Zirconium Oxide Supported Palladium Nanoparticles as a Highly Efficient Catalyst in the Hydrogenation– Amination of Levulinic Acid to Pyrrolidones

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The selective hydrogenation-amination of levulinic acid into pyrrolidones is regarded as one of the most important reactions to transform biomass-derived lignocellulose feedstocks into valuable chemicals. Here we report on ZrO_2 -supported Pd nanoparticles as a highly active, chemoselective, and reusable catalyst for the hydrogenation-amination of levulinic acid with H_2 and various amines under mild reaction conditions. The

Pd/ZrO₂ catalyst exhibited a marked increase in activity compared with conventional Pd catalysts and a significant enhancement in pyrrolidone selectivity. The excellent catalytic performances are reasonably attributed to the ZrO₂ support, which has strong Lewis acidity to enhance the hydrogenationamination reaction and hinder side reactions.

attention because pyrrolidones are used widely as solvents

and raw materials for the production of surfactants and fibers. $^{\scriptscriptstyle [5,16-19]}$ To date, various metal complex catalysts have

been used to catalyze the LA-to-pyrrolidone processes,^[16,18] but

their homogeneous nature makes catalyst separation and re-

generation from the reaction system difficult. Supported Pt

and Au metal nanoparticles are regarded as active and recycla-

ble catalysts, but most reactions with these heterogeneous cat-

alysts are performed at a high reaction temperature and/or with solvents,^[5, 18, 19] which limit their wide applications because

of the high energy cost in the reaction process and product separation from the solvents. Recently, a molybdenum oxide modified Pt catalyst was reported for LA hydrogenation-ami-

Supported Pd nanoparticles are well known as highly active catalysts for industrial hydrogenation^[45] but their use is challenging in the hydrogenation–amination of LA because of their disadvantages such as poor pyrrolidone selectivity.^[17] If we consider that Pd catalysts, which have lower costs than Au and Pt catalysts, have been used widely in industrial processes, the development of highly efficient Pd catalysts for the hydrogenation–amination of LA to pyrrolidones is important for sus-

In this work, we report for the first time a heterogeneous Pd nanocatalyst that can efficiently catalyze the hydrogenationamination of LA to pyrrolidones. We employed ZrO_2 as a support, and the Pd/ZrO₂ catalyst exhibits a superior catalytic activity and pyrrolidone selectivity at a very mild reaction temperature (90 °C) and solvent-free conditions. For example, in the hydrogenation-amination of LA with *n*-octylamine, the Pd/ZrO₂ catalyst gives a yield of pyrrolidone of over 98% to afford a turnover number (TON) of 5625, which is 2–40 times

that of catalysts reported previously.^[5a, 16-19] Importantly, the

nation under mild reaction conditions.^[17]

tainable chemical synthesis from biomass.

Introduction

The selective transformation of renewable biomass-derived feedstocks is very important for the sustainable production of fuels and fine chemicals.^[1,2] In particular, levulinic acid (LA), which could be obtained easily from lignocelluloses in an environmentally friendly way, has been recognized as one of the top 10 most promising platform molecules derived from biomass by the U.S. Department of Energy.^[3,4] Recently, many successful routes have been developed for the efficient transformation of LA to valuable chemicals.^[5-44] Particularly, the hydrogenation–amination of LA to pyrrolidones has attracted much

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 Pd/ZrO_2 catalyst is stable and recyclable and offers a good opportunity for potential applications.

Results and Discussion

Pd/ZrO₂ was synthesized by impregnation. Typically, ZrO₂ was added to a mixed solution of Na₂PdCl₄ and urea. After the mixture was stirred at 90 °C for 4 h, the solid was separated from the liquor and treated by calcination and reduction. Finally, Pd/ZrO₂ with a Pd loading of 2.1% was obtained. For comparison, the Al₂O₃- and TiO₂-supported Pd catalysts were synthesized by the same method and were denoted as Pd/Al₂O₃ and Pd/TiO₂ with Pd loadings of 2.1 and 1.9%, respectively.

A TEM image of Pd/ZrO_2 is presented in Figure 1, which shows direct evidence that the Pd nanoparticles are highly dis-



Figure 1. A) TEM image of Pd/ZrO_2 and B) HRTEM image of a Pd nanoparticle.

persed on the ZrO_2 support. Furthermore, the high-resolution transmission electron microscopy (HRTEM) image shows that the Pd nanoparticles have well-defined lattice spacing of 0.223 nm, which is associated with the Pd{111} plane.^[46-48] The Pd nanoparticle size distribution was estimated to be in the range of 3–7 nm from more than 80 nanoparticles (Figure S1).

XRD patterns of Pd/ZrO₂, Pd/TiO₂, and Pd/Al₂O₃ are shown in Figure S2. In these samples it is difficult to observe the peaks related to Pd nanoparticles, which suggests the high dispersion of the Pd nanoparticles. We used CO adsorption tests to measure the fraction of exposed Pd atoms in these catalysts, which is denoted as the Pd dispersion degree (Table 1). Pd/ZrO₂ has a dispersion degree of 21.5%, which is very similar to that of Pd/Al₂O₃ and a little lower than that of Pd/TiO₂. The Pd nanoparticles on the Al₂O₃ and TiO₂ supports were further

Table 1. Structural parameters of various Pd catalysts.						
Sample	S_{BET} [m ² g ⁻¹]	Pd loading [wt%] ^[a]	Pd nanoparticle size [nm] ^[b]	Dispersion [%] ^[c]		
Pd/ZrO ₂	< 10	2.1	3–7	21.5		
Pd/TiO ₂	42	1.9	2-4	30.1		
[a] Measured by using ICP-OES. [b] Measured by using TEM. [c] Measured by using CO adsorption.						

characterized by using TEM, which confirmed the high dispersion of the Pd nanoparticles on the support (Figures S3 and S4).

The catalytic tests began with the hydrogenation-amination of LA with *n*-octylamine under 0.5 MPa of H₂ at 90 °C as a model reaction, in which various side reactions of hydrogenation and dehydration might occur during the process (Scheme 1). The catalytic data in the hydrogenation-amination of LA over various supported Pd catalysts are presented in Figure 2. Notably, the catalyst support is very sensitive to the activity and selectivity. Pd/ZrO₂ exhibits a full conversion of LA with a pyrrolidone (5-methyl-1-octylpyrrolidin-2-one) selectivity as high as 98.7% (Figure 2A), whereas Pd/Al₂O₃ shows a LA conversion of 76.1% and a pyrrolidone selectivity of 87.0%.



Scheme 1. Catalytic hydrogenation–amination of LA and the possible side reactions.



Figure 2. A) LA conversion (blue) and pyrrolidone selectivity (red) and B) TON in the hydrogenation–amination of LA with *n*-octylamine over various oxide-supported Pd catalysts. Reaction conditions: 5 mmol of LA, 5 mmol of amine, S/C at 1000, reaction time at 12 h, 90 °C, and 0.5 MPa of H₂.

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Additionally, Pd/SiO₂ and Pd/C exhibit an extremely low pyrrolidone selectivity (<4.5%). Particularly, Au/ZrO₂, Pt/C, and Pt/MoO_x/TiO₂, which were reported as very efficient catalysts for the hydrogenation-amination of LA,^[5a, 17, 19] exhibit pyrrolidone yields of 24.4, 61.8 and 92.1%, respectively (Table S1). The Pt/ZrO₂ exhibits a high pyrrolidone yield of 99.0% (Table S1), which is similar to that of Pd/ZrO₂ (98.7%), but the lower cost of Pd than Pt suggests that Pd/ZrO₂ is more favorable than Pt/ZrO₂ for the hydrogenation-amination reaction. After the calculation of TON, it is clear that the TON of the Pd/ZrO₂ could reach as high as 5625, which is much higher than that of the other oxide-supported Pd catalysts (222-1077; Figure 2B). This value is even higher than that of other metalbased catalysts (Au, Pt, Ir, and Ru, 115-2150; Table S2) reported previously.^[5a, 16a, 17, 18, 19a] These results demonstrate the excellent activity for LA conversion and the high selectivity for the formation of pyrrolidone in hydrogenation-amination over the Pd/ZrO₂ catalyst.

The dependence of LA conversion and product yield on the reaction time over the Pd/ZrO₂, Pd/Al₂O₃, and Pd/TiO₂ catalysts is shown in Figure 3. If Pd/ZrO₂ is used as a catalyst, a conversion of 94% is reached quickly at 6 h (Figure 3 A-a) accompanied by the formation of amine (m/e = 229.2, GC-MS) and pyrrolidone. The amine appears at the start of the reaction (Table S3) and reaches the highest yield (28.2%) at 3 h. After almost the full conversion of LA (>99%) at 8 h, the pyrrolidone is still formed continuously until the yield is higher than 99.0% at 10 h with the complete consumption of amine in the reaction. This implies that the pyrrolidone product is formed through an amine intermediate. In addition, there is nearly no γ -valerolactone product in the reaction (Table S3 and Figure 3A-d), which means that the direct hydrogenation-esterification of LA is avoided completely over the Pd/ZrO₂ catalyst. Conversely, if Pd/Al₂O₃ and Pd/TiO₂ were used as catalysts, γ -valerolactone is formed at the start of the reaction and formed continuously (Table S3, Figure 3B and 3C), which suggests a direct hydrogenation route from LA to γ -valerolactone.

Based on these experimental data and the possible mechanism for LA conversion suggested previously,^[6,17] it is proposed that the hydrogenation–amination of LA to pyrrolidone comprises steps of (i) amination of LA to form imine, (ii) hydrogenation of imine to amine, and (iii) condensation of amine to pyrrolidone (Scheme 2). In these steps, the formation of amine should be regarded as the rate-limiting step because the order of the yields of the amine intermediate formed in the reaction is $Pd/ZrO_2 > Pd/Al_2O_3 > Pd/TiO_2$. To confirm this order, the catalytic activities of the Pd/ZrO_2 , Pd/Al_2O_3 , and Pd/TiO_2 in the amination of 2-hexanone with aniline were compared, and their turnover frequencies (TOFs) are presented in Table 2. Clearly, Pd/ZrO_2 (2600 h⁻¹) is much more active than Pd/TiO_2 and Pd/Al_2O_3 (756 and 1900 h⁻¹), which demonstrates the stronger ability for amination over Pd/ZrO_2 than Pd/Al_2O_3 and Pd/TiO_2 .

As a major side reaction, the conversion of LA to γ -valerolactone occurs easily through tandem steps of (i) reduction of the C=O group on LA to C–OH and (ii) esterification to form γ - valerolactone (Scheme S1), in which the reduction of C=O is regarded as a key step.^[8] Notably, in the reduction of

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Figure 3. Dependence of a) LA conversion and selectivity to b) pyrrolidone, c) amine, and d) γ -valerolactone on time in the hydrogenation–amination of LA with *n*-octylamine over A) Pd/ZrO₂, B) Pd/Al₂O₃, and C) Pd/TiO₂. The decrease of the γ -valerolactone yield is because of the further hydrogenation to alcohols.



Scheme 2. Proposed reaction pathways for the hydrogenation-amination of LA to pyrrolidone.

2-hexanone to 2-hexanol, Pd/ZrO_2 exhibits a much lower activity than Pd/Al_2O_3 and Pd/TiO_2 (entries 1–3 in Table 3). After the



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Table 2. Catalytic activities in the conversion of 2-hexanone and aniline
to the corresponding amine over Pd/ZrO2, Pd/Al2O3, and Pd/TiO2 in the
presence of H2.^[a]O
Image: Harrier of H2.^[a]Image: Harrier of H2.^[a]O
Image: Harrier of H2.^[a]Image: Harrier of H2.^[a]O
Image: Harrier of H2.^[a]Image: Harrier of H2.^[b]Image: Harrier of H2.^[a]Image: Harrier of H2.^[b]Image: Harrier of H2.^[b]



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Pd/TiO₂



addition of aniline in the starting 2-hexanone, Pd/ZrO₂ is completely inactive for C=O reduction, whereas Pd/Al₂O₃ and Pd/TiO₂ still give TOFs of 270 and 455 h⁻¹, respectively (entries 4–6 in Table 3). These results indicate that Pd/ZrO₂ is highly selective in the tandem amination and hydrogenation of the C=O group to amine rather than the direct hydrogenation of the C=O group to C–OH species, which can explain why the byproduct γ -valerolactone is inhibited with Pd/ZrO₂.

It is well known that ZrO_2 , Al_2O_3 , and TiO_2 supports are Lewis acidic oxides that could react with the C=O group by an acid–base interaction to influence the reaction pathways in the conversion of C=O groups in the compounds.^[49] To understand the activities over various catalysts, we compared the NMR spectra of adsorbed probe molecules, trimethylphosphine (TMP) and 2^{-13} C-acetone, to characterize their acidic properties.^[50]

The ³¹P NMR spectra of TMP adsorbed on ZrO₂, Al₂O₃, and TiO₂ are presented in Figure 4A. The main peaks at $\delta = -45$, -49, and -57 ppm could be assigned to the interaction of TMP with Lewis acid sites. In these spectra, no clear signals at $\delta = -2$ to -5 ppm associated with the interaction of TMP with Brønsted acidic protons could be observed, which indicates that the Brønsted acidic sites are absent in these oxides. ¹³C

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Figure 4. A) ³¹P NMR spectra of TMP and B) ¹³C NMR spectra of $2^{-13}C$ -acetone adsorbed on a) ZrO_{2r} b) Al_2O_{3r} and c) TiO_{2r} . The asterisks in the ¹³C NMR spectra denote spinning side bands.

magic-angle-spinning (MAS) NMR spectra of 2-¹³C-acetone adsorbed on ZrO₂, Al₂O₃, and TiO₂ are shown in Figure 4B. In these spectra, the peak at $\delta = 224$ ppm is caused by the strong interaction of Lewis acidic sites with acetone, the peak at $\delta = 216$ ppm is attributed to the relatively weak interaction of Lewis acidic sites with acetone, and the peak at $\delta = 210$ ppm is assigned to the physical sorption of acetone. The signals at $\delta = 181-167$, 109–70, 42, and 34 ppm are related to the products of the bimolecular and trimolecular reactions of 2-¹³C-acetone. Interestingly, ZrO₂ shows a much more intense peak at $\delta = 224$ ppm than Al₂O₃ and TiO₂, which indicates that ZrO₂ has much stronger Lewis acidic sites than Al₂O₃ and TiO₂.

The temperature-programmed desorption (TPD) profiles of acetone on ZrO₂, Al₂O₃, and TiO₂ are shown in Figure S5. All three samples exhibit peaks in the low-temperature region of 70.6–72.8 °C, which is assigned to the desorption of physically adsorbed acetone. Interestingly, ZrO₂ and Al₂O₃ exhibit additional peaks in the high-temperature region (> 250 °C), which are assigned to acetone adsorbed strongly on the metal oxides by acid–base interaction. Notably, the desorption temperature on ZrO₂ (309.1 °C) is higher than that of Al₂O₃ (272.8 °C), which indicates the stronger interaction of acetone with ZrO₂ than with Al₂O₃.

The IR spectra of acetone adsorbed on ZrO₂, Al₂O₃, and TiO₂ were measured to understand the interaction between acetone and the metal oxides (Figure 5). The spectra of TiO₂ and Al₂O₃ exhibit peaks at $\tilde{\nu} = 1724$ and 1715 cm^{-1} assigned to the C=O bond of acetone. Interestingly, the vibration of the C=O bond appeared at $\tilde{\nu} = 1675 \text{ cm}^{-1}$ in the spectrum of ZrO₂, which is a redshift of 49 and 40 cm⁻¹ from that of TiO₂ and Al₂O₃, respectively. The redshift is consistent with the stronger interaction of the basic C=O group with the Lewis acids on





Figure 5. IR spectra of acetone adsorbed on a) ZrO₂, b) Al₂O₃, and c) TiO₂.

 ZrO_2 than those on TiO₂ and Al_2O_3 .^[49,51] This phenomenon is in good agreement with that observed from the acetone-TPD profiles (Figure S5) and acetone-adsorption ¹³C NMR spectra (Figure 4).

Possibly, the abundant strong Lewis acid–base interaction increases the electrophilicity of the C=O group in the compounds significantly, which promotes amination for the formation of amine intermediates and prevents the hydrogenation of the C=O group to C–OH species in the hydrogenation–amination. These features make the Pd/ZrO₂ catalyst highly active and selective for the hydrogenation–amination of LA to pyrrolidones (Scheme 3).

Recyclability tests in the hydrogenation–amination of LA with *n*-octylamine over Pd/ZrO₂ are shown in Figure 6. After the sixth run, Pd/ZrO₂ still gives a LA conversion of 98.5% and a pyrrolidone selectivity of 98.0%. Further observation shows that the LA conversion (~14.5%) and reaction rates (~290 mol_{LA}mol_{Pd}⁻¹ h⁻¹) at the beginning of each run (25 min) are very similar. All of these results indicate the excellent recyclability of the Pd/ZrO₂ catalyst. Additionally, inductively coupled plasma optical emission spectroscopy (ICP-OES) shows that the Pd species is undetectable in the reaction liquor, TEM images of used Pd/ZrO₂ catalyst (Figure S6) show a similar Pd



Scheme 3. The role of ZrO₂ in two pathways of LA conversion.

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Figure 6. Recycling tests (LA conversion: blue; pyrrolidone selectivity: red; initial reaction rate: green) in the hydrogenation–amination of LA with *n*-oc-tylamine over Pd/ZrO₂. The reaction conditions are the same as those stated for Figure 2A. The reaction rates were calculated from the LA conversion in the first 25 min of the reaction.

3

Runs

0

1

2

nanoparticle size distribution to that of the as-synthesized catalyst, which suggests the good stability of the Pd nanoparticles on the ZrO_2 support.

Encouraged by the successful hydrogenation-amination of LA with *n*-octylamine, we employed various amines as reactants in the hydrogenation-amination reactions. As expected, Pd/ZrO₂ exhibits very high yields of the corresponding pyrrolidone products (Table 4). The high activity, superior selectivity, excellent stability, and general applicability show the potential of Pd/ZrO₂ in hydrogenation-amination reactions in the future.





Conclusions

We demonstrate that ZrO_2 -supported Pd nanoparticles are highly efficient for the selective production of pyrrolidones from the hydrogenation–amination of levulinic acid (LA) with amines and H₂. The excellent properties are attributed to the presence of strong Lewis acidity in the catalyst, which is very favorable for LA amination and hinders the side reaction of direct LA hydrogenation–esterification. This work is important for the development of highly efficient catalysts for the conversion of LA.

Experimental Section

Materials: All the chemicals are commercially available and used directly without any treatment.

Synthesis of ZrO_2 support: $ZrOCI_2$ (3 g) was dissolved in deionized H_2O (500 mL). Then, NaOH aqueous solution (1 m) was dropped into the above solution until white precipitate was fully formed. After hydrothermal treatment in an autoclave at 200 °C overnight, filtration at RT, washing with a large amount of water, drying at 80 °C, and calcination at 500 °C for 2 h, the ZrO_2 support was obtained.

Loading of Pd on the support: Typically, the solid support (1 g) was added to Na₂PdCl₄ solution (50 mL) with the desired Pd concentration. After the addition of urea (molar ratio of urea/Pd at 100), stirring at 90 °C for 4 h in a closed reactor, filtration at RT, washing with a large amount of water, drying at 100 °C for 12 h, calcination at 400 °C for 3 h, and reduction by H₂ at 250 °C for 2 h, the supported Pd catalyst was obtained, which was designed as Pd/ZrO₂. The Pd loading for Pd/ZrO₂, Pd/Al₂O₃, Pd/TiO₂, Pd/SiO₂, and Pd/C was 2.1, 2.1, 1.9, 2.0, and 5.0 wt %, respectively. The supported Pt and Au catalysts were synthesized by the same method except with the use of H₂PtCl₆ and HAuCl₄ as the metal precursors.

Characterization: XRD patterns were collected by using a Rigaku D/MAX 2550 diffractometer with CuK_{α} radiation ($\lambda = 1.5418$ Å). Pd contents were determined by using ICP-OES (PerkinElmer 3300DV). TEM was performed by using a JEM-2100F electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. NMR spectroscopy was performed by using a Bruker Ascend-500 spectrometer at resonance frequencies of 125.88 and 202.63 MHz for ¹³C and ³¹P, respectively. The experiments were recorded using a 4 mm tripleresonance MAS probe at a spinning rate of 10 kHz. The pulse width ($\pi/2$) for ¹³C was measured to be 4.3 μ s. A contact time of 5 ms and a recycle delay of 3 s were used for the ¹H-¹³C cross polarization (CP) MAS measurement. ³¹P MAS NMR spectra with highpower proton decoupling were recorded by using a $\pi/2$ pulse length of 4.1 μ s and a recycle delay of 30 s. The chemical shift of ¹³C was referenced externally to hexamethylbenzene, and that of ³¹P was referenced to 1 м aqueous H₃PO₄. The CO chemisorption of the samples was measured by using a Finetec Finesorb-3010 instrument equipped with a thermal conductivity detector (TCD). Typically, 0.1 g of the sample was pretreated in a pure He flow (20 mLmin⁻¹) at 200 °C for 0.5 h and then cooled to 25 °C. Pulse chemisorption measurements were performed at 25 °C with 20% $CO/He (20 \text{ mLmin}^{-1}).$

Catalytic tests: The hydrogenation-amination was performed in a high-pressure autoclave with a magnetic stirrer. Typically, the

substrate and catalyst were mixed in the reactor. Then the reaction system was heated quickly to a given temperature (the temperature was measured with a thermometer in an oil bath). Then hydrogen was introduced and kept at desired pressure (the hydrogen pressure in the autoclave was recorded at the reaction temperature). After the reaction, the product was diluted and analyzed by using gas chromatography using a flame ionization detector with a flexible quartz capillary column coated with FFAP (Free Fatty Acid Phase). The conversion of LA (C_{LA}), the TON, the yield (Y), and the selectivity to pyrrolidone ($S_{pyrrolidone}$) were calculated from Equations (1)–(4), respectively:

$$C_{\text{LA}} \ [\%] = \left[1 - (M_{\text{LA after reaction}} / M_{\text{LA before reaction}})\right] \times 100 \% \tag{1}$$

$$TON = (M_{LA before reaction} - M_{LA after reaction}) / M_{Pd}$$
(2)

$$Y_{\text{pyrrolidone}} \left[\%\right] = \left(M_{\text{pyrrolidone}}/M_{\text{LA before reaction}}\right) \times 100\% \tag{3}$$

$$S_{\text{pyrrolidone}} \left[\%\right] = \left(Y_{\text{pyrrolidone}}/C_{\text{LA}}\right) \times 100\,\% \tag{4}$$

in which $M_{\text{LA before reaction}}$ and $M_{\text{LA after reaction}}$ are the molar amount of LA before and after reaction, respectively. M_{Pd} is the molar amount of total Pd atoms in the reaction system. $M_{\text{pyrrolidone}}$ is the molar amount of pyrrolidone product after reaction. $M_{\text{LA after reaction}}$, $M_{\text{LA after reaction}}$, and $M_{\text{pyrrolidone}}$ were determined by using GC with bromobenzene as an internal standard.

The recyclability of the catalyst was tested by separating it from the reaction system by centrifugation, washing with large quantity of ethanol/cyclohexane, and drying at 120 °C for 2 h.

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Zirconium Oxide Supported Palladium
 Nanoparticles as a Highly Efficient
 Catalyst in the Hydrogenation–
 Amination of Levulinic Acid to
 Pyrrolidones



Selectivity secrets: ZrO₂-supported Pd nanoparticles (Pd/ZrO₂) are highly efficient for the selective conversion of

levulinic acid to pyrrolidones by the hydrogenation-amination route.