates a change in the structure of the bimetallic nanoparticle at elevated temperatures. The high propylene selectivity similar to the intermetallic catalyst suggests there are very few Pd ensembles left on the surface. In order to verify this conclusion, the 3%Pd-1.8%Zn catalyst was first reduced at 550 °C and reactions of neopentane at 275 °C were conducted. Although the catalyst was active after reduction at low temperature, there is no neopentane conversion after reduction at high temperature.

The above results are summarized by the scheme shown in Fig. 9. The structure of the 3%Pd–1.8%Zn catalyst reduced at 275 °C has a Pd core with a small number of surface Zn (metallic) atoms. The high ratio of linear-bound CO peaks in the DRIFTS suggests that this PdZn film has an intermetallic alloy structure. The catalytic performance suggests that approximately 90% of the surface is the Pd–Zn alloy with the remaining 10% of the surface consisting of Pd ensembles. At 550 °C, there is an increase in the surface coverage of the PdZn intermetallic alloy with few remaining Pd ensembles, although the nanoparticle core is still Pd-rich [58]. The inability to form a fully intermetallic PdZn alloy nanoparticle is due to a limited amount of Zn interacting with the Pd. Datye et al. and van Bokhoven et al. have also shown that PdZn intermetallic formation increases with reduction temperature [46,59].

For the 3%Pd–1.8%Zn catalyst, there is a high surface coverage of the PdZn alloy with a Pd-rich core at 275 °C. For both Pd–Zn catalysts, it appears that even under conditions which lead to a small amount of reduced Zn, the PdZn surface forms an ordered alloy structure rather than a random distribution of metallic Pd and Zn



Fig. 9. Simplified cross section of Pd and PdZn catalysts showing structure change as reduction temperature increased.

surface atoms. At 550 °C, there is little change in the DRIFTS spectra, but the EXAFS shows an increase in the number of PdZn bonds with near complete formation of the PdZn alloy nanoparticles. For each PdZn catalyst with complete surface coverage of the PdZn intermetallic alloy, the isolated Pd atoms are active for structure-insensitive reactions, but are inactive for structure-sensitive reactions. The large change in catalytic performance is due to a geometric effect, i.e., isolation of the active Pd atoms, rather than an electronic effect due to alloy formation.

5. Conclusion

Bimetallic PdZn on silica catalysts can form an intermetallic alloy with isolated active palladium atoms. At low reduction temperature and with limited amounts of zinc near the Pd nanoparticles, there are small regions of the surface with Pd ensembles and catalytic selectivity similar to that of monometallic Pd. At higher Zn loadings, or higher reduction temperatures, the PdZn nanoparticle surface is fully covered by the PdZn alloy, which is inactive for structure-sensitive reactions like neopentane hydrogenolysis/ isomerization and propane hydrogenolysis. The PdZn intermetallic surface alloy, however, has high catalytic activity for structureinsensitive reactions like propane dehydrogenation. The high propane dehydrogenation to propylene selectivity results from the geometric isolation of the active Pd atoms, which have only metallic Zn neighbors. From this work, catalytic reactions where there are both structure-sensitive (hydrogenolysis) and structure-insensitive (propane dehydrogenation) reactions and the structureinsensitive reaction leads to the desired products, the ideal catalyst will have single metallic sites with few ensemble sites.

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