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Selective hydrogenation of 1,3-butadiene on Pd—Ni bimetallic catalyst: From model surfaces to supported catalysts



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ABSTRACT

The selective hydrogenation of 1,3-butadiene serves as a means to purify the butene stream generated from cracking naphtha or gas oil. To identify selective hydrogenation catalysts, 1,3-butadiene was studied on single crystal Ni/Pd(111) bimetallic surfaces, utilizing density functional theory (DFT) calculations and temperature-programmed desorption (TPD). DFT calculations predicted that the Pd-terminated bimetallic surface should be more active and selective to produce 1-butene, which were verified experimentally using TPD. The promising results on model surfaces were extended to γ -Al₂O₃-supported catalysts using both batch and flow reactors. Extended X-ray absorption fine structure (EXAFS) and transmission electron microscopy (TEM) confirmed the formation of bimetallic nanoparticles. The Pd—Ni bimetallic catalysts showed higher hydrogenation activity and 1-butene selectivity than the monometallic catalysts. The excellent correlation between model surfaces and supported catalysts demonstrates the feasibility of designing effective bimetallic catalysts for selective hydrogenation reactions.

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1. Introduction

Selective hydrogenation is one of the critical reactions to remove alkynes and dienes in polymer synthesis. The hydrocarbon streams from cracking units typically contain $\sim 1\%$ alkynes or dienes, which must be removed below 10 ppm for polymerization processes because they poison the catalysts and degrade the product quality. For example, the hydrogenation of 1,3-butadiene is used for the purification of butene streams. Among the products of 1,3-butadiene hydrogenation, 1-butene is the desired product for manufacturing polybutene and polyethylene. In this paper, 1,3-butadiene was chosen as a probe molecule to identify catalysts for the selective hydrogenation of one C=C bond in dienes.

Pd- [1–5] and Pt- [1,6–9] based catalysts are commonly studied for the selective hydrogenation of unsaturated C—C bonds. For the selective hydrogenation of dienes, Pd-based catalysts are more active and selective than their Pt-based counterparts [10]. The Pt- and Pd-based bimetallic catalysts typically display higher selectivity than the corresponding monometallic catalysts [9,11–24]. For example, Pd—Ag showed higher selectivity to butenes, but lower hydrogenation activity [12]. The effect of bimetallic formation in Pd—Au appeared to be dependent on the reaction temperature and 1,3-butadiene conversion. At low temperature, 294 K, Pd-Au was reported to have a lower activation barrier for 1,3butadiene hydrogenation. The Pd-Au bimetallic catalysts showed higher selectivity to 1-butene than Pd at 1,3-butadiene conversions higher than 30%. However, at conversions lower than 30%, the Pd-Au catalyst was less selective than Pd to 1-butene formation [15]. The Pd—Cu catalyst had higher 1-butene selectivity, but maintained similar activity to that of Pd [18]. Pd-Sn was studied on different alumina supports, which showed that the addition of Sn to Pd increased the butene selectivity, but had an insignificant effect on the catalyst activity [22]. The inclusion of Mo in Pd supported on zeolites decreased the initial catalytic activity of 1,3butadiene hydrogenation, while the selectivity to butene was improved [23]. Overall, most of the Pd-based bimetallic catalysts reported in the literature showed improved butene selectivity, but often at the expense of activity. Therefore, it is important to identify bimetallic catalysts that increase both selectivity and activity.

Previous studies on model surfaces of Pd_5Ni_{95} [25] and Pd_8Ni_{92} [26] showed higher activity for 1,3-butadiene hydrogenation (based on surface Pd atoms) than Pd(111) and Pd(110) surfaces, and the selectivities to butene on these Pd-Ni surfaces were the same as on Pd surfaces. Furthermore, when the Ni surface was



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modified with 0.5 ML Pd, the catalytic activity for 1,3-butadiene hydrogenation increased by an order of magnitude [27]. These surface science studies suggest that Pd—Ni bimetallic catalysts have higher selectivity for 1-butene production and higher activity for 1,3-butadiene hydrogenation.

The objective of this work was to correlate Pd—Ni bimetallic surfaces with supported catalysts for 1,3-butadiene hydrogenation. Surface science experiments and density functional theory (DFT) calculations were performed on Ni-modified Pd(111) surfaces to determine the effect of Pd—Ni bimetallic bonds on the hydrogenation pathway of 1,3-butadiene. In parallel, supported Pd—Ni catalysts were characterized and evaluated in both batch and flow reactors to verify the predictions from the model surfaces.

2. Theoretical and experimental methods

2.1. DFT calculations

All DFT calculations of binding energies were performed with the Vienna ab initio Simulation Package (VASP) [28-31]. The PW 91 functional [32] was used in the generalized gradient approximation (GGA) [33] calculation, and a kinetic cutoff energy of 396 eV was chosen for the plane wave truncation. The surfaces were modeled using a periodic 4×4 unit cell and the calculations used a $3 \times 3 \times 1$ Monkhorst–Pack *k*-point grid. The clean Pd(111) surface was modeled by adding six equivalent layers of vacuum onto four Pd layers, in which the two bottom layers were frozen at metal distances of 2.80 Å in each layer and 2.3 Å between the layers, while the top two layers were allowed to relax to reach the lowest energy configuration. The Pd-terminated bimetallic surface, designated as PdNiPd(111), was derived by replacing the second layer of Pd atoms with Ni atoms. The binding energy of adsorbed molecules on the surface was calculated by subtracting the energies of the bare slab and of the free molecule from the total energy of the slab plus the adsorbed molecule. The configurations from VASP calculations were further optimized using the Cambridge Serial Total Energy Package (CASTEP) suite of programs to identify the transition state and calculate the activation energy for each reaction step.

2.2. Measurements of model surfaces

TPD measurements were performed in an ultrahigh vacuum (UHV) chamber with a base pressure of 1×10^{-10} Torr, equipped with an Auger electron spectroscopy (AES), a mass spectrometer, a sputter gun, and a Ni metal source, as described previously [34]. A Pd(111) single crystal (Princeton Scientific, 99.99%, 2 mm thick and 10 mm in diameter) was placed at the center of the UHV chamber by directly spot-welding the crystal to two tantalum posts, for resistive heating and cooling with liquid nitrogen. A chromel–alumel K type thermocouple was welded to the back of the Pd sample for temperature measurements. The Pd(111) surface was cleaned using sputtering–annealing cycles.

The Ni-terminated, NiPdPd(111) and Pd-terminated, PdNiPd(111) bimetallic surfaces were prepared by controlling the current of the Ni source, the temperature of the Pd(111) surface, and the deposition time. The NiPdPd(111) surface was prepared by depositing Ni onto the Pd(111) surface, while the surface was maintained at 300 K. The ratio of Ni and Pd peak intensities (I_{Ni}/I_{Pd}) from Auger measurements is plotted in Fig. 1a as a function of deposition time. Breaks were found at 4 min (point A) and 8 min (point B), suggesting that the deposition of the Ni atoms on the Pd(111) surface was in a layer-by-layer [35] growth mode. At point A, one layer of Ni atoms was deposited on the Pd(111) surface, referred to as the NiPdPd(111) surface. After preparation



Fig. 1. (a) Deposition time vs AES Ni/Pd peak ratio and (b) thermal stability of the monolayer Ni surface (Regime I: NiPdPd(111) configuration; Regime II: transition from NiPdPd(111) to PdNiPd(111) configuration; Regime III: diffusion of Ni into bulk phase).

of the NiPdPd(111) surface, it was heated to higher temperatures, and Auger measurements [36] were performed every 50 K. The change in the Ni/Pd Auger peak ratio was plotted as a function of the surface temperature in Fig. 1b. The slope of the $I_{\rm Ni}/I_{\rm Pd}$ curve changed when the surface was heated between 550 K (point C) and 650 K (point D), which indicated that Ni atoms started to diffuse into the Pd substrate [37,38]. Based on the previous studies of the thermal behavior of Ni/Pt(111), heating to approximately 600 K led to diffusion of Ni between the first and second layers of Pt to produce a subsurface PtNiPt(111) structure, followed by diffusion of Ni further into the bulk at higher temperatures [39]. The observation of two distinct slopes in Fig. 1b suggested that two thermally induced diffusion regimes, subsurface and bulk diffusion, might exist for the Ni/Pd(111) surface. In the current paper, the NiPd surface annealed to 600 K is referred to as the subsurface PdNiPd(111) structure in DFT calculations and TPD measurements. However, the slope of Ni subsurface diffusion is greater than that of the Ni bulk diffusion, which is uncommon compared with the previous studies of metal/Pt(111) surfaces [40]. The only plausible explanation is that the decrease in the Ni AES signal is related to the term of $\exp[-d/\lambda]$, where d is the thickness of Pd layers screening the Ni atoms and λ the mean free path of Ni Auger electrons. Because the mean free path of the Ni(LMM) electrons is relatively large, it is possible that Ni can still be detected by AES, although at a reduced intensity of $\exp[-d/\lambda]$, even after Ni atoms diffuse several layers deep in the bulk. However, it is difficult to quantify

the slope without knowing the rate and depth of Ni diffusion into the bulk Pd(111). The surface structure and elemental composition of the 300 K and 600 K Ni/Pd(111) surfaces have been characterized using scanning tunneling microscopy (STM) and low-energy ion scattering (LEIS) [41]. The LEIS results confirmed the thermally induced diffusion of Ni, leading to a Pd-terminated surface after annealing to 600 K.

All gases used in this work, 1,3-butadiene, hydrogen, and neon, were of research purity and were used without further purification. The reagents were dosed into the UHV chamber through a stainless steel tube, and the purity was verified with mass spectrometry before UHV experiments.

2.3. Preparation of supported catalysts

The γ -Al₂O₃ (Alfa Aesar, 244 m²/g) supported catalysts were synthesized using incipient wetness impregnation. The precursor solutions were prepared by dissolving $Pd(NO_3)_2 \cdot 2H_2O$ (Alfa Aesar) and/or Ni(NO₃)₂·6H₂O (Alfa Aesar) in an amount of water just sufficient to fill the pores of 3 g of the support. The precursor solution was then added to the support by dropwise addition and was stirred thoroughly between droplets. The catalysts were dried at 373 K for 10 h and calcined at 563 K for 2 h. A ramp rate of 0.4 K/min was used up to 373 K and 0.8 K/min up to 563 K. A co-impregnation synthesis procedure was used for the bimetallic catalysts to produce the greatest extent of bimetallic bond formation, as verified previously for supported Pt-Ni catalysts [24]. The corresponding monometallic Ni and Pd catalysts were prepared to serve as control samples. The compositions of the synthesized catalysts are as follows: 1.51 wt% Ni/ γ -Al₂O₃, 0.91 wt% Pd/ γ -Al₂O₃, and 1.51 wt% Ni–0.91 wt% Pd/ γ -Al₂O₃, corresponding to a Ni:Pd atomic ratio of 3:1.

2.4. Catalyst characterization

2.4.1. Pulse CO chemisorption

The number of active sites on each catalyst was measured through CO uptake with an AMI-200ip (Altamira). A quartz reactor was loaded with 100 mg of catalyst and reduced in 40 sccm of 50% H_2 in He at 723 K for 1 h. After reduction, the catalyst was cooled to room temperature in He before pulsing CO. The amount of CO flowing out of the reactor was measured with a thermal conductivity detector. Each adsorbed CO molecule was assumed to correspond to one active site, which provided a means to quantitatively compare the number of active sites between catalysts.

2.4.2. Transmission electron microscopy (TEM)

TEM measurements were performed using a JEOL2010F equipped with a Schottky field emission gun at 200 keV. All TEM

images were taken in scanning (STEM) mode with a 12-nm camera length and a 1-nm diameter nanoprobe. The TEM samples were prepared by first reducing the catalyst samples, then grinding the reduced sample into fine powders, and suspending them in acetone. Droplets of the suspension were placed onto a carbon coated copper grid. The grid was dried overnight before loading the sample into the TEM.

2.4.3. Extended X-ray absorption fine structure (EXAFS)

EXAFS measurements were used to confirm the presence of Pd—Ni bimetallic bonds. Measurements of the Pd K-edge were performed on the X18B beamline at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The catalyst samples were pressed into a pellet with a thickness twice the absorption length to maximize the signal to noise ratio. The catalysts were reduced in situ in 40 sccm of 50% H_2 in He at 723 K for 1.5 h, and the EXAFS spectra were collected at room temperature. The EXAFS spectra were calibrated to the Pd K-edge energy from a Pd reference foil.

The X-ray signal was analyzed using the IFEFFIT 1.2.11 data analysis package (Athena, Aretmis, Atoms, and FEFF6) [42,43]. The structural information was obtained by Fourier-transforming the absorbance signal into R-space and then fitting each data set to the theoretical standards generated in FEFF6 [44]. The theoretical monometallic photoelectron amplitude and phase were calculated for the bulk Pd fcc structure. The passive electron reduction factor S_0^2 was found to be 0.878 from fitting the Pd foil data. The seven parameters used in the fitting procedure were the correction to the edge energy, the coordination numbers of the Pd—Pd and Pd—Ni bonds, corrections to their model interatomic distances, and the mean square deviations in interatomic distances (EXAFS Debye–Waller factors).

2.5. Catalytic evaluation of supported catalysts

2.5.1. Batch reactor

Fourier transform infrared (FT-IR) spectroscopy was used to monitor the gas-phase concentrations of reactants and products during the hydrogenation 1,3-butadiene. The FT-IR spectra were recorded with 4-cm⁻¹ resolution using a Thermo Nicolet Nexus 470 spectrometer equipped with a mercury cadmium telluride (MCT-A) detector. The details of the batch reactor cell and the sample preparation procedure have been previously reported [24]. For all FT-IR experiments, ~13.6 mg of supported catalyst was loaded into the IR cell, which was then evacuated for 12 h, until the system reached a pressure below 10^{-6} Torr. The catalysts were reduced at 723 K in 30 Torr hydrogen for 30 min, the cell was then evacuated, and a high-temperature flash (723 K) was performed to remove any surface species generated during the reduction period.



Fig. 2. Top and side views of optimized adsorption geometry of C₄H₆, C₄H₇, C₄H₈, C₄H₉, and C₄H₁₀ species on PdNiPd(111) surfaces.



$$C_4H_6 \xrightarrow[\leftarrow]{+H1.04}{-H0.64} C_4H_7 \xrightarrow[\leftarrow]{+H0.92}{-H0.49} C_4H_8 \xrightarrow[\leftarrow]{+H1.01}{-H0.49} C_4H_9 \xrightarrow[\leftarrow]{+H0.87}{-H1.05} C_4H_{10}$$

On PdNiPd(111) surface:

$$C_{4}H_{6} \xrightarrow[-H 0.60]{+H 0.68} C_{4}H_{7} \xrightarrow[-H 1.03]{+H 0.88} C_{4}H_{8} \xrightarrow[-H 0.81]{+H 0.88} C_{4}H_{9} \xrightarrow[-H 1.52]{+H 0.80} C_{4}H_{10}$$

Scheme 1. The reaction pathways for 1,3-butadiene hydrogenation on Pd(111) and PdNiPd(111) surfaces. The activation barriers are in eV.

Table 1

Table 2

The binding energies on Pd(111) and PdNiPd(111) surfaces.

Surface	Pd(111)	PdNiPd(111)
d-Band center (eV) Binding energy (eV)	-1.9	-2.25
C ₄ H ₆	-1.49	-0.83
C ₄ H ₇	-1.62	-0.58
C ₄ H ₈	-0.55	-0.13
C ₄ H ₉	-1.58	-1.29
C ₄ H ₁₀	-0.11	-0.11

The reduction cycle was repeated three times before performing 1,3-butadiene hydrogenation experiments.

After reducing the catalyst, 7.8 Torr C_4H_6 , 17.2 Torr H_2 , and 25 Torr He were introduced into the reaction vessel simultaneously, with a 1,3-butadiene to hydrogen ratio of 1:2.2. The reaction proceeded at a catalyst temperature of 308 K. During the reaction, the gas-phase reactants and products were monitored by recording IR spectra (32 scans) every 30 s. The concentrations

of the reactant and products were estimated using the absorbance intensities of their characteristic vibration modes as follows: v(C=C-C=C) at 1586 cm⁻¹ for 1,3-butadiene, v(C=C) at 1655 cm⁻¹ for 1-butene, and v(-CH₃) at 1466 cm⁻¹ for *n*-butane. No 2-butene characteristic vibration modes (1697 cm⁻¹ and 1540 cm⁻¹) were found in the gas-phase products. Details of the calculation of the gas-phase concentrations of molecules from 1,3-butadiene hydrogenation were reported previously [24]. All carbon atoms were accounted for by performing a carbon balance, confirming the absence of 2-butenes and any other hydrocarbon fragments. At present, we do not understand why 2-butene was not detected in the batch reactor. One potential explanation is that, in the batch environment, gas-phase products constantly undergo re-adsorption and reaction. More detailed study is needed to understand such phenomena: however, because our batch reactor results are primarily used for activity comparison, the absence of 2-butene does not affect our batch reactor conclusions of trends in hydrogenation activity.



Fig. 3. TPD spectra of (a) H₂ (b) 1-butene, and (c) butane following 2.0 L predosed H₂ and 2.0 L 1,3-butadiene on NiPdPd(111), Pd(111) and PdNiPd(111) surfaces.

O chem	isorptions results a	nd first-order consum	ption rate constants	for the hydrogenatio	n of 1.3-butadiene o	ver the monometallic an	id bimetallic catalysts.
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Catalysts	Average particle size (nm)	CO uptake (µmol g ⁻¹ cat)	Normalized k_r (by weight) (min ⁻¹ g ⁻¹ cat)	Normalized k_r (by CO uptake) (10 ⁻² min ⁻¹ µmol CO ⁻¹)	Normalized k_r (by total metal loading) (10 ⁻³ min ⁻¹ g ⁻¹ metal)
$PdNi/\gamma - Al_2O_3$	5.9	29.3	2.32	7.92	9.59
$Pd/\gamma - Al_2O_3$	5.1	15.2	1.08	7.11	11.87
Ni/γ - Al_2O_3	5.2	12.3	0.038	0.31	0.25

2.5.2. Flow reactor

The catalyst was mixed with guartz particles in a ratio of 1:29 (100 mg catalyst and 2.9 g quartz particles) in a fixed bed reactor. Prior to the reaction, the catalysts were reduced in pure hydrogen at 723 K for 3 h and then cooled to reaction temperature. The total flow rate of 1,3-butadiene and hydrogen was 9.6 mL/min, and the 1,3-butadiene to hydrogen ratio was 1:2.2 or 1:4. The reaction temperatures studied were from 313 to 373 K at intervals of \sim 20 K. The catalyst was left on stream for 1.5 h at each temperature to achieve steady state. The outlet stream was analyzed online by a gas chromatograph equipped with a FID detector (GC 7900, Techcomp Ltd.) and an HP-Al/S PLOT column (Agilent, $30 \text{ m} \times 0.53 \text{ }\mu\text{m}$). Only the C4 species (1,3-butadiene, 1-butene, trans-2-butene, cis-2-butene, and butane) were observed in the outlet, with the gas-phase carbon balance above 95%. The selectivity of each product was calculated by dividing its concentration by the total products. The total butene selectivity was obtained by summing the selectivities of all butene species.

3. Results

3.1. Model surface results

3.1.1. DFT calculations

DFT calculations were performed on Pd(111) and PdNiPd(111) surfaces to compare the adsorption and reaction network of 1,3-butadiene. The adsorption geometries of 1,3-butadiene and its hydrogenation products used in this work are the same as those reported on Pd(111) in the literature [45], and the geometries on PdNiPd(111) are shown in Fig. 2. As shown in the activation barrier of each step (Scheme 1), the hydrogenation of 1,3-butadiene to 1-butene on Pd(111) needs to overcome a relatively high activation barrier of 1.04 eV for the first step and 0.92 eV for the second step. In comparison, lower reaction barriers are required on the PdNiPd(111) surface, with barriers for the first and second steps being 0.68 eV and 0.88 eV, respectively. The lower activation barriers on PdNiPd(111) suggest higher hydrogenation activity on the bimetallic surface.

The binding energies of 1,3-butadiene and its hydrogenation products are summarized in Table 1. The PdNiPd(111) surface exhibits a surface d-band center further away from the Fermi level and correspondingly lower binding energies for the adsorbed molecules. On the PdNiPd(111) surface, 1-butene shows a very low binding energy (-0.13 eV), indicating that 1-butene should readily desorb from the surface after its formation rather than undergo further hydrogenation. This suggests that 1,3-butadiene should be selectively hydrogenated to 1-butene rather than to butane. Using DFT calculations, Gomez et al. found that the binding energy of 1-butene was significantly lower on Pd₁Ni₃(111) than on Pd(111) and Pd₃Ni₁(111) surfaces [46]. They also proposed that the Pd₁Ni₃(111) structure should give higher 1-butene selectivity.

3.1.2. TPD results

To verify the DFT results, TPD experiments of 1,3-butediene hydrogenation were performed on the Pd(111) and PdNiPd(111) surfaces. For comparison, the Ni-terminated, NiPdPd(111) surface was also studied. Fig. 3 shows the TPD results following the reaction of 1,3-butadiene with pre-adsorbed atomic hydrogen on the three surfaces. Fig. 3a shows the TPD spectra of hydrogen on the three surfaces. The hydrogen desorption peak areas indicate the amount of unreacted hydrogen on each surface. In Fig. 3b, a desorption peak of 1-butene is observed around 230 K on the PdNiPd(111) surface, indicating the formation of 1-butene from the hydrogenation of 1,3-butadiene. In comparison, only a small peak around 230 K is observed from Pd(111), and no peak is

observed from NiPdPd(111). In Fig. 3c, no butane desorption peak is observed on the three surfaces, suggesting that there is no butane formed during the TPD experiments. The TPD results demonstrate that the PdNiPd(111) bimetallic surface shows the highest activity for 1,3-butadiene hydrogenation, while the Pd(111) and NiPdPd(111) surfaces are not active. Furthermore, no butane formation is observed on the PdNiPd(111) surface, suggesting that the Pd-terminated bimetallic structure should have both high activity and selectivity toward 1-butene.

Previous studies have revealed the potential effect of hydrides on hydrogenation, as demonstrated previously on the Pd_8Ni_{92} surface. For example, Valcarcel et al. [47] have demonstrated that hydrogen dissolution is a major reason for lower activity on Pd surfaces in a gas-phase static reactor. Additionally, according to Rupprechter and Somorjai [48], although the dissolved hydrogen can be available for surface hydrogenation, the reaction rate with dissolved hydrogen is much lower than with the gas-phase hydrogen. The TPD spectra in Fig. 3 suggest that hydride formation might not be the reason for the lack of 1,3-butadiene hydrogenation on Pd(111).

As shown in Fig. 3a, two H₂ desorption peaks are observed at \sim 300 K and \sim 400 K from both Pd(111) and PdNiPd(111) surfaces, which correspond to the subsurface hydrogen and surface hydrogen, respectively [49,50]. The onset of H₂ desorption occurred at around 200 K from both Pd(111) and PdNiPd(111) surfaces, which was in the temperature range of 1,3-butadiene hydrogenation on PdNiPd(111). The desorption temperatures for both the subsurface (\sim 300 K) and surface (\sim 400 K) remain similar on the two surfaces. The peak area of the subsurface hydrogen on PdNiPd(111) is



Fig. 4. HAADF TEM micrographs and particle size distributions for the catalysts: (a) $PdNi/\gamma-Al_2O_3$, (b) $Pd/\gamma-Al_2O_3$, (c) $Ni/\gamma-Al_2O_3$.



Fig. 5. Pd K-edge XANES spectra before and after reduction (a), Fourier transformed (magnitude) k^2 weighted EXAFS function ($\chi(k)$) before and after reduction (b), Pd K-edge Fourier transformed (magnitude) k^2 weighted EXAFS function ($\chi(k)$) after reduction with first shell fit (c). The Pd foil is included in (a) to serve as a reference for metallic Pd.

Table 3	
Summary of EXAFS analysis of Pd K-edge catalysts supported on γ -Al ₂ O ₃ .	

Pd/γ - Al_2O_3	$PdNi/\gamma - Al_2O_3$
9.77 ± 0.38	8.34 ± 0.74
/	1.44 ± 0.50
2.83 ± 0.002	2.79 ± 0.01
/	2.64 ± 0.01
0.008 ± 0.001	0.010 ± 0.001
1	0.016 ± 0.004
	Pd/γ-Al ₂ O ₃ 9.77 ± 0.38 / 2.83 ± 0.002 / 0.008 ± 0.001 /

reduced by only about 25% from that of Pd(111), indicating that the formation of bimetallic surface does not significantly suppress hydride formation compared to Pd(111). Significant amounts of subsurface and surface hydrogen are present on Pd(111) and are available to react with 1,3-butadiene if Pd(111) has comparable activity with PdNiPd(111). These results suggest that the lower hydrogenation activity on the Pd(111) surface is not entirely due to hydride formation.

Moreover, as pointed out in the previous studies by Filhol et al., strain relaxation effects in the Pd—Ni surfaces also contributed to alkene hydrogenation [51]. Similar strain effects should also play a role in the higher hydrogenation activity on PdNiPd(111).

3.2. Characterization of supported catalysts

The CO uptake values are 29.3, 15.2, and 12.3 μ mol g⁻¹ for PdNi/ γ -Al₂O₃, Pd/ γ -Al₂O₃, and Ni/ γ -Al₂O₃, respectively, as shown in Table 2. The high-angle annular dark field (HAADF) TEM images of the catalysts are shown in Fig. 4. The particle size distributions were calculated by measuring horizontal particle diameters in several different images for each catalyst. The three catalysts have similar particle size distributions, as shown in Fig. 4 and Table 2.

Fig. 5a shows the Pd K-edge X-ray absorption near-edge structure (XANES) spectra of the Pd/ γ -Al₂O₃ and PdNi/ γ -Al₂O₃ catalysts before and after reduction, along with the spectra of the Pd foil for reference. The background-subtracted, edge-step normalized and k^2 -weighted Pd K-edge EXAFS data ($\chi(k)$) are shown in R-space in Fig. 5b, along with the fits obtained using FEFF6 theory shown in Fig. 5c.



Fig. 6. The consumption of (a) 1,3-butadiene, production of (b) 1-butene, and production of (c) n-butane during the hydrogenation of 1,3-butadiene at 308 K.

Careful examination of the Pd K-edge XANES and EXAFS reveals information regarding the extent of oxidation of the catalysts. Relatively intense peaks are present in Fig. 5a at 24,350 eV prior to reduction and are attributed to the Pd—O bond, which is confirmed by the peaks at low radial distribution in Fig. 5b. After reduction in H₂, the spectra are more similar to that of the Pd foil in Fig. 5a, and the Pd—O peaks are not present in Fig. 5b. The Pd—O peaks are replaced by Pd—Ni peaks at slightly larger values of *R*. Together, these changes in the spectra indicate that Pd is in a metallic state after reduction in H₂.

Fig. 5c presents the Fourier transformed (R-space) data of the reduced catalysts and their associated fits from FEFF6. Fits were obtained by only including Pd—Pd and Pd—Ni contributions. The results from the fitting procedure are shown in Table 3. For both the Pd/ γ -Al₂O₃ and PdNi/ γ -Al₂O₃ catalysts, the Pd—Pd distances (2.83 Å and 2.79 Å, respectively) are larger than the bulk Pd—Pd distance (2.75 Å), possibly due to the formation of Pd hydride and the expansion of Pd—Pd bond [52,53]. For the PdNi/ γ -Al₂O₃ catalyst, the Pd—Pd distance is 2.79 Å, which is 0.04 Å smaller than the monometallic Pd—Pd distance (2.83 Å), while the Pd—Ni distance is 2.64 Å, which is 0.15 Å larger than the metallic Ni—Ni distance (2.49 Å). These changes in bond distance are most likely

related to the strain of the larger Pd atoms residing on top of smaller Ni atoms. A similar effect was observed previously from EXAFS studies of the PtNi/ γ -Al₂O₃ catalyst [24]. The EXAFS results confirm that Pd—Ni bimetallic bonds are formed in the catalysts because the bimetallic bond lengths are between that of either parent metal. In addition to the observed attenuation in bond lengths, the CN of Pd—Ni is 1.44, which indicates that bimetallic bonds are present in the Pd—Ni/ γ -Al₂O₃ catalyst. During data fitting, good fits to the Pd K-edge experimental data could only be obtained by including both Pd—Pd and Pd—Ni contributions in the model, which further suggest that bimetallic bonds are present.

The overall coordination number is 9.77 on Pd/ γ -Al₂O₃ and 9.78 on PdNi/ γ -Al₂O₃ (N(Pd—Pd) + N(Pd—Ni)). The similarity between the coordination numbers indicates that the metallic particles on each catalyst should be of similar size, consistent with the particle size statistics from TEM images as listed in Table 2. In the bimetallic catalyst, the ratio of Pd—Pd to Pd—Ni coordination numbers (CN(Pd—Pd):CN(Pd—Ni) = 8.34:1.44 = 5.79:1) is much larger than the atomic ratios of Pd:Ni (1:3). This implies that a considerable amount of remaining Ni atoms is located as monometallic Ni nanoparticles, dispersed across the γ -Al₂O₃ support, or present in the form of NiAl₂O₄.

3.3. Catalytic evaluation of supported catalysts

3.3.1. Batch reactor

Fig. 6 shows the changes in gas-phase concentrations of 1,3butadiene, 1-butene, and *n*-butane with reaction time over the PdNi/ γ -Al₂O₃, Pd/ γ -Al₂O₃, and Ni/ γ -Al₂O₃ catalysts. The Pd—Ni bimetallic catalyst exhibits a higher hydrogenation activity than both the Pd and Ni monometallic catalysts, as illustrated in the 1,3-butadiene consumption rates in Fig. 6a, which is consistent with the model surface studies. After two hours of reaction, 1,3butadiene is completely converted over PdNi/ γ -Al₂O₃, ~80% over Pd/ γ -Al₂O₃, and only ~7% over Ni/ γ -Al₂O₃. Fig. 6b and c show once again that the bimetallic catalyst outperforms the monometallic Pd and Ni catalysts. A broad peak of 1-butene appears between 40 and 60 min over PdNi/ γ -Al₂O₃, which indicates the possibility of producing the maximum amount of 1-butene within short contact time on the bimetallic catalyst.

To make a quantitative analysis, the hydrogenation reaction rates are estimated by a first-order rate law for the consumption of 1,3-butadiene and are normalized by catalyst weight, by CO uptake, and by metal loading, as shown in Table 2. The rate constant of PdNi/ γ -Al₂O₃, normalized by weight, is twice that of Pd/ γ -Al₂O₃, while that of Ni/ γ -Al₂O₃ is smaller by two orders of magnitude. This suggests that Ni/γ -Al₂O₃ is almost inactive for 1,3butadiene hydrogenation. The rate constants normalized by CO uptake follow the same trend of $PdNi/\gamma-Al_2O_3 > Pd/\gamma-Al_2O_3 > Ni/\gamma$ γ -Al₂O₃. The rate constant of PdNi/ γ -Al₂O₃ normalized by CO uptake is only slightly larger than that of Pd/γ -Al₂O₃ and that of Ni/γ -Al₂O₃ is still smaller by orders of magnitude. The rate constant of PdNi/ γ -Al₂O₃ normalized by metal loading is even smaller than that of Pd/ γ -Al₂O₃. However, the normalizations by CO uptake or metal loading are not very suitable in the current case. According to the EXAFS results, not all Ni atoms are alloyed with Pd on the bimetallic catalyst. Some Ni particles are isolated on the support. These Ni particles have CO uptake values but barely contribute to hydrogenation activity. Therefore, the rate constants normalized by weight are more suitable for the activity comparison among the different catalysts. The higher rate constant of $PdNi/\gamma-Al_2O_3$ verifies the prediction of higher hydrogenation activity in the TPD results and the lower activation barrier in the DFT calculations on the Pd-terminated PdNiPd(111) surface. Previous DFT calculations of Pd-Ni bimetallic systems have indicated that, in the presence of adsorbed hydrogen, the Pd-terminated surface is the thermodynamically stable structure [40,54], which contributes to the good correlation between the supported catalysts and model surfaces.

3.3.2. Flow reactor

To verify the batch reactor results and to test the catalytic selectivity under steady-state conditions, 1,3-butadiene hydrogenation was performed in a flow reactor at different temperatures from 315 to 375 K. Higher temperature evaluations of Ni/ γ -Al₂O₃ were measured to obtain selectivity over a broad range of conversions to compare selectivity with Pd/ γ -Al₂O₃ and PdNi/ γ -Al₂O₃. As shown in Fig. 7, the trend in the conversion of 1,3-butadiene at different temperatures is consistent with the batch reactor results. For both H₂/C₄H₆ ratios, PdNi/ γ -Al₂O₃ exhibits higher activity than Pd/ γ -Al₂O₃ at all temperatures, while Ni/ γ -Al₂O₃ shows no hydrogenation activity below 373 K.

To further evaluate the selective hydrogenation of 1,3-butadiene on different catalysts, the selectivities to total butene, 1-butene, *trans*-2-butene, and *cis*-2-butene were plotted at conversions of 10% and 60% in Fig. 8. The butene selectivities are independent of the H_2/C_4H_6 ratios. Similar product distribution and product selectivities are obtained for $H_2/C_4H_6 = 2.2$ and for $H_2/C_4H_6 = 4$, so only selectivities at $H_2/C_4H_6 = 2.2$ are shown in Fig. 8. The total butene selectivity is 100% at conversions below 60% over the three catalysts.

Moreover, the selectivities to 1-butene, *trans*-2-butene, and *cis*-2-butene are different over the three catalysts. The PdNi/ γ -Al₂O₃ catalyst is ~20% more selective to 1-butene at conversions below 60% than its monometallic counterparts. As shown in Fig. 8, the steady-state product distribution showed the following trend: PdNi/ γ -Al₂O₃ > Pd/ γ -Al₂O₃ ~ Ni/ γ -Al₂O₃ for 1-butene production, Pd/ γ -Al₂O₃ > Pd/ γ -Al₂O₃ ~ PdNi/ γ -Al₂O₃ for *trans*-2-butene, and Ni/ γ -Al₂O₃ > Pd/ γ -Al₂O₃ ~ PdNi/ γ -Al₂O₃ for *cis*-2-butene. The enhanced selectivity for 1-butene formation over PdNi/ γ -Al₂O₃ is consistent with the DFT and TPD results that the bimetallic structure promotes the production and subsequent desorption of 1-butene. However, more studies are needed to understand the trends for the *cis*- and *trans*-2-butene production.

As 1-butene is the most desirable product from 1,3-butadiene hydrogenation, $PdNi/\gamma-Al_2O_3$ is superior than $Pd/\gamma-Al_2O_3$ because it has higher hydrogenation activity and better performance in suppression of both complete hydrogenation and isomerization reactions.

4. Discussion

Several parallels between model surfaces and supported catalysts can be drawn based on the results presented above. In the



Fig. 7. Conversion of 1,3-butadiene in flow reactor at different temperatures. (a) $H_2:C_4H_6$ = 2.2:1; (b) $H_2:C_4H_6$ = 4:1.



Fig. 8. Selectivities of total butene, 1-butene, *trans*-2-butene, and *cis*-2-butene in flow reactor at conversion of (a) 10% (b) 60%. ($H_2:C_4H_6$ = 2.2:1, similar product distribution is obtained for $H_2:C_4H_6$ = 4:1).

TPD experiments of model surfaces, the Pd-terminated PdNiPd(111) surface shows much higher activity for 1.3-butadiene hydrogenation than Pd(111) and NiPdPd(111) surfaces. This trend is consistent with DFT calculations, which show that the activation barrier for each hydrogenation step is lower on PdNiPd(111) than on Pd(111). The catalytic evaluation of the supported catalysts in both batch and flow reactors shows that $PdNi/\gamma-Al_2O_3$ exhibits higher activity than its monometallic catalysts, demonstrating an excellent correlation between model surfaces and supported catalysts. The selectivity also shows similarities between model surfaces and supported catalysts. The PdNiPd(111) surface does not produce butane from 1-butene under the UHV-TPD experimental conditions. DFT calculations show that 1-butene has much lower binding energy on PdNiPd(111) than on Pd(111), indicating a higher 1-butene selectivity due to its facile desorption from the PdNiPd(111) surface. Both DFT calculations and TPD experiments predict that the Pd-terminated bimetallic structure should give higher 1-butene selectivity than the monometallic catalysts. This is validated by the evaluation of supported catalysts using the flow reactor, where $PdNi/\gamma$ -Al₂O₃ shows a higher 1-butene selectivity over Pd/ γ -Al₂O₃ at similar 1,3-butadiene conversions.

The results in the present work successfully bridge the "pressure gap" and "materials gap" between surface science studies under UHV conditions and reactor evaluations of supported catalysts under catalytic conditions. Equally important, this paper reports a more effective catalyst for the selective hydrogenation of 1,3-butadiene. The PdNi/ γ -Al₂O₃ catalyst has both higher hydrogenation activity and higher selectivity to 1-butene, which is the most desirable product in the purification of butane streams.

However, an inconsistency has been found between model surfaces and supported catalysts. The activity increase by the addition of Ni is not as significant in supported catalysts as suggested from surface science studies. This is most likely due to the relatively low degree of bonding between Ni and Pd in the supported catalysts. According to the EXAFS results, the coordination number of Pd—Ni is only 1.44, which is much lower than common bimetallic catalysts [55]. A similar coordination number of 1.35 is found on 0.18%Pd–1.5%Ni/ γ -Al₂O₃ (atomic ratio 1:15; EXAFS results not shown), indicating the difficulty of Ni insertion into Pd nanoparticles. To better understand the bimetallic effect and to promote the formation of Pd—Ni bimetallic bonds, Pd—Ni nanoparticle structures on other oxide supports should be further explored.

5. Conclusions

Hydrogenation of 1,3-butadiene has been studied on Pd-Ni bimetallic catalysts using a combination of DFT calculations and TPD experiments on model surfaces and reactor evaluation over supported catalysts. The results show that the Pd-Ni bimetallic structure has higher hydrogenation activity than its monometallic counterparts. The activity of the catalysts follows the trend of Pd—Ni > Pd > Ni. The selectivity is evaluated with supported catalysts in both batch and flow reactors. The Pd-Ni, Pd and Ni catalysts supported on γ -Al₂O₃ show similar total selectivity to butenes, while Pd—Ni/ γ -Al₂O₃ gives the highest 1-butene selectivity at similar conversions. The high hydrogenation activity and 1butene selectivity make PdNi/ γ -Al₂O₃ a better catalyst for 1,3butadiene removal than the Pd monometallic catalyst. The good correlation between model surfaces and supported catalysts demonstrates the feasibility of designing selective hydrogenation catalysts using well-defined single crystal surfaces.

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