

# Pd/NbOPO<sub>4</sub> Multifunctional Catalyst for the Direct Production of Liquid Alkanes from Aldol Adducts of Furans\*\*

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**Abstract:** Great efforts have been made to convert renewable biomass into transportation fuels. Herein, we report the novel properties of NbO<sub>x</sub>-based catalysts in the hydrodeoxygenation of furan-derived adducts to liquid alkanes. Excellent activity and stability were observed with almost no decrease in octane yield (>90 % throughout) in a 256 h time-on-stream test. Experimental and theoretical studies showed that NbO<sub>x</sub> species play the key role in C–O bond cleavage. As a multifunctional catalyst, Pd/NbOPO<sub>4</sub> plays three roles in the conversion of aldol adducts into alkanes: 1) The noble metal (in this case Pd) is the active center for hydrogenation; 2) NbO<sub>x</sub> species help to cleave the C–O bond, especially of the tetrahydrofuran ring; and 3) a niobium-based solid acid catalyzes the dehydration, thus enabling the quantitative conversion of furan-derived adducts into alkanes under mild conditions.

The overall goal of the conversion of biomass resources into transportation fuels is the removal of oxygen, and great effort has been devoted worldwide to the development of efficient conversion processes.<sup>[1]</sup> Herein, we report the novel activity of a Pd/NbOPO<sub>4</sub> multifunctional catalyst for the direct conversion of furans into alkanes under mild conditions. The aldol adduct of furfural with acetone was directly and almost entirely converted into octane at 170 °C and 2.0 MPa, and the catalyst lasted for 256 h without deactivation. This excellent performance was attributed to the unique ability of NbO<sub>x</sub> as an early-transition-metal oxide to cleave the C–O bond in the furan ring and function as a solid acid catalyst for the dehydration.

Several integrated processes have been proposed for upgrading biomass platforms into liquid hydrocarbons on the

basis of different strategies and catalysts.<sup>[2–4]</sup> Among them, an important strategy is to increase the length of the carbon chain by C–C coupling reactions, for example, first through the base-catalyzed aldol condensation or dimerization of  $\alpha$ -angelica lactone to give angelica lactone dimer<sup>[2]</sup> or acid-catalyzed hydroxyalkylation/alkylation,<sup>[3]</sup> followed by removal of the oxygen atoms of the resulting oxygenates to produce liquid alkanes by hydrodeoxygenation over various noble-metal-based catalysts at relatively high temperature and pressure. However, harsh conditions would lead to severe C–C bond cleavage and coke formation. It has been reported that ReO<sub>x</sub>, MoO<sub>x</sub>, and WO<sub>x</sub> species can effectively promote the activity of a Rh/SiO<sub>2</sub> or Rh/C catalyst for the selective hydrogenolysis of cyclic ethers and polyols to  $\alpha,\omega$ -diols.<sup>[5]</sup> Burch et al.<sup>[6]</sup> also confirmed the promotion effect of Re on the Pt/TiO<sub>2</sub> catalyst during the hydrogenolysis of *N*-methylpyrrolidin-2-one to *N*-methylpyrrolidine through C=O bond cleavage both theoretically and experimentally. Furthermore, we found that CoO<sub>x</sub> species could effectively work together with the noble metal platinum to open the furan ring of furfural alcohol and 4-(2-furyl)-3-buten-2-one (furfural acetone single aldol adduct) under mild conditions.<sup>[7]</sup> However, we also noticed that CoO<sub>x</sub> species have weak acidity and are not active enough for the dehydration of octanediols. Therefore, we then used the metal/solid-acid bifunctional catalyst Pt/NbOPO<sub>4</sub> and found that under mild conditions (175 °C, 2.5 MPa) it not only converted octanediols into octane, but also partially converted the saturated furanic compound into octane through C–O bond cleavage in the tetrahydrofuran ring.<sup>[7b]</sup> Thus, we speculated that besides its acidity, NbO<sub>x</sub> may have the ability to break a C–O bond in the furan ring.<sup>[8]</sup> Thus, the niobium-based-solid-acid-supported noble metal can be used as a multifunctional catalyst for the direct production of targeted alkanes from aldol adducts of furfural and/or 5-hydroxymethylfurfural (HMF) (Scheme 1).

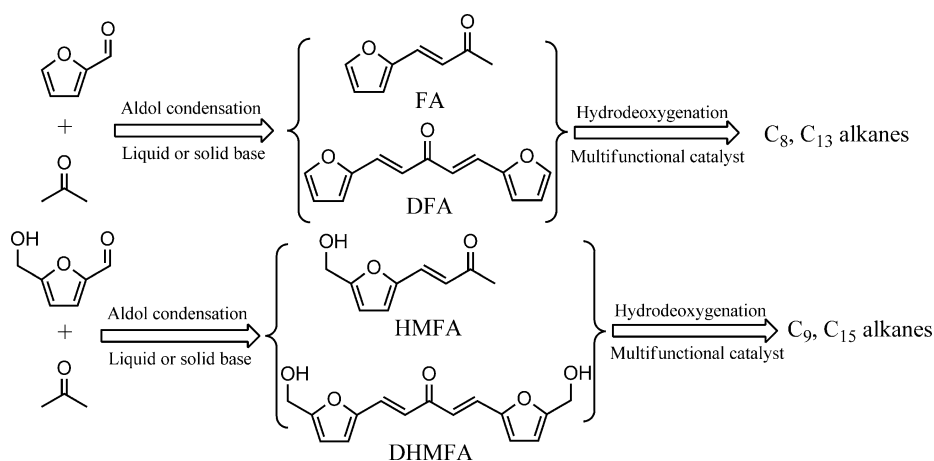
The aldol condensation of furfural and/or HMF with acetone can be carried out with a liquid or solid base. In this study, NaOH was used to enable the complete conversion of furfural and/or HMF during the aldol condensation and enhance the selectivity toward double adducts (a strong base favors double-condensation products at a specific ketone-to-furfural ratio; see the Supporting Information for details of the reaction and product distributions).<sup>[2a,b]</sup> After aldol condensation, the single adduct of furfural with acetone, furfural acetone [4-(2-furanyl)-3-buten-2-one, FA], was fed through a fixed-bed reactor filled with the Pd/NbOPO<sub>4</sub> catalyst. The 256 h time-on-stream result is presented in Figure 1. There were no oxygen-containing products detected in the reaction effluents by GC–MS (see Figure S11), and the

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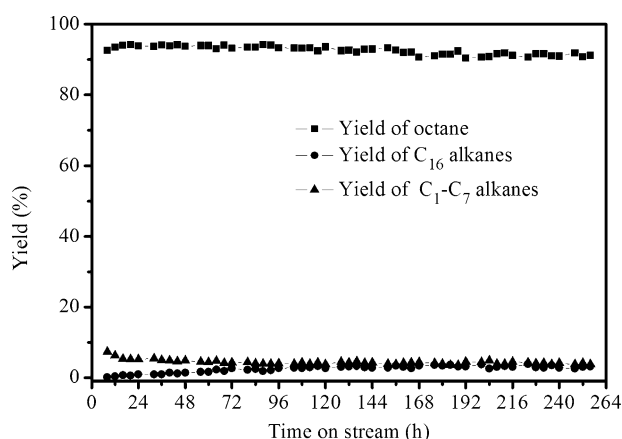
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**Scheme 1.** Reactions involved in the conversion of biomass-derived platform chemicals into liquid alkanes.



**Figure 1.** Production of octane by the direct hydrodeoxygenation of a solution of FA (3 wt%) in cyclohexane in a fixed-bed reactor over a Pd/NbOPO<sub>4</sub> catalyst. Reaction conditions: 170 °C, 2 MPa, weight hourly space velocity: 1.2 h<sup>-1</sup>, gas-flow rate: 20 mL min<sup>-1</sup>.

main product was octane (>90%), accompanied by small amounts of C<sub>1</sub>–C<sub>7</sub> (produced by C–C cleavage) and C<sub>16</sub> alkanes (probably produced by the hydrodeoxygenation of the intermolecular aldol adducts of C<sub>8</sub> intermediates). Surprisingly, the catalyst showed excellent activity and stability with almost no decrease in octane yield (>90% throughout). Owing to the mild reaction conditions, less C–C cracking occurred, and the amounts of CH<sub>4</sub> (ca. 0.3–0.5%) and CO<sub>2</sub> (ca. 0.1–0.3%) in the gas phase were very small. This result is quite different from those obtained at higher temperature and pressure, under which conditions severe C–C cleavage always occurs.<sup>[2a,b,3a]</sup> Hence, besides reducing the cost and energy consumption of biorefining, the mild conditions in our process can also improve the stability of the catalyst and restrain C–C cleavage, thus making the whole process more cost-effective and energy-efficient.

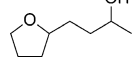
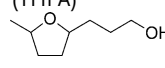
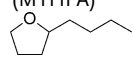
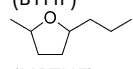
To investigate the role of each component in the catalyst, we carried out the reactions in batch reactors with various oxide-supported Pd catalysts, as well as NbOPO<sub>4</sub> combined with different noble metals. The catalytic performance of

various oxide-supported Pd catalysts in FA hydrodeoxygenation, as well as the BET surface area of these supports, is summarized in Table 1. The final products of the reactions over these oxide-supported Pd catalysts were drastically different. Over the Pd/NbOPO<sub>4</sub> catalyst, FA was quantitatively converted into alkanes, with an octane yield of 94%. However, on the common Pd/Al<sub>2</sub>O<sub>3</sub> catalyst, FA was only converted into the hydrogenated products 4-(2-tetrahydrofuryl)-2-butanol (THFA) and 3-(5-methyl-2-tetrahydrofuryl)-1-propanol (MTHFA), without any deoxygenation or ring-opening products.

Interestingly, the mechanical blending of NbOPO<sub>4</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> gave a much better catalytic activity than Pd/Al<sub>2</sub>O<sub>3</sub> alone, although the hydrodeoxygenation was not complete (51% yield of octane), probably owing to the weak interaction between Pd and NbOPO<sub>4</sub>. This result suggests that the NbOPO<sub>4</sub> support played a vital role in ring opening and hydrodeoxygenation. Moreover, on the Pd/H-ZSM-5 catalyst, octane was produced in only 25% yield along with oxygen-containing products in over 69% yield. Considering that the BET surface area and acidic properties of H-ZSM-5 were similar to those of NbOPO<sub>4</sub> (Table 1; see also Figure S6), although the high number of acidic sites and large BET surface area might have played important catalytic roles, they may not be the main reason for high hydrodeoxygenation activity. This hypothesis was confirmed by the reaction with the supported Pd catalyst Pd/Nb<sub>2</sub>O<sub>5</sub>, which despite having the smallest BET surface area and the lowest acid-site density exhibited excellent catalytic performance (96% octane yield; see Figure S12 for GC–MS results). Therefore, we propose that NbO<sub>x</sub> species can actually break or assist in breaking the C–O bond and thus promote the high-yielding formation of octane.

The catalytic performance of different noble-metal-loaded NbOPO<sub>4</sub> catalysts was also investigated. Pt/NbOPO<sub>4</sub> and Pd/NbOPO<sub>4</sub> showed the best performance with a total yield of alkanes of over 99% and an octane yield of over 93%; the remaining alkanes obtained in 6–7% yield were mainly *n*-heptane and isohexadecane, consistent with the results obtained in the fixed-bed reactor. Over a Ru/NbOPO<sub>4</sub> catalyst, alkanes were obtained in a total yield of 88%, along with a small amount of oxygenates. Surprisingly, even the non-noble-metal-loaded NbOPO<sub>4</sub> catalyst Ni/NbOPO<sub>4</sub> showed moderate hydrodeoxygenation activity to produce octane in 8% yield under these mild conditions. When the temperature was increased to 200 °C, the octane yield was raised to 54%, with products still containing the tetrahydrofuran ring produced in only 12% yield. The by-products were mainly dioctyl ether (DOE) and 1-octanol. These results (see Table S1 in the Supporting Information for details) indicate that besides expensive Pt and Pd, much cheaper Ru or even

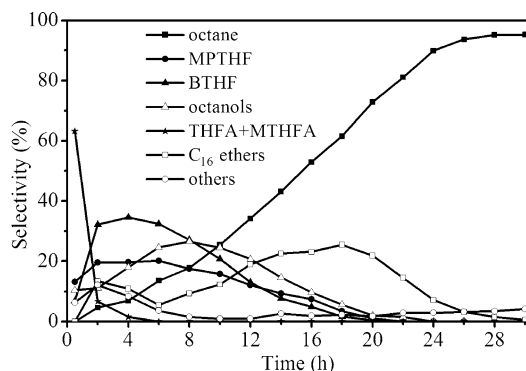
**Table 1:** The BET surface area and catalytic performance of different supported Pd catalysts for the direct hydrodeoxygenation of FA.<sup>[a]</sup>

Catalyst <sup>[b]</sup>	Pd/NbOPO <sub>4</sub>	Pd/Al <sub>2</sub> O <sub>3</sub>	NbOPO <sub>4</sub> & Pd/Al <sub>2</sub> O <sub>3</sub> <sup>[c]</sup>	Pd/H-ZSM-5	Pd/Nb <sub>2</sub> O <sub>5</sub>
<i>S</i> <sub>BET</sub> [m <sup>2</sup> g <sup>-1</sup> ]	360	198	ND <sup>[d]</sup>	318	86
Conversion [%]	> 99.9	> 99.9	> 99.9	> 99.9	> 99.9
Selectivity [%] <sup>[e]</sup>	> 99.9	0	54	25	> 99.9
Yield [%]					
octane	94	0	51	24	96
other alkanes	6	0	3	1	4
 (THFA)	0	73	0	0	0
 (MTHFA)	0	27	0	0	0
 (BTHF)	0	0	2	17	0
 (MPthf)	0	0	16	37	0
octanols	0	0	8	10	0
diethyl ether (DOE)	0	0	20	5	0
other oxygenates	0	0	0	6	0

[a] Reaction conditions: catalyst (0.1 g), FA (0.2 g), cyclohexane (6.46 g), 170 °C, initial H<sub>2</sub> pressure: 2.0 MPa, reaction time: 24 h. [b] Pd loading: 5 wt%. All Pd catalysts were reduced in situ. [c] The reaction was carried out with NbOPO<sub>4</sub> (0.1 g) and Pd/Al<sub>2</sub>O<sub>3</sub> (0.1 g). [d] Not determined. [e] Selectivity for the formation of alkanes.

the non-noble metal Ni loaded on NbOPO<sub>4</sub> can be used as multifunctional catalysts for the efficient hydrodeoxygenation of biomass-derived oxygenates, owing to the significant promotional effect of NbO<sub>x</sub> species on C–O cleavage.

Considering that the reaction could be too fast and that some of the intermediates may not be detected at 170 °C, we conducted the direct conversion of FA under the catalysis of Pd/NbOPO<sub>4</sub> at a slightly lower temperature of 150 °C and a H<sub>2</sub> pressure of 1.5 MPa. The determined reaction profile (see Figure 2) shows that during the first 0.5 h, the main products were THFA and MTHFA, and no unsaturated products were found (see Figure S14 for GC–MS results), thus suggesting that the hydrogenation, which is catalyzed by



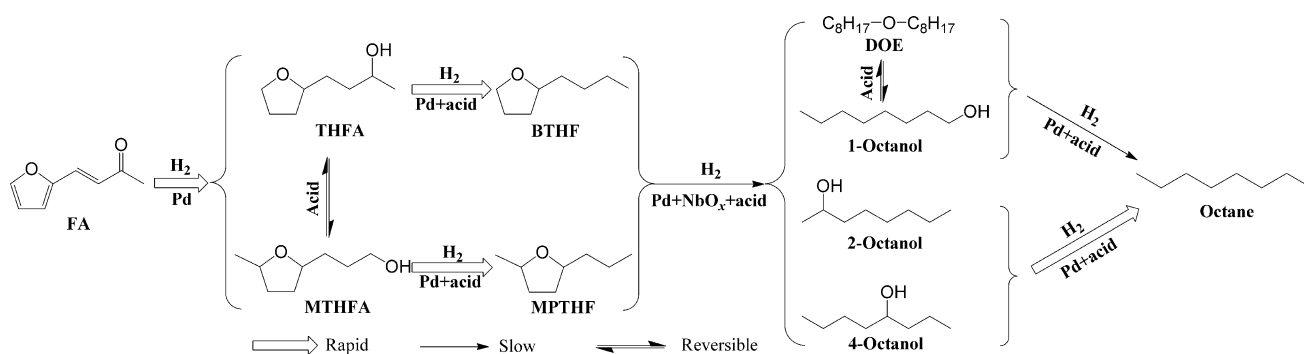
**Figure 2.** Product distribution from the direct conversion of FA over Pd/NbOPO<sub>4</sub> versus the reaction time at 150 °C and 1.5 MPa.

Pd, is a facile and fast process. The content of the dehydroxylation intermediates (MPthf and BTHF) then increased and that of the hydrogenated products (THFA and MTHFA) decreased rapidly between 0.5 and 4 h, thus indicating that the hydrogenolysis of the hydroxy group (by acid-catalyzed dehydration and palladium-catalyzed hydrogenation) is also a fast process. After 4 h, with the opening of the tetrahydrofuran ring (catalyzed by NbO<sub>x</sub> species), octanols (mainly 1-octanol) and C<sub>16</sub> ethers (mainly DOE) first accumulated and then diminished in quantity as the reaction progressed. This plot suggests that the sequence of the Pd/NbOPO<sub>4</sub>-catalyzed reactions was as follows: 1) hydrogenation of unsaturated bonds, 2) dehydration/hydrogenation of the secondary hydroxy group, 3) tetrahydrofuran-ring-opening reaction, and 4) dehydration/hydrogenation of the primary hydroxy group. This order is consistent with the relative difficulty of each step in the reaction pathway (see Figure S15).

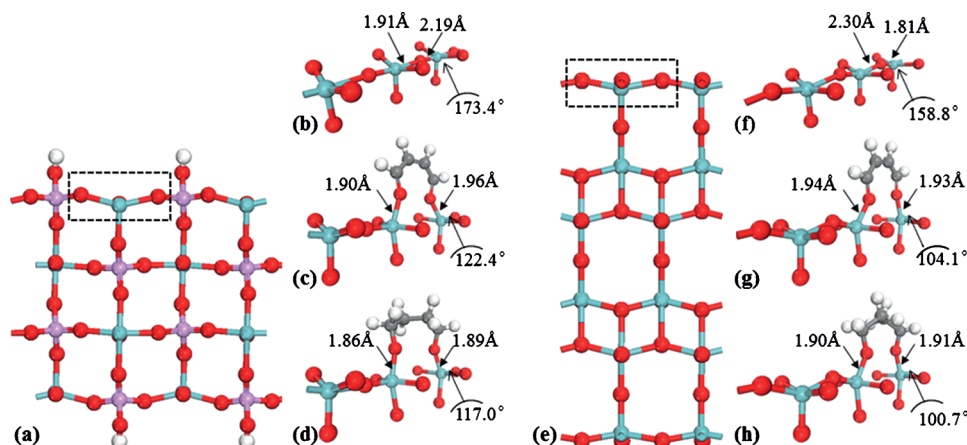
According to the product distribution versus reaction time, we tentatively propose the reaction pathway shown in Scheme 2.

To better understand the origin of the high activity of niobium-based supports toward the ring opening of furans, we also performed a first-principles simulation of the corresponding reaction processes at characteristic NbOPO<sub>4</sub> and Nb<sub>2</sub>O<sub>5</sub> surfaces. NbOPO<sub>4</sub>(100) and Nb<sub>2</sub>O<sub>5</sub>(001) surfaces, which both exhibit well-ordered flat structures, were chosen as the substrates. The bulk-truncated NbOPO<sub>4</sub>(100) surface includes singly coordinated O atoms (Figure 3a), which were therefore saturated with H atoms for our calculation, whereas Nb<sub>2</sub>O<sub>5</sub>(001) (Figure 3e) took the original conformation with doubly coordinated O (O<sub>2c</sub>) and pentacoordinated Nb (Nb<sub>5c</sub>). Nevertheless, the NbOPO<sub>4</sub>(100) and Nb<sub>2</sub>O<sub>5</sub>(001) surfaces both contain NbO chains (see the dashed black squares in Figure 3a,e and corresponding local structures in Figure 3b,f) with similar atomic structures.

For surface reactions, we first considered the adsorption of furan at NbOPO<sub>4</sub>(100). In the calculated structure (Figure 3c), the C–O bond of furan is actually broken, and a bidentate adsorption configuration is observed with a calculated adsorption energy of 0.66 eV. At the same time, the surface Nb–O–Nb chain at the adsorption site also opens up to accommodate the adsorbate, and as a result, two Nb–O bonds, one between surface Nb and O atoms and the other between surface a Nb atom and the O atom of furan, occur with nearly identical distances of 1.90 and 1.96 Å. We also calculated the tetrahydrofuran adsorption and obtained



**Scheme 2.** Proposed reaction pathway for the direct conversion of FA into octane.



**Figure 3.** Calculated structures (side view) of a) hydrogenated  $\text{NbOPO}_4(100)$ , e) clean  $\text{Nb}_2\text{O}_5(001)$ , b,f) the Nb-O-Nb chains highlighted in dashed squares on both surfaces, and c,d,g,h) the corresponding structures with one adsorbed furan (c,g) or tetrahydrofuran molecule (d,h). The Nb atoms are shown in light blue, P in pink, O in red, C in black, and H in white.

a similar bidentate structure (Figure 3d), but with a much higher adsorption energy of 1.39 eV. For the  $\text{Nb}_2\text{O}_5(001)$  surface (Figure 3e), the calculated structures of adsorbed furan and tetrahydrofuran are illustrated in Figure 3g,h, and the corresponding adsorption energies were estimated to be 0.38 and 1.02 eV, respectively. The calculations at both surfaces gave consistent results regarding the adsorption structures and energetics. In particular, owing to the inherent large stress within the Nb-O-Nb chain at the surface (as seen from the large angle), the local Nb-O bond tends to break to release the stress. Correspondingly, the “free” Nb and O atoms can bind with the O and C atoms of the adsorbing (tetrahydro)furan and promote its ring opening. These results can therefore explain the ring-opening activity of  $\text{NbO}_x$ -based catalysts, and indicate the reaction order as furan hydrogenation by supported metal clusters, followed by ring opening of tetrahydrofuran at the substrate. This reaction order is consistent with our experimental findings reported above.

We then calculated the subsequent hydrogenation processes of adsorbed tetrahydrofuran on the  $\text{Nb}_2\text{O}_5(001)$  surface. The corresponding energy profile is illustrated in Figure 4. We assumed that  $\text{H}_2$  can readily dissociate at Pt and then transfer to the surface of the  $\text{Nb}_2\text{O}_5$  support. As we

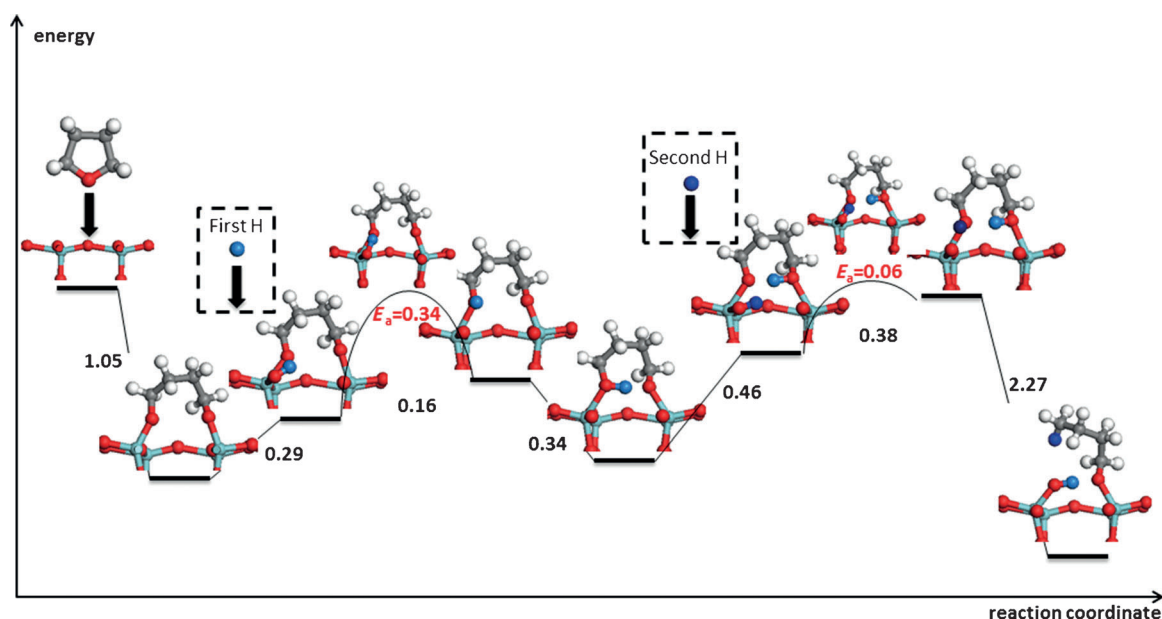
can see, the first hydrogen atom favors bonding to  $\text{O}_{2c}$  beside the Nb-O bond with a negative adsorption energy of -0.23 eV, which indicated that this hydrogen atom is unstable. By performing climbing image nudged elastic band (CI-NEB) calculations, we located the transition state for the diffusion of the adsorbed H atom to bond with the O atom of the Nb-O-C linkage and found an energy barrier of 0.34 eV. A stable intermediate state resulted in which the H atom is located in the middle of two Nb-O-C linkages and shared by the two O atoms. Afterwards, the

second hydrogen atom diffuses onto the O atom of the Nb-O-C linkage; for this step, the energy barrier is only 0.06 eV. This H atom can then transfer to the C atom of the same linkage to help break the C-O bond with almost no barrier; the resulting surface species can be viewed as dissociative adsorbed butanol. Afterwards, one H atom can transfer via the O atom of the left Nb-O-C linkage to the C atom to promote the formation and desorption of butane as the desired product. Further hydrogenation of the residual O atom would lead to water formation and desorption, with the surface ending up in the original state to finish the catalytic cycle. In general, as can be seen from the calculated energy profile, these processes should be able to occur under rather mild conditions.

To further confirm the role of  $\text{NbO}_x$  and investigate the detailed reaction mechanism of the hydrodeoxygenation, a series of in situ DRIFTS experiment were conducted with tetrahydrofuran (THF) as the model compound. The resulting spectra (see Figure S9) indicated the chemisorption of THF on  $\text{Pd/NbOPO}_4$  as a bidentate intermediate, and then its transformation into adsorbed butanol by the addition of  $\text{H}_2$ , in agreement with the result of the DFT calculation.

For the production of long-chain alkanes from biomass without complicated separation, other aldol-condensation





**Figure 4.** Calculated energy profile for hydrogen diffusion and the hydrogenation of tetrahydrofuran on the Nb<sub>2</sub>O<sub>5</sub>(001) surface. All of the calculated elementary steps are illustrated with the energy differences in black, the energy barriers in red, and the reacting H atoms in blue.

products with similar structures to that of FA, such as difurfural acetone (DFA), 5-hydroxymethylfurfural acetone (HMFA), di-5-hydroxymethylfurfural acetone (DHMFA), or mixtures of these compounds, were also considered as candidates for hydrodeoxygenation. Long-chain alkanes (> 90 %) were obtained in very high yield in each case with less C–C bond cleavage, thus indicating that this process provides an approach to the production of long-chain alkanes that is not only applicable to FA, but also to other biomass-derived ketones. The composition of the alkanes can be tuned by simply changing the nature (e.g., furfural versus HMF) and the molar ratio of the biomass-derived reactants (e.g., furfural or HMF/acetone = 1:10–1.5:1; see Figure S17).

This process does consume a lot of hydrogen for the production of alkanes. For example, 8 mol of hydrogen are consumed for the hydrodeoxygenation of 1 mol of 4-(2-furyl)-3-buten-2-one to octane. However, the heat of octane combustion is 5518 kJ mol<sup>−1</sup>; much higher than that of 8 mol of H<sub>2</sub> (285.8 × 8 = 2286 kJ mol<sup>−1</sup>). Thus, with respect to the final products, the transformation of all the reactants, including H<sub>2</sub>, still gives rise to an increase in energy.

In summary, we have reported a direct and efficient approach for the production of liquid alkanes from biomass-derived aldol adducts (FA, HMFA, DFA, and DHMFA) over a multifunctional Pd/NbOPO<sub>4</sub> catalyst under mild conditions. Octane is obtained in very high yield (94 %) from the direct conversion of FA, and the catalyst can be used for 256 h without deactivation at 170 °C and 2 MPa, which is the best performance reported so far. Further studies verified that NbO<sub>x</sub> species could effectively promote the C–O bond cleavage, which is very important for the high-yielding production of alkanes under mild conditions. A DFT calculation also showed that the Nb–O–Nb chains in both NbO<sub>x</sub> and NbOPO<sub>4</sub> have a strong ability to break the C–O bond on the (tetrahydro)furan ring, as this process can efficiently relieve

the surface tension of the oxide bonding network. Moreover, the complete hydrogenation process has been calculated and appears to be very facile. In general, Pd/NbOPO<sub>4</sub> as a multifunctional catalyst plays three roles in the conversion of aldol adducts into alkanes: 1) The supported noble metal is the active center for hydrogenation; 2) NbO<sub>x</sub> species aid in C–O bond cleavage, especially of the tetrahydrofuran ring; and 3) the niobium-based solid acid catalyzes the dehydration.

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