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A facile route toward the synthesis of ethyl-4-ethoxy pentanoate in high yield: reductive etherification of ethyl levulinate in ethanol on Pd/SiO₂-C catalysts

Qianqian Cui^a, Yinshuang Long^a, Yun Wang^a, Haihong Wu^a, Yejun Guan^{a*}, Peng Wu^a

Abstract: Facile synthesis of biomass-derived ethers useful as biofuels or biofuel-additives has attracted great attention. We have recently reported the synthesis of a novel etherified ester ethyl-4ethoxy pentanoate (EEP) from gamma-valerolactone (GVL) in ethanol catalyzed by H-Beta zeolite. In this continuous study, we report an alternative route to prepare EEP in high yield by reductive etherification of ethyl levulinate (EL) in ethanol at 140 °C under 0.5 MPa H_2 with silica modified Pd/C catalyst. The ether production likely follows a tandem acetalization-hydrogenolysis process with ethyl-4,4diethoxy pentanoate (EDEP) as intermediate. The acetalization step can be favored by introducing acidic materials, SiO₂-carbon or Beta zeolite as a cocatalyst. The combination of Pd/SiO2-C and Beta mixture leads to 100% EL conversion and 93% EEP selectivity under optimized reaction conditions. We have for the first time measured the standard molar combustion enthalpy of as-prepared EEP by static oxygen-bomb, and the value of which is determined to be about -5658 kJ/mol, much larger than that of EL (-2650 kJ/mol).

Introduction

As the worldwide supply of petroleum diminishes, it is becoming increasingly important to produce both chemicals and transportation fuels economically from biomass that can be utilized as a renewable carbon source.1-6 Three classes of feedstocks derived from biomass are considered to be appropriate for the production of renewable fuels: starchy (including sugars), triglyceride, and lignocellulosics.⁷ Among these feedstocks, lignocellulosic biomass is the most inexpensive and abundant class of renewable, which can be converted to socalled platform chemicals such as furfural, alkyl levulinate, and gamma-valerolactone (GVL).3, 8-10 This methodology affords a greater degree of flexibility in downstream processing of biomass derived oxygenates such as ethanol, furan, ester, acetal, and ether. More importantly, adding oxygenated additives into transportation fuel can remarkably improve combustion and reduce the emissions of some regulated pollutants originating from transportation, which allows the clean air standards to be met.^{11, 12} In this regard, bio-derived ethers have been identified as a representative category of valuable fuel-additives.² Therefore

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synthesis of bio-ethers such as 5-ethoxymethylfurfural^{13, 14} and glycerol ethers^{15, 16} via acid-catalyzed etherification of biomassderived alcohols has attracted great attention. We have recently reported the synthesis of a novel bio-derived etherified ester, ethyl-4-ethoxy pentanoate (EEP), by simply heating GVL in ethanol in the presence of solid-acid catalyst of Beta zeolite.¹⁷ The EEP yield and selectivity reached 86% and 97%, respectively at reaction temperature of 160 °C. However, the EEP yield could not be further increased because (a) the GVL conversion is limited by the reaction equilibrium between GVL and ethyl-4-hydroxyl pentanoate (EHP), and (b) several dehydration by-products such as ethyl pentenates were formed at higher reaction temperatures (Scheme S1). Therefore, developing alternative route is desirable in the viewpoint of green and sustainable chemistry.

Reductive etherification of carbonyl compounds provides an alternative methodology for the preparation of biomass-derived ethers.¹⁸⁻²⁰ Balakrishnan et al.¹⁸ have reported the reductive etherification of 5-(hydroxymethyl)furfural catalyzed by supported Pt/alumina catalyst in presence of Amberlyst-15. This method also applies to furfural in both methanol and ethanol by using carbon-supported noble metal nanoparticles as catalyst, though under different reaction conditions.^{19, 20} We have found that Pd/C can efficiently catalyze the reductive etherification of furfural in ethanol under mild conditions (0.3 MPa H₂ and 60 °C).²⁰ Tulchinsky and Briggs recently reported the synthesis of alkyl 4alkoxypentanoates by simultaneous esterification and reductive etherification by using levulinic acid as precursor, where Pd/C was used as catalyst under hydrogen pressure 100-700 psig at 200-220 °C.²¹ However, the yield of etherified esters were limited due to the high temperature used.²¹ The results in this work demonstrate that Pd/C shows moderate activity for EL conversion but high selectivity toward EEP via reductive etherification. The EL conversion over Pd/C can be enhanced by modifying amorphous SiO₂ onto the carbon surface. Moreover, the EEP yield was further increased to 93% when Beta was introduced as a cocatalyst at 140 °C. The EEP formation most likely undergoes a two-step (acetalization and hydrogenolysis) process. The introduction of amorphous SiO2 and Beta accelerates the acetalization owing to their acidic nature. The combustion value of as-prepared EEP has been determined in a static-bomb thermometer. This work gives another example for preparation of bio-derived etherified ester from carbonyl compounds via reductive etherification.

Results and Discussion

Effect of temperature, Pd loading, and hydrogen pressure on the reductive etherification of EL over Pd/C catalyst

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As an initial study, we tested the reductive etherification of EL over 2.1 wt% Pd/C catalyst at reaction temperatures ranging from 50 to 140 °C under 0.5 MPa H₂ and the results are shown in Figure 1. The 2.1 wt% Pd/C catalyst was active for EL hydrogenation at 50 °C in ethanol, giving EL conversion of 16% after reaction for 4 h. The product selectivities are as follows: 73% to EEP, 20% to EHP, 7% to GVL. To our delight, the formation of etherified ester, EEP, was readily observed at temperature as low as 50 °C. Further increase of temperature led to the increase of both EL conversion and EEP selectivity. When the reaction temperature was 140 °C, the EL conversion and EEP selectivity were 60% and 90%, respectively. It should be noted that the hydrogenation of EL in ethanol over 2.0 wt% Ru/C catalyst at 140 °C gives GVL as the main product with a selectivity as high as 98% (Table S1). This result points to the specific role of Pd nanoparticles in reductiveetherification.



Figure 1. Effect of reaction temperature on the catalytic activity of 2.1 wt% Pd/C catalyst for the reductive etherification of ethyl levulinate (EL). Reaction conditions: 350 μ L of EL in 9.65 mL of ethanol; 0.5 MPa H₂; 50 mg of 2.1Pd/C catalyst; 4 h. EV: ethyl valerate; GVL: gamma-valerolate; EHP: ethy-4-hydroxyl pentanoate; EEP: ethyl-4-ethoxy pentanoate.

Table 1. Effects of Pd Loading, H₂ Pressure on the Reductive Etherification of Ethyl Levulinate (EL) over Pd/C Catalyst.

		H ₂	Conv	Sel. (%)			
Entry	Catalyst	Pressure (MPa)	(%)	EEP	EV	GVL	
1	0.5Pd/C	0.5	16	70	30	0	
2	1.0Pd/C	0.5	22	86	9	5	
3	1.5Pd/C	0.5	42	92	4	4	
4	2.1Pd/C	0.5	60	90	5	5	
5	3.1Pd/C	0.5	75	92	3	5	
6	2.1Pd/C	0.3	37	90	2	6	
7	2.1Pd/C	1	82	91	1	8	

Reaction conditions: 350 µL of EL in 9.65 mL of ethanol; 140 °C; 50 mg of Pd catalyst; 4 h. EV: ethyl valerate; GVL: gammavalerolate; EEP: ethyl-4-ethoxy pentanoate.

We next explored the effect of Pd loading on the etherification activity of Pd/C catalyst at 140 °C and 0.5 MPa H₂ and the results are displayed in Table 1 (Entries 1-5). One can see that as the Pd loading increases from 0.5 wt% to 3.1%, the EL conversion increases from 16% to 75%. EEP was observed as the

dominating product for all catalysts. The by-products were found to be ethyl valerate (EV) and GVL. When the Pd loading was 3.1 wt%, EL conversion reached 75% and the selectivity of EEP was as high as 90%. We further investigated the effect of H₂ pressure on the reductive etherification over 2.1 wt% Pd/C catalyst. The results shown in Table 1 (Entries 4, 6, and 7) suggest that the higher H₂ pressure benefits the EL conversion, meanwhile, the EEP selectivity remains above 90%. The EL conversion reached 82% under H₂ pressure of 1 MPa with EEP selectivity of 91%.

Effect of modifying inorganic oxides on the catalytic activity of Pd/C catalyst

The above-mentioned results demonstrate that Pd/C catalyst shows moderate activity but high selectivity toward EEP in reductive etherification of EL. It has been shown recently that the activity and stability of carbon supported metal nanoparticles can be remarkably increased by modifying inorganic oxides.²²⁻²⁸ Therefore, we have prepared several inorganic oxide and carbon composites (MO_x-C) by introducing SiO₂, Al₂O₃, TiO₂, CeO₂, ZrO₂, and Nb₂O₅ onto C surface via impregnation or hydrolysis methods with MO_x loading about 20 wt%. The catalytic activity of Pd supported on these supports are listed in Table 2.

Table 2.	Catalytic Activity	of Pd/C modifi	ed with V	arious Ox	ides
(20 wt%)	for the Reductive	Etherification	of Ethyl Le	evulinate (EL).

Catalyata	Conv.	Sel. (%)				
Catalysis	(%)	EV	EEP	GVL	EHP	
2.6Pd/Al ₂ O ₃ -C	17	11	75	14	-	
2.7Pd/CeO2-C	25	2	26	62	10	
2.5Pd/Nb ₂ O ₅ -C	33	10	86	4	-	
2.5Pd/ZrO ₂ -C	28	5	85	6	4	
2.5Pd/TiO ₂ -C	45	3	91	6	-	
2.5Pd/SiO ₂ -C	65	1	93	6	-	

Reaction conditions: 350 µL of EL in 9.65 mL of ethanol; 140 °C; 50 mg of Pd catalyst; 0.5 MPa H₂; 4 h. EV: ethyl valerate; GVL: gamma-valerolate; EEP: ethyl-4-ethoxy pentanoate.

One can clearly see that Pd/C catalyst modified with different oxides showed distinct activities. The 2.6Pd/Al₂O₃-C catalyst only gave 17% EL conversion with EEP selectivity of 75% and the byproducts mainly included EV and GVL. The catalysts modified with CeO₂, ZrO₂, Nb₂O₅, and TiO₂ gave EL conversion of 25%, 28%, 33%, and 45%, respectively. These catalysts all showed much lower activity than Pd/C catalyst (60%). It should also be noted that the major product over Pd/CeO2-C was GVL instead of EEP. Different to these metal oxides based Pd/MOx-C, Pd/SiO2-C showed slightly higher activity (65%) than Pd/C (60%). Inspired by this result, we then compared the catalytic activity of Pd/SiO₂-C with varying SiO₂ content and the results are shown in Fig. 2. When 2.5 wt% SiO₂ was loaded, the EL conversion was about 68%. Further increase of SiO₂ led to higher EL conversion. A maximum EL conversion about 73% was achieved for both Pd/5SiO₂-C and Pd/10SiO₂-C. By contrast, Pd/SiO₂ only gave EL conversion and EEP selectivity of 4% and 57%, respectively. This finding suggests that modifying SiO₂ onto the carbon surface may affect the catalytic activity of SiO₂-C composite as well as the Pd/SiO₂-C catalyst. It can be concluded that the modified oxides

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influence the catalytic performance and product distribution. We next followed the EL conversion and product distributions during the reaction course by choosing Pd/C, Pd/CeO₂-C, and Pd/SiO₂-C as examples and the results are shown in Tables S2-S4, respectively. One can see that in the early stage of the reaction (10 min), the acetalization product, ethyl 4,4-diethyoxypentanoate (EDEP), was detected with varying selectivity ranging from 10 to 26% depending on the nature of support. This phenomenon suggests that acetalization of EL as shown in Equation 1 takes place on all catalysts in the beginning of the reaction.

 $EL + 2C_2H_5OH \rightleftharpoons EDEP + H_2O$ -----Equation 1



Figure 2. Effect of SiO₂ loading on the catalytic performance of 2.1 wt% Pd/C, 3.0 wt% Pd/SiO₂, and 2.5 wt% Pd/xSiO₂-C (x=2.5, 5, 10, 20, and 30 wt%) catalysts in reductive etherification of EL. Reaction conditions: 350 μ L of EL in 9.65 mL of ethanol; 140 °C; 50 mg of catalyst; 0.5 MPa H₂; 4 h. EV: ethyl valerate; GVL: gamma-valerolate; EEP: ethyl-4-ethoxy pentanoate.

It should also be noted that the selectivity to EHP at 10 min for Pd/CeO₂-C catalyst was about 62%, while minute or very little amount of EHP was observed for Pd/C and Pd/SiO₂-C catalyst. This result means that Pd nanoparticles on CeO₂-C are more active toward saturation of carbonyl bond, thus forming large amount of EHP. As a result, the lactonization of EHP will undoubtedly lead to the formation of GVL, which explains the low EEP yield on Pd/CeO₂-C catalyst. This phenomenon is consistent with a previous report that Pd/CeO₂ is an active catalyst for GVL production.²⁹

The mechanism of reductive-etherification of EL

The above-mentioned results demonstrate that EEP can be successfully synthesized via reductive-etherification of EL on Pd/C modified with various oxides, though with different activity and selectivity. The reductive-etherification of carbonyl compounds generally undergoes a consecutive acetalization-hydrogenolysis pathway.³⁰⁻³² For instance, acetal of cyclohexanone, octanal and furfural have been observed in large amount without exceptionally in the early stage of their reductive-etherification process. Taking furfural as an example, it is highly likely that most furfural was first converted to furfural acetal, which is then converted to furfuryl ethyl ether. By contrast, the amount

of EDEP is rather low during the reductive-etherification process of EL. To clarify the role of EDEP in the production of EEP, we have investigated the hydrogenation activity of EDEP without catalyst or in presence of Pd catalysts (Table S5). The EDEP was synthesized according to a previous report³³. The ¹H-NMR and GC-MS spectra is consistent with literature^{33, 34} and its purity was determined to be about 94% (Figure S1). Upon heating at 140 °C, the EDEP turns back to EL in ethanol with 100% conversion and 100% selectivity without any catalyst, meaning that the EDEP is not stable in ethanol under the reaction conditions. This is in line with the fact that the synthesis of EDEP in high yield requires the usage of triethyl orthoformate as reactant, which acts as a dehydration reagent³³. When Pd catalysts were present, the conversions were 97% and EEP was observed as one of the major product with selectivity ranging from 15 to 35%. The EEP selectivity over Pd/C, Pd/CeO2-C and Pd/SiO2-C are 23%, 15%, and 35%, respectively. This result clearly indicates that the EEP can be produced by hydrogenolysis of EDEP. Moreover, modifying SiO₂ onto carbon significantly improves the EEP yield. The positive role of SiO₂ might be two-fold. First, the acetalization is likely catalyzed by either the Pd-H species on Pd/C catalyst²⁰ or by Brønsted acid sites when solid acidic materials such as Amberlyst-15 were present¹⁸. Second, the acidic sites catalyze the protonation of acetal leading to the formation of enolether intermediate, which is eventually hydrogenated to ether.³² In this regard, introducing SiO₂ increases the amount of acidic sites of carbon material, e.g. lactonlic and phenolic groups, according to a recent study by Gatti and coworkers²⁷.

In accordance with this assumption, we then tested the catalytic activity of Pd/xSiO₂-C in presence of 25 mg of Beta zeolite for EL hydrogenation and the results are shown in Table 3 and Table S6. One can see that the EL conversions over Pd/C, Pd/SiO₂ and Pd/xSiO₂-C are all significantly improved. As an example, EL conversion increased from 60% to 87% over 2.1Pd/C in the presence of Beta. For Pd/SiO₂, the EL conversion also increased from 4% to 16%. It should be noted that for the combinations of Pd/xSiO₂-C and Beta, the 2.5Pd/20SiO₂-C and Beta showed the highest EL conversion of 95%, with EEP yield of 88% at 140 °C. This value is much higher than that obtained (55%) for Betacatalyzed ring-opening of GVL in ethanol at the same temperature¹⁷. These results agree with the above-mentioned assumption that acidity favors the reductive-etherification. We tested the catalytic performance of 2.5Pd/20SiO2-C in the presence of other commonly used zeolites, namely, USY (SAR=25) and ZSM-5 (SAR=58). The results in Table S7 demonstrate that USY and ZSM-5 also showed promotion effect but not as pronounced as that observed in case of Beta. The EL conversion over USY and ZSM-5 were 74 and 79% under the same reaction conditions, respectively. The total acidity of three zeolites is as follow: Beta (2.2 mmol/g) > ZSM-5 (1.8 mmol/g) > USY-6 (0.45 mmol/g)¹⁷, which is in good agreement with the trend of EL conversions. Therefore, we consider that it is highly likely that the acidic zeolites are involved in the reductive etherification. It should be pointed out that the intimate contact between Pd nanoparticles and acidic sites of zeolites is not necessary since Pd/20SiO₂-C and zeolites were physically mixed. Another observation should be noted is that lower EEP selectivity was

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noticed after introducing USY and ZSM due to the formation of EV. This result is consistent with our previous finding that strong Brønsted acid sites contribute to the production of EV.³⁵

Table 3. The Catalytic Performance of Pd/C, Pd/SiO₂, and Pd/xSiO₂-C Catalysts in Presence of 25 mg of Beta Zeolite.

Catalvat	$C_{OD}(0/1)$	Sel. (%)			
Catalyst	COIIV. (%)	EV	EEP	GVL	
2.1Pd/C	87	12	85	3	
2.5Pd/2.5SiO ₂ -C	88	6	89	5	
2.5Pd/5SiO ₂ -C	82	21	77	2	
2.5Pd/10SiO ₂ -C	90	7	89	4	
2.5Pd/20SiO2C	95	3	93	4	
2.5Pd/30SiO ₂ -C	88	5	91	4	
3.0Pd/SiO ₂	16	8	87	5	

Reaction conditions: 350 μ L of EL in 9.65 mL of ethanol; 140 °C; 50 mg of Pd catalyst; 25 mg of Beta (SAR=25); 0.5 MPa H₂; 4 h. EV: ethyl valerate; GVL: gamma-valerolate; EEP: ethyl-4-ethoxy pentanoate.

We next studied the effect of Beta loading on the reductive etherification activity of Pd/20SiO₂-C catalyst and the results are shown in Table 4. It can be seen that the EL conversion increased to 77% when 5 mg of Beta was added in the reaction mixture while the EEP selectivity was not changed significantly. The EL conversion further increased to about 91% when the amount of Beta was 15 mg. The addition of more amount of Beta did not significantly change the EL conversion. With respect to the role of Beta in this reaction, it is worthy of noting that Verhoef and coworkers³⁶ have found that H-MCM-22 itself may catalyze the reductive etherification of substituted cyclohexanones with secondary alcohols. They suggested that the protons or Lewis sites in zeolites might be able to catalyze this reaction. However, our control experiment showed that Beta alone did not show catalytic activity in converting EL to EEP. Moreover, the 2.5 wt% Pd/Beta catalyst also gave very low EL conversion of 14% under the identical reaction conditions. Therefore we believe that Beta serves as cocatalyst of Pd/xSiO₂-C for this process, likely enhancing the forward reaction of acetalization and the protonation of acetal intermediate. Moreover, increasing H₂ pressure to 1 MPa led to almost complete conversion of EL and the EEP yield could reach 93%. Provided the excellent performance of the 2.5Pd/20SiO₂-C and Beta mixture, we have further explored their reusability for the reductive etherification. Results shown in Figure 3 suggest that after four sequential reactions, the EL conversion dropped slightly from 90% to 80%, while the EEP selectivity attained above 95%. This result means that the reductive etherification pathway is very promising compared with the acid-catalyzed etherification that undergoes deactivation due to the coke formation.¹⁷ The spent catalyst was characterized by TEM analysis and the result is shown in Figure S3. One can see that the aggregation of Pd nanoparticles occurred during the hydrogenation process, which accounts for the decrease of EL conversion.

The combustion value and miscibility of EEP

Bio-ether has been considered as potential fuel-additive. In this regard, energy content is one of the most important features accounting for its practical application. Therefore, we have prepared about 2 g of crude EEP with purity close to 95% after evaporating the solvent and trace amount of EV. Figure S2 shows the ¹H NMR spectroscopy of the crude product, which confirms the chemical structure of EEP molecule. We next tested its standard (p°=0.1 MPa) molar enthalpy of combustion in oxygen at 25 °C ($\Delta_c H_m^{\circ}$) by a static oxygen-bomb calorimetry with benzoic acid as reference. The $\Delta_c H_m{}^o$ of EEP is estimated to be -5658 kJ/mol, which is much larger than that of GVL (-2650 kJ/mol).37 More importantly, the density of EEP determined at 20 °C by measuring the weight of 1 mL of EEP is found to be about 1.239 g/mL, suggesting that EEP has high-volume energy density. The miscibility is another factor regarding to its application as fueladditive. Figure S4 shows the solubility of 2 mL of EL, GVL, EEP, and MTBE with 6 mL of n-heptane. One can see that a homogenous solution was obtained when EEP or MTBE was mixed with n-heptane, whereas this is not the case for EL and GVL, which means that the etherification strongly increases the solubility of ester in hydrocarbon. The boiling point of EEP has also been determined under 1 atm and it is found to be about 138±2 °C.

Table 4. Catalytic Activity of 2.5 wt% Pd/20SiO₂-C in Presence of Various Amount of Beta zeolite for the Reductive Etherification of EL.

	Beta		Sel. (%)		
Catalysts	loading (mg)	Conv. (%)	EV	EEP	GVL
2.5Pd/Beta	-	14	3	97	0
2.5Pd/20SiO ₂ -C	5	77	2	94	4
2.5Pd/20SiO ₂ -C	15	91	3	93	4
2.5Pd/20SiO ₂ -C	25	95	3	93	4
2.5Pd/20SiO ₂ -C	100	91	4	92	4
2.5Pd/20SiO ₂ -C ^a	25	>99	3	93	4

Reaction conditions: 350 μ L of EL in 9.65 mL of ethanol; 0.5 MPa H₂; 9.65 mL ethanol, 140 °C; 50 mg of Pd/20SiO₂-C catalyst; 4 h. ^a 1 MPa H₂.



Figure 3. The reusability of 2.5wt% Pd/20SiO₂-C and Beta mixture for the reductive etherification of EL. Reaction conditions: 350 μ L

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of EL aqueous solution; 0.5 MPa H_2 , 9.65 mL ethanol; 140 °C; 50 mg of Pd/20SiO₂-C catalyst and 25 mg of Beta; 4 h.

BET, XRD, CO chemisorption and TEM characterization of supported Pd catalysts

The above results have shown that supporting SiO₂, a well-known inert material, onto Pd/C improves the catalytic activity in reductive etherification of EL to EEP. We then characterized the Pd/C, Pd/SiO₂, and Pd/20SiO₂-C catalyst and the major textural properties are listed in Table 5. The XRD patterns of Pd/C with different Pd loading, Pd/MO_x-C and Pd/xSiO₂-C catalysts are also shown in Figures S5-7.

Table 5. Chemical Composition, Textural and StructuralProperties of Various Catalysts.

Catalyst	Pd (wt.%)ª	SSA⁵ (m²/g)	V _{total} (cm³/g)	D ^c (%)	Size ^d (nm)
Pd/SiO ₂	3.1	209	1.34	4.8	7.2
Pd/C	2.1	1297	0.88	40	6.3
Pd/20SiO ₂ -C	2.5	1330	0.89	47	5.0

^a Pd loading Determined by ICP.

^b Specific surface area Calculated using BET method.

^c Dispersion estimated by CO chemisorption.

^d Average particle size given by TEM investigation.

All Pd catalysts show dispersion higher than 34% except for Pd/SiO₂ (4.8%) and Pd/Beta (4.0%). Figure 4A shows the N_2 adsorption/desorption isotherms of Pd/C, Pd/SiO₂, and Pd/SiO₂-C catalysts. Pd/C and Pd/SiO₂-C show very similar surface area of about 1300 m²/g, while Pd/SiO₂ shows the lowest surface area of 209 m²/g. The powder X-ray diffraction patterns in Figure 4B suggest that the diffraction peak at 40° assigned to Pd nanoparticles is clearly observed for Pd/SiO₂, while no obvious diffractions of Pd are found for Pd/C and Pd/SiO2-C. We next determined the Pd particle size by TEM analysis. As shown in Figure 4C, the average Pd particle size of Pd/SiO₂, Pd/C, and Pd/SiO₂-C is estimated to be 7.2, 6.3, and 5.0 nm, respectively. The dispersion of these Pd nanoparticles was also determined by CO chemisorption (Table S8). Pd/20SiO₂-C shows the highest dispersion of 47%, while Pd/SiO₂ shows the lowest dispersion of 4.8%. This trend is in line with the TEM analysis and explains the highest activity of Pd/SiO2-C in EL reductive etherification. This result also gives another example in emphasizing the advantages of oxide-carbon composites their application in catalysis, especially in liquid phase hydrogenation. The presence of carbon ensures the high dispersion of Pd nanoparticles and meanwhile, the oxides tune the acidic properties of the catalyst. These composites are expected to find wide application in biomass conversion.38



Figure 4. N_2 adsorption/desorption isotherms (A), XRD patterns (B) and TEM images (C) of Pd/C, Pd/20SiO₂-C, and Pd/SiO₂ catalysts.

Conclusions

In summary, we have demonstrated another example of preparing etherified ester via reductive etherification of biomassderived platform compound containing carbonyl group. With ethyl levulinate (EL) as starting reagent, ethyl-4-ethoxy pentanoate (EEP) can be synthesized with yield about 75% in ethanol at 140 °C for 4 h under 1 MPa H₂ over Pd/C catalyst. The EEP yield can be significantly improved to 93% by introducing amorphous SiO₂ onto carbon surface and adding Beta as cocatalyst in the reaction mixture under mild conditions. It is likely that the acidity of SiO₂/C and Beta is beneficial to the reductive etherification, possibly enhancing the forward reaction of acetalization equilibrium. The standard molar combustion enthalpy of asprepared crude EEP with purity about 95% is determined to be - 5658 kJ/mol, which suggests that EEP may serve as a fuel-additive with great potential.

Experimental Section

Materials synthesis

Activated carbon (C) was obtained from STREM Chemicals with a surface area about 1400 m²/g. The SiO₂-C composites with different SiO₂ loadings ranging from 0 to 30 wt% were prepared by hydrolysis of tetraethyl orthosilicate (TEOS). In a typical synthesis, 1 g of activated carbon was dispersed in 30 mL of ethanol and stirred for one hour. Desired amount of TEOS was added into the mixture dropwise and the resulted solution was stirred overnight allowing for the complete hydrolysis of TEOS. The slurry was filtered, washed with deionized water, dried at 60 °C for 12 h, and then calcined at 500 °C for 3 h with a ramp rate of 3 °C/min under a N₂ flow. The sample was denoted as xSiO₂-C (x stands for the silica loading in wt.%). For comparison, C supported metal oxides, namely Al₂O₃-C, CeO₂-C, ZrO₂-C and Nb₂O₅-C, have also been prepared by incipient impregnation with the corresponding metal salts (Al(NO₃)₃·9H₂O, Ce(NO₃)₃·6H₂O, ZrOCl₂·6H₂O, Niobium(V) oxalate hydrate). The

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preparation of TiO₂-C can be referred to our previous study³⁹, except that tetrabutyl titanate was used as Ti precursor in this work. Beta (SAR=25, 646 m²/g) and ZSM-5 (SAR=58, 401 m²/g) were supplied from Nankai Catalyst Company, China. USY-6 (SAR=24, 623 m²/g) was offered by Huahua Catalyst Manufacturing Company, China. The detailed textural and acidic properties of three zeolites can be referred to our previous work.¹⁷

Preparation of supported Pd catalysts

The Pd catalysts with Pd loading of 0~3 wt% were prepared via a deposition–precipitation method.^{39, 40} In a typical synthesis, 0.3 g of support was distributed in 75 ml of H₂O with vigorous stirring for 2 h. An appropriate amount of H₂PdCl₄ aqueous solution was added into the mixture. After being stirred for another 2 h, the final pH value of the mixture was adjusted to 10~10.5 by adding NaOH solution (1 M). Then, NaBH₄ aqueous solution (NaBH₄/Pd = 15, molar ratio) was added into the suspension to reduce the Pd²⁺. The slurry was stirred for another 2 h, filtered, washed with deionized water, and finally dried at 60 °C for 12 h. The supports used in this study included SiO₂-C, Al₂O₃-C, TiO₂-C, CeO₂-C, ZrO₂-C, and Nb₂O₅-C.

Catalyst characterizations

The powder X-ray diffraction (XRD) patterns were collected at 35 kV and 25 mA on a Rigaku Ultima IV X-ray diffractometer using Cu K α radiation (λ =1.5405 Å). Transmission electron microscopy (TEM) images were taken on a FEI Tecnai G2 F30 microscope operating at 300 kV. Nitrogen adsorption-desorption isotherms at -196 °C were obtained using BELSORP-Max equipment. Prior to the measurement, the samples were first degassed at 150 °C under vacuum for 6 h. Specific surface areas were calculated according to the BET-method using five relative pressure points at an interval of 0.05-0.30. The BJH model was applied to the adsorption branch of the isotherm obtained the pore size distribution. Pulse CO chemisorption was performed on a Micromeritics AutoChem 2910 to determine the metal dispersion of the reduced catalysts. Prior to measurement, 200 mg catalyst was reduced in a flow of 100 mL/min 10 vol% H₂ in Ar at 200 °C for 2 h and then flushed in He for 2 h. After cooled down to 30 °C in He, the CO gas pulses (5 vol.% CO in He) were introduced in a flow of 100 mL/min. A thermal conductivity detector (TCD) was used to follow the changes in the CO gas phase concentration.

Catalytic Tests

Reductive-etherificiation of ethyl levulinate in ethanol

Catalytic reactions for conversion of ethyl levulinate (EL) to ethyl-4-ethoxy pentanoate (EEP) were conducted in a Teflon-lined (100 mL) steel batch reactor at a stirring speed of 800 rpm for 4 h. The reactor was charged with 0.35 mL of EL, 9.65 mL of ethanol, and 50 mg of Pd catalyst. Then, the reactor was pressured to 0.5 MPa with H₂ and heated at 140 °C for 4 h. Once the reactor was cooled down to room temperature, the products were diluted with ethanol and analyzed with flame ionization detector (FID) and a capillary column DM-5 (30 m length and 0.25 mm internal diameter). The following temperature program was used for GC analysis: kept at 120 °C for 16 min, heated to 220 °C with a ramp rate of 20 °C/min and kept at 220 °C for another 10 min. For reusability test, the used catalyst was seperated by centrifuge, washing with ethanol two times and finally drying at 80 °C overnight. GC-MS analysis was carried out on Agilent 6890 equipped with an Agilent 5973 mass selective detector. ¹H NMR spectra were recorded with Bruker Ultrashield 400 Plus NMR.

Synthesis of ethyl 4,4-diethoxypentanoate (EDEP)

To shed light on the reaction mechanism of reductive-etherification of EL, the possible intermediate, ethyl 4,4-diethyoxypentanoate (EDEP), was synthesized according to a previous report³². In a typical synthesis, to a solution of EL (2.84 mL, 20 mmol) in absolute ethanol (8 mL) were added triethyl orthoformate (3.29 mL, 20 mmol) and 10 mg of p-toluenesulfonic acid. The solution was heated at 145 °C for 2 h. After neutralization with NEt₃ and evaporation of the solvent, EDEP was obtained as a pale-yellow oil with yield about 94%. The ¹H-NMR and GC-MS spectra of the obtained EDEP are in agreement with the reported data (Figure S2).^{33, 34}

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Keywords: bioether • biofuel • levulinate • palladium • silicacarbon composite

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A facile reductiveetherification method over a combination of Pd/SiO₂-C and Beta catalysts has been developed for preparing a bioether based fuel additive, ethyl-4-ethoxy pentanoate, in high yield.



Yinshuang Long, Yun Wang, Haihong Wu, Yejun Guan*, Peng Wu

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Qianqian Cui,

A facile route toward the synthesis of ethyl-4ethoxy pentanoate in high yield: reductive etherification of ethyl levulinate in ethanol on Pd/SiO₂-C catalysts