Pd/Nb₂O₅/SiO₂ Catalyst for the Direct Hydrodeoxygenation of Biomass-Related Compounds to Liquid Alkanes under Mild Conditions

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A simple Pd-loaded Nb₂O₅/SiO₂ catalyst was prepared for the hydrodeoxygenation of biomass-related compounds to alkanes under mild conditions. Niobium oxide dispersed in silica (Nb₂O₅/SiO₂) as the support was prepared by the sol-gel method and characterized by various techniques, including N₂ adsorption, XRD, NH₃ temperature-programmed desorption (TPD), TEM, and energy-dispersive X-ray spectroscopy (EDAX) atomic mapping. The characterization results showed that the niobium oxide species were amorphous and well dispersed in silica. Compared to commercial Nb₂O₅, Nb₂O₅/SiO₂ has significantly more active niobium oxide species exposed on the surface. Under mild conditions (170 °C, 2.5 MPa), Pd/10%Nb₂O₅/

SiO₂ was effective for the hydrodeoxygenation reactions of 4-(2-furyl)-3-buten-2-one (aldol adduct of furfural with acetone), palmitic acid, tristearin, and diphenyl ether (model compounds of microalgae oils, vegetable oils, and lignin), which gave high yields (>94%) of alkanes with little C–C bond cleavage. More importantly, owing to the significant promotion effect of NbO_x species on C–O bond cleavage and the mild reaction conditions, the C–C cleavage was considerably restrained, and the catalyst showed an excellent activity and stability for the hydrodeoxygenation of palmitic acid with almost no decrease in hexadecane yield (94–95%) in a 150 h time-on-stream test.

Introduction

With the diminishment of fossil-fuel resources and the growth of environmental concerns, the conversion of biomass into liquid transportation fuels has attracted a lot of attention. As comprehensively described by Dumesic et al.,^[1] Lercher et al.,^[2] and Bitter et al.,^[3] lignocellulose, inedible vegetable oils, and microalgae oils are the three general feedstocks for the production of "second-generation" biofuels. The conversion of biomass to hydrocarbon fuels requires the removal of oxygen to improve energy density.^[1]

In the works of the groups of Dumesic^[4] and Huber,^[5] C₈–C₁₅ oxygenates were produced by the aldol condensation of acetone with furfural (and/or 5-hydroxymethylfurfural) derived from lignocellulose. The C₈–C₁₅ alkanes were obtained by subsequent hydrogenation to remove the unsaturated C=C and C=O bonds over Pd/Al₂O₃ (4–5.5 MPa H₂) and hydrodeoxygenation on a Pt-loaded solid acid catalyst (250–265 °C, 5.2–6.0 MPa H₂). Very recently, Sutton et al.^[6] developed a new process for the hydrodeoxygenation of bioderived furans into alkanes under mild conditions using a Pd catalyst under acidic conditions. Firstly, the C=C bond outside furan ring was saturated,

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the furan rings were then opened to form polyketones, and finally the polyketones were hydrodeoxygenated to alkanes. Corma^[7] and Zhang^[8] also developed new processes for alkane formation. After the C–C coupling reaction of 2-methylfuran and lignocellulose-derived carbonyl compounds, the highly unsaturated oxygenates were directly hydrodeoxygenated to branched alkanes over carbon-supported noble-metal (Pt, Pd, and Ir) catalysts at 350–370 °C and 5–6 MPa H₂. All of these strategies are creative, but the hydrodeoxygenation process is complicated (multiple steps) or is operated at high temperature and pressure.

Fatty acids and triglycerides from inedible oil crops such as microalgae and jatropha are considered as promising renewable sources of biodiesel.^[2,3,9] Currently, three methods can be utilized for the deoxygenation of fatty acids and triglycerides to alkanes. The first relies on supported Group 9 and 10 metal catalysts, such as Ni/ZrO₂, Pd/C, and Pt/C, for the decarbonylation and decarboxylation of carboxylic acids to alkanes at 260-330 °C.^[10] However, the decarbonylation and decarboxylation not only require high temperatures but also produce hydrocarbons with one less carbon atom. The second utilizes conventional hydrodesulfurization catalysts (sulfide NiMo or CoMo), which are more selective to hydrodeoxygenation at 300- $450\,^\circ\text{C},^{[11]}$ however, the metal sulfide catalysts can suffer from sulfur leaching, which leads to contaminated products and deactivation. The third employs zeolite-supported metal catalysts, such as Ni/HBEA (HBEA = protonated zeolite beta)^[12] and Pt-Re/H-ZSM-5,^[13] which have high selectivity for the hydrodeoxygenation of fatty acids to alkanes at 250-300 °C, but a considerable selectivity for decarbonylation/decarboxylation still exists



(> 20 %) for triglyceride conversion owing to the high temperature and ${\rm H}_2$ pressure.

In our previous work,^[14] we developed a direct and efficient approach for the production of liquid alkanes from furfural-derived aldol adducts under mild conditions (170°C, 2 MPa) over a Pd/NbOPO₄ catalyst. We found that NbO_x species promote the C-O bond cleavage significantly, especially the bonds of tetrahydrofuran rings, as was further confirmed by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments and DFT calculations. Herein, we report a simple Pd-loaded 10%Nb2O5/SiO2 catalyst for the quantitative hydrodeoxygenation of 4-(2-furyl)-3-buten-2-one to noctane under mild conditions (170°C, 2.5 MPa). The 10%Nb₂O₅/SiO₂ support was prepared readily by the sol-gel method without any surfactant; therefore, it can be synthesized on a large scale at a low cost. We also demonstrated that the Pd-loaded 10%Nb2O5/SiO2 catalyst can convert palmitic acid, tristearin, and diphenyl ether (Scheme 1) quantitatively



Scheme 1. Biomass-related compounds used in this work.

into alkanes with less C–C cleavage through hydrodeoxygenation under the same mild conditions; these are model compounds for microalgae oils, vegetable oils, and lignin, respectively. In addition, the reaction pathway for palmitic acid hydrodeoxygenation and the stability of 4%Pd/10%Nb₂O₅/SiO₂ catalyst were investigated.

Results and Discussion

Characterization

The X-ray powder diffraction patterns of various Nb₂O₅/SiO₂ materials and reference commercial Nb₂O₅ are shown in Figure 1. For commercial Nb₂O₅, all of the diffraction peaks could be indexed to orthorhombic Nb₂O₅ (JCPDS card 30-0873). The SiO₂ sample prepared by the sol–gel method is amorphous, as only one broad band was detected from $2\theta = 15^{\circ}$ to 40°. As no reflections were observed in the low-angle range (1° < 2 θ < 10°), long-range ordering is absent in these mesoporous Nb₂O₅/SiO₂ materials. The appearance of only one very broad band (2 $\theta = 15^{\circ}$ -40°) in the wide-angle 2 θ region implies the amorphous characteristic of these materials. As no





Figure 1. XRD patterns of various Nb_2O_5/SiO_2 materials: a) $5 \% Nb_2O_5/SiO_2$, b) $10\% Nb_2O_5/SiO_2$, c) $20\% Nb_2O_5/SiO_2$, d) $10\% Nb_2O_5/SiO_2$ -im, and e) commercial Nb_2O_5 .

crystalline Nb₂O₅ phase was detected in these Nb₂O₅/SiO₂ samples, the amorphous niobium oxide species were well dispersed in the silica. For the 10%Nb₂O₅/SiO₂-im sample, which was prepared by impregnating SiO₂ with niobium citrate solution, the clear observation of some small Nb₂O₅ peaks indicates that the Nb₂O₅ on the SiO₂ surface was crystalline.

The N₂ adsorption–desorption isotherms and pore size distributions of the Nb₂O₅/SiO₂ materials are shown in Figure S1. All of the samples with different Nb content exhibit typical type IV isotherms (IUPAC definition), which are characteristic of mesoporous materials.^[15] The appearance of H2-type hysteresis loops at a relative pressure of 0.4–0.8 indicates the presence of "ink-bottle-type" pores in these materials. All of the Nb₂O₅/SiO₂ samples possess mesoporous characteristics with pore size distributions in the range 2–5 nm (Figure S1 b). The BET surface areas, pore volumes, and average pore diameters are summarized in Table 1. The specific surface areas and pore volumes in-

Table 1. Texture properties of Nb_2O_5/SiO_2 prepared by the sol-gel method and other materials.						
Sample	S_{BET} [m ² g ⁻¹]	Pore volume [cm ³ g ⁻¹]	Pore size ^[a] [nm]			
SiO ₂	786	0.65	3.5			
5%Nb ₂ O ₅ /SiO ₂	927	0.75	3.5			
10%Nb ₂ O ₅ /SiO ₂	794	0.68	3.5			
20%Nb ₂ O ₅ /SiO ₂	490	0.58	4.5			
10%Nb ₂ O ₅ /SiO ₂ -im	411	0.35	3.8			
commercial Nb_2O_5	6	-	-			
[a] Average pore diameters calculated from the desorption branches by						

crease first and then decrease with increasing Nb₂O₅ content, as was also observed for $TiO_2/SiO_2^{[16]}$ and WO₃/SiO₂^[17] materials prepared by the sol–gel method.

The TEM images of the $10\%Nb_2O_5/SiO_2$, $20\%Nb_2O_5/SiO_2$, and Pd-loaded Nb_2O_5/SiO_2 catalysts are shown in Figure 2. No clear phase separation can be observed in the whole detected

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Figure 2. TEM images of a) 10%Nb2O5/SiO2, b) 20%Nb2O5/SiO2, c) 4%Pd/ $5\,\% Nb_2O_5/SiO_2,\,d)\,4\,\% Pd/10\,\% Nb_2O_5/SiO_2,\,and\,e)\,4\,\% Pd/20\,\% Nb_2O_5/SiO_2;$ f) histogram of the Pd particle size distribution (for 300 particles).

region (Figure 2a and b), which implies that the niobium oxide species are dispersed uniformly in the Nb₂O₅/SiO₂ materials. It is also clear from the Nb atomic maps (Figure S3 f) that the Nb atoms were uniformly dispersed in the silica. The histogram of the Pd particle size distribution shows that most of the Pd particles are distributed in the range 2-9 nm (Figure 2 f). According to the statistical analysis, the average Pd particle sizes in 4%Pd/5%Nb₂O₅/SiO₂, 4%Pd/10%Nb₂O₅/SiO₂ and 4%Pd/ 20%Nb₂O₅/SiO₂ were 5.9, 5.1, and 4.5 nm, respectively, and decreased gradually as Nb₂O₅ content increased.

Hydrodeoxygenation of 4-(2-furyl)-3-buten-2-one

The results for the hydrodeoxygenation of 4-(2-furyl)-3-buten-2-one over different Pd-based catalysts in a batch reactor are summarized in Table 2. The Pd/10%Nb2O5/SiO2 catalyst showed the highest catalytic activity, and the octane yield was 95.5% (Table 2, entry 3), which is as good as that of Pd/ NbOPO₄,^[14b] therefore, the Pd/10%Nb₂O₅/SiO₂ has an excellent ability to catalyze the hydrodeoxygenation of furan-based compounds under mild reaction conditions. The other 3.6% alkanes were mainly *n*-heptane and isohexadecane. Without the addition of niobium oxide species, Pd/SiO₂ showed much lower activity, and the octane yield was only 16% (Table 2, entry 6). Through the impregnation of Nb₂O₅ in SiO₂, the yield of octane improved to 31.2% for the 4%Pd/10%Nb₂O₅/SiO₂-im catalyst (Table 2, entry 7). These results suggest that the high hydrodeoxygenation activity for furan-based compounds over the Pd/10%Nb₂O₅/SiO₂ catalyst should be ascribed mainly to the presence of niobium oxide species. This behavior agrees well with the previous report^[14b] that NbO_x species could promote the C-O bond cleavage effectively. However, there were still 64.1% oxygenates unconverted over the 4%Pd/ 10%Nb₂O₅/SiO₂-im catalyst. This is because the Nb₂O₅ impregnated in the SiO₂ crystallized to larger particles and, therefore, there were less niobium oxide species exposed on the surface of the catalyst. In addition, the much weaker acidity of 10%Nb₂O₅/SiO₂-im than that of 10%Nb₂O₅/SiO₂ may be another reason for the poor hydrodeoxygenation activity of 4%Pd/ 10%Nb₂O₅/SiO₂-im. The Pd/5%Nb₂O₅/SiO₂ catalyst was slightly less active than Pd/10%Nb₂O₅/SiO₂, as its lower Nb content led to a slightly slower reaction rate. For an extended reaction time of 30 h, the octane yield increased to 90.1% (Table 2, entries 1 and 2). For the Pd/20%Nb₂O₅/SiO₂ catalyst with a higher Nb content, 95.3% octane yield was obtained in a shorter time (16 h), and no oxygenates remained (Table 2, entry 4). These results further confirmed that NbO_x species could promote the C-O bond cleavage and assist the hydrodeoxygenation process. The Pd/commercial Nb₂O₅ catalyst showed the lowest activity with only 1.9% octane yield (Table 2, entry 5) owing to its small specific surface area and crystallinity.

Entry	Catalyst	t	Conversion	Yield [%]							
		[h]	[%]	octane	other alkanes	THFA ^[b]	MTHFA ^[c]	BTHF ^[d]	MPTHF ^[e]	octanols	dioctyl ether
1	Pd/5%Nb ₂ O ₅ /SiO ₂	24	100	84.1	6.0	0	0	0	0	0	9.9
2	Pd/5%Nb ₂ O ₅ /SiO ₂	30	100	90.1	6.3	0	0	0	0	0	3.6
3	Pd/10%Nb ₂ O ₅ /SiO ₂	24	100	95.5	3.6	0	0	0	0	0	0.9
4	Pd/20%Nb ₂ O ₅ /SiO ₂	16	100	95.3	4.7	0	0	0	0	0	0
5	Pd/commercial Nb ₂ O ₅	24	100	1.9	0	49.0	41.5	4.6	1.7	0.3	0
6	Pd/SiO ₂	24	100	16.0	1.1	0	0	19.3	24.1	27.4	5.4
7	Pd/10%Nb ₂ O ₅ /SiO ₂ -im	24	100	31.2	1.4	0	0	17.8	18.5	23.5	4.3

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[e] 2-Methyl-5-propyltetrahydrofuran.

Hydrodeoxygenation of other compounds with different oxygen-containing functional groups

The 4%Pd/10%Nb₂O₅/SiO₂ catalyst was also tested in the hydrodeoxygenations of palmitic acid, tristearin, and diphenyl ether, which are model compounds for microalgae oils, vegetable oils, and lignin, respectively. These three model compounds contained three different oxygen-containing functional groups, namely, carboxy, ester, and ether groups. The results are shown in Table 3. The reactions of palmitic acid and tristearin

Table 3. Hydrodeoxygenation of diphenyl ether, palmitic acid, and tristearin by 4% Pd/10%Nb ₂ O ₅ /SiO ₂ . ^[a]							
Entry	Substrate	Product	Conversion [%]	Selectivity [%]			
1	palmitic acid	$n-C_{16}$ alkane	100	95.3			
2	tristearin	<i>n-</i> C ₁₈ alkane	100	94.2			
3 ^[b]	diphenyl ether	cyclohexane	100	98.2			
[a] Reaction conditions: catalyst $(0,2,\alpha)$ substrate $(0,2,\alpha)$ cyclohexane							

[a] Reaction conditions: catalyst (0.2 g), substrate (0.2 g), cyclohexane (6.46 g), 170 °C, initial H_2 pressure: 2.5 MPa, reaction time: 24 h; catalysts were reduced in situ. [b] The solvent was dodecane (6.46 g) rather than cyclohexane.

under mild conditions (170 °C, 2.5 MPa H₂ pressure) resulted in high yields (>94%) of alkanes with the same chain length as that of the starting compound, and the 5–6% byproducts were the alkanes with one carbon atom less than the main product, which were produced by the terminal C–C cleavage. Therefore, it can be suggested that the 4%Pd/10%Nb₂O₅/SiO₂ catalyst could catalyze efficiently the hydrodeoxygenation of a fatty acid and a fatty acid ester with the C–C cleavage reac-

tion suppressed. In addition, the hydrodeoxygenation of diphenyl ether to cyclohexane with 98.2% yield indicated that the 4%Pd/10%Nb₂O₅/SiO₂ catalyst can also be used in the hydrodeoxygenation of ether groups.

A non-noble-metal Ni-loaded $10\%Nb_2O_5/SiO_2$ catalyst was also investigated for the hydrodeoxygenation of palmitic acid to test the effect of $10\%Nb_2O_5/SiO_2$ on C–O cleavage, and the results are shown in Table 4. Notably, a high yield (97%) of hexadecanol

was obtained, and this compound is used widely in surfactants, lubricants, plasticizers, emulsifiers, cosmetics, and biofuels.^[18] As the temperature increased to $220\,^\circ$ C, the palmitic

Table 4. Hydrodeoxygenation of palmitic acid over $10\%Ni/10\%Nb_2O_5/SiO_2^{[a]}$							
Entry	<i>Т</i> [°С]	Conversion [%]	<i>n-</i> C ₁₆ alkane	Yield [%] <i>n-</i> C ₁₅ alkane	hexadecanol		
1 2	180 220	100 100	1.8 86.1	1.2 13.9	97.0 0		
[a] Reaction conditions: catalyst (0.2 g), palmitic acid (0.2 g), cyclohexane (6.46 g), initial H_2 pressure: 2.5 MPa, reaction time: 24 h.							

acid was completely converted to alkanes with a yield of 86.1% for $n-C_{16}$ alkane. These results suggest that the 10%Ni/10%Nb₂O₅/SiO₂ catalyst can be used for the highly selective hydrodeoxygenation of fatty acids to fatty alcohols or alkanes, owing to the promotion effect of 10%Nb₂O₅/SiO₂ on C–O cleavage.

The reaction pathways of the hydrodeoxygenation of palmitic acid were investigated by products analysis at different reaction times. The time course of the conversion of palmitic acid catalyzed by 4%Pd/10%Nb₂O₅/SiO₂ is shown in Figure 3. Hexa-



Figure 3. The time course of the hydrodeoxygenation of palmitic acid catalyzed by 4%Pd/10%Nb₂O₅/SiO₂. Reaction conditions: catalyst (0.2 g), palmitic acid (0.2 g), cyclohexane (6.46 g), 170 °C, initial H₂ pressure 2.5 MPa.

decanol first accumulated to 63.2% at 3 h and then diminished gradually as the reaction processed; this indicates that the palmitic acid was initially hydrogenated rapidly to hexadecanol. For prolonged reaction times, the yield of $n-C_{16}$ alkane increased gradually as the hexadecanol decreased gradually. The proposed pathways are shown in Scheme 2. According to the

$$\begin{array}{c} C_{15}H_{31}\text{-}COOH \xrightarrow{H_2} (C_{15}H_{31}\text{-}CHO) \xrightarrow{H_2} C_{15}H_{31}\text{-}CH_2OH \xrightarrow{H_2} C_{16}H_{34} \\ \hline \\ -H_2O \xrightarrow{-H_2} C_{15}H_{31}\text{-}CH_2OH \xrightarrow{-H_2O} C_{16}H_{34} \end{array}$$

Scheme 2. Proposed reaction pathway for the hydrodeoxygenation of palmitic acid into C_{16} alkane.

product distribution versus reaction time, the hydrodeoxygenation of palmitic acid to $n-C_{16}$ alkane is a consecutive reaction, and palmitic acid hydrogenation to hexadecanol is followed by hexadecanol hydrogenolysis to $n-C_{16}$ alkane; this is consistent with the proposal by Lercher for the hydrodeoxygenation of stearic acid to octadecane over Ni/HBEA catalyst.^[12]

Stability test of 4%Pd/10%Nb₂O₅/SiO₂

The stability of the catalyst is important for its practical usage; therefore, a cycle usage test of $4\%Pd/10\%Nb_2O_5/SiO_2$ for the hydrodeoxygenation of palmitic acid was conducted, and the results are shown in Figure 4. The nearly constant activity of the $4\%Pd/10\%Nb_2O_5/SiO_2$ catalyst after reuse five times at

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Figure 4. The cycle usage test and hydrothermal stability test of 4%Pd/ 10%Nb₂O₅/SiO₂ for the hydrodeoxygenation of palmitic acid. Reaction conditions: catalyst (0.2 g), substrate (0.2 g), cyclohexane (6.46 g), 170 °C, initial H₂ pressure: 2.5 MPa, reaction time: 5 h. The catalyst in the hydrothermal stability test was 4%Pd/10%Nb₂O₅/SiO₂ catalyst after hydrothermal treatment at 200 °C for 24 h.

170 °C for 5 h in each cycle indicates the good stability of the catalyst. In addition, the hydrothermal stability of the 4%Pd/ 10%Nb₂O₅/SiO₂ catalyst was investigated, because water is ubiquitous in biomass conversion. The 4%Pd/10%Nb₂O₅/SiO₂ catalyst was first treated hydrothermally at 200 °C for 24 h and then tested for the hydrodeoxygenation of palmitic acid at 170 °C for 5 h. The reaction result (Figure 4) shows that the catalytic performance of 4%Pd/10%Nb₂O₅/SiO₂ remains almost the same after the hydrothermal treatment. No crystalline phases of niobium oxide species appeared in the XRD pattern of the hydrothermally treated 4%Pd/10%Nb₂O₅/SiO₂ catalyst (Figure 5 c). The addition of silica can inhibit the crystallization



Figure 5. XRD patterns of 4%Pd/10%Nb₂O₅/SiO₂: a) fresh catalyst, b) used catalyst after the 150 h time-on-stream test in a fixed-bed reactor, and c) catalyst hydrothermally treated at 200 °C for 24 h.

of niobia in niobia-silica catalysts to improve the hydrothermal stability.^[19] Therefore, the 4%Pd/10%Nb₂O₅/SiO₂ catalyst has a good hydrothermal stability.

The hydrodeoxygenation of palmitic acid was also investigated in a continuous-flow system with a fixed-bed reactor at 170 °C, 2.5 MPa, 2.4 h^{-1} weighted hourly space velocity (WHSV), and a gas flow rate of 20 mLmin⁻¹. The results obtained from the fixed-bed reactor were almost consistent with those from



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Figure 6. Product distribution in the direct hydrodeoxygenation of a 3 wt% palmitic acid in dodecane solution in a fixed-bed reactor over 4%Pd/ $10\%Nb_2O_5/SiO_2$ catalyst. Reaction conditions: 170 °C, 2.5 MPa, 2.4 h⁻¹ WHSV, and 20 mLmin⁻¹ gas flow rate.

the batch reactor; the yield of hexadecane reached 94–95%, and the other 5–6% product was pentadecane (Figure 6). Clearly, the catalyst showed high activity and good stability with almost no decrease in hexadecane yield throughout the 150 h test. Owing to the mild reaction conditions, there was no clear growth or aggregation of Pd particles after the 150 h time-on-stream test on the basis of the TEM image and the histogram for the Pd particle size distribution shown in Figure 7. There was only a little Pd leaching according to the inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis, and the Pd loadings of the fresh catalyst and used catalyst



Figure 7. a) TEM image of used 4%Pd/10%Nb₂O₅/SiO₂ catalyst after the 150 h time-on-stream test in a fixed-bed reactor; b) histogram of Pd particle size distribution of fresh 4%Pd/10%Nb₂O₅/SiO₂ (black) and used 4%Pd/10%Nb₂O₅/SiO₂ (red) after the 150 h time-on-stream test (for 300 particles).

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were 4.0 and 3.8 wt%, respectively. In addition, the XRD patterns (Figure 5) showed that no crystalline phases of niobium oxide species appeared, and the niobium oxide species remained amorphous. The above evidence indicates that the 4%Pd/10%Nb₂O₅/SiO₂ demonstrated excellent activity and stability for the hydrodeoxygenation reaction.

Conclusions

We have reported a simple and effective Pd/10 $\% Nb_2O_5/SiO_2$ catalyst for hydrodeoxygenation reactions under mild conditions. The Nb₂O₅/SiO₂ support material prepared by the sol-gel method possesses mesoporous characteristics with pore size distributions in the range 2-5 nm, and amorphous niobium oxide species were well dispersed in the silica. The Pd/ 10%Nb₂O₅/SiO₂ catalyst showed excellent activity for the hydrodeoxygenation of 4-(2-furyl)-3-buten-2-one (furan ringbased compound) with a 95.5% yield of octane at 170°C and a H₂ pressure of 2.5 MPa. Palmitic acid and tristearin can also be converted under the same conditions and gave high yields (>94%) of alkanes with the same chain length as those of the starting compounds. The catalyst can last for either 150 h time-on-stream test or five reuse cycles without deactivation in the hydrodeoxygenation of palmitic acid. The hydrodeoxygenation of diphenyl ether to cyclohexane with 98.2% yield indicates that the 4%Pd/10%Nb₂O₅/SiO₂ catalyst can also be used for the hydrodeoxygenation of ether groups. In conclusion, the Pd/10%Nb₂O₅/SiO₂ catalyst can catalyze efficiently the hydrodeoxygenation of furan-ring-based compounds, fatty acids, fatty acid esters, and ethers. Therefore, Pd/10%Nb₂O₅/SiO₂ is a versatile catalyst for the hydrodeoxygenation of biomass-related compounds to alkanes under mild conditions.

Experimental Section

Materials

 $Pd(NO_3)_2 \times H_2O$ solution was purchased from Heraeus Materials Technology Shanghai Co., Ltd, palmitic acid and tristearin were purchased from TCI, diphenyl ether was purchased from Aladdin, and commercial Nb_2O_5 was purchased from Sinopharm Chemical Reagent Co., Ltd. 4-(2-Furyl)-3-buten-2-one was prepared by the aldol condensation of furfural with acetone according to the literature procedure.^[14b] All other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without purification.

Catalyst preparation

The Nb precursor (niobium citrate) was prepared according to the literature procedure,^[20] and a niobium citrate solution with a Nb concentration of 0.4 mol L^{-1} was prepared for use.

 Nb_2O_5/SiO_2 with different Nb_2O_5 content was prepared by a sol-gel method in the presence of citric acid, which is an effective method for the synthesis of thermally stable mesoporous aluminophosphate materials or mesoporous silica-based materials.^[17,21] The detailed process is as follows: A certain amount of citric acid (CA) and distilled water were added to niobium citrate solution (0.4 molL⁻¹, 11.26 g), and then tetraethyl orthosilicate (TEOS, 20 mL) was added under stirring to afford a mixture with a TEOS/

CA/H₂O molar ratio of 1.0:0.31:11. After aging for 2 h, the mixture was heated at 50 °C in the open air to remove water and all other volatiles to afford the as-synthesized precursor. Finally, the dried solid was calcined at 600 °C for 3 h (heating rate 10 Kmin⁻¹), and the 10 wt %Nb₂O₅/SiO₂ sample was obtained. The 5 wt %Nb₂O₅/SiO₂ and $20wt \%Nb_2O_5/SiO_2$ catalysts were prepared by the same method with the amount of niobium citrate changed to 5.34 and 25.35 g, respectively, and the volume of TEOS and the TEOS/CA/ H₂O molar ratio of 1:0.31:11 were unchanged. As a reference sample, pure mesoporous silica (SiO₂) was prepared under the same conditions in the absence of niobium citrate. For comparison, a 10 wt %Nb₂O₅/SiO₂-im sample was also prepared by the incipient wetness impregnation method. After the impregnation of SiO₂ (prepared as above) with the calculated amount of an aqueous solution of niobium citrate, the sample was dried at 50°C for 12 h and then calcined at 500 °C for 3 h.

The Pd- and Ni-based catalysts were prepared by the incipient wetness impregnation method with appropriate amounts of aqueous solutions of Pd(NO₃)₂·xH₂O and Ni(NO₃)₂·6H₂O, respectively. The obtained sample was dried at 50 °C for 12 h and then calcined at 500 °C for 3 h (heating rate 1 Kmin⁻¹). The Pd loading was 4 wt%, and the Ni loading was 10 wt%. The Ni-based catalysts were reduced previously in a flowing 10% H₂/Ar mixture at 500 °C for 3 h.

Characterization

The powder XRD patterns were recorded with a Rigaku D/max-2550VB/PC diffractometer by using CuK_{\alpha} (\lambda\!=\!0.15406~\text{nm}) radiation.

The N_2 adsorption–desorption isotherms were measured at 77 K by using a NOVA 4200e analyzer (Quantachrome Co. Ltd). Before the measurements, the samples were outgassed at 200 °C for 12 h under vacuum to remove moisture and volatile impurities.

The TEM images were recorded with a FEI Tecnai F20s-TWIN instrument, and the electron-beam accelerating voltage was 200 kV.

Catalytic reactions and product analysis

The batch reactions for the direct hydrodeoxygenation of 4-(2-furyl)-3-buten-2-one were performed in a 50 mL stainless-steel autoclave. Typically, 4-(2-furyl)-3-buten-2-one (0.2 g) and the catalyst (0.2 g) were mixed with cyclohexane (6.46 g) in the autoclave. The reactor was then sealed, purged three times with nitrogen, and charged to 2.5 MPa H₂. The reactor was then heated to 170 °C under magnetic stirring at 600 rpm for 24 h. After the completion of the reaction, the reactor was guenched in a water bath to room temperature. The liquid solution was separated from the solid catalyst by centrifugation and analyzed by GC–MS (Agilent 7890A-5975C) with an HP-5 column. Tridecane was used as the internal standard for the quantification of the liquid products. The batch hydrodeoxygenation reactions of palmitic acid, tristearin, and diphenyl ether were conducted in the same way.

The direct hydrodeoxygenation of palmitic acid was also tested in a fixed-bed reactor system. A feed composed of a 3 wt% solution of palmitic acid in dodecane and a H₂ co-feed were used for the continuous-flow reaction test. The pelletized catalyst (1.0 g, 40– 60 mesh) was loaded into the stainless-steel tubular reactor (inner diameter 6 mm, length 55 cm). Crushed quartz granules were placed into both ends of the catalyst to maintain the bed height and reduce the dead volume. After the loading, the reaction temperature and pressure were adjusted to the desired value, and the



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feed flow was injected using an HPLC pump at a H_2 flow of 10 mL min⁻¹. The WHSV was determined by dividing the mass flow rate of the liquid by the mass of the catalyst used. The liquid phase was separated from the gas phase and collected with a gas–liquid separator. The liquid phase analysis was performed with an Agilent 7890A GC–MS instrument equipped with an HP-5 column. Tridecane was used as the internal standard for the quantification of the liquid products.

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Y. Shao, Q. Xia, X. Liu, G. Lu,* Y. Wang*

Pd/Nb₂O₅/SiO₂ Catalyst for the Direct Hydrodeoxygenation of Biomass-**Related Compounds to Liquid Alkanes** under Mild Conditions



Mild mannered: Under mild conditions (170 °C, 2.5 MPa), Pd/10 %Nb₂O₅/SiO₂ is effective for the hydrodeoxygenation reactions of 4-(2-furyl)-3-buten-2-one (the aldol adduct of furfural with acetone),



Mild conditions: 170 °C, 2.5 MPa H₂ High yield of alkanes without C-C cleavage

without C-C cleavage

palmitic acid, tristearin, and diphenyl ether (model compounds of vegetable oils, microalgae oils, and lignin) and gives high yields (>94%) of alkanes with little C–C bond cleavage.

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