Cooperative Catalysis for Direct Hydrodeoxygenation of Vegetable Oils into Diesel-range Alkanes over Pd/NbOPO₄†

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Near quantitative carbon yields of diesel-range alkanes were achieved from the hydrodeoxygenation of triglycerides over Pd/NbOPO₄ under mild conditions with no catalyst deactivation: catalyst characterization and theoretical calculations suggest that the high hydrodeoxygenation activity is originated from synergistic effect of Pd and strong Lewis acidity with unique structure of NbOPO₄.

The sustainable production of liquid fuels from renewable biomass is one of the possible ways to reduce our reliance on fossil fuels and alleviate the concerns about global warming.¹ Vegetable oils are widely available in nature and are being considered as a promising renewable energy source, with the potential to be transformed to diesel fuels.²

So far, several strategies have been reported to convert vegetable oils (triglycerides) into diesel fuels. The commercial approach is the transesterification of triglycerides with methanol to form fatty acid methyl ester (FAME), with glycerol as the by-product.³ FAME as a first generation biodiesel is one of the most extensively used biofuels nowadays and has been in practice with a large scale.⁴ However, FAME as a transportation fuel has several drawbacks, such as high viscosity and poor calorific value, which obviously limits its application.⁵ In addition, the by-product, glycerol with low demand has created serious environmental problems.⁶ The catalytic cracking of triglycerides over zeolites, such as HZSM-5 to produce gasoline- and diesel-range fuel is an alternative,⁷ but the low selectivity limits its application. Hydrotreating of triglycerides at high temperature over supported metal sulfide catalysts, such as NiMo and CoMo sulfide catalysts have also been attempted.⁸ This process is selective and existing infrastructure and application experience from the petroleum industry can be used. However, the leaching of sulfur

from sulfide catalysts is an issue at high temperature, which will inevitably contaminate the products and deactivated the catalysts. As an alternative, decarboxylation and/or decarbonylation of carboxylic acids at high temperature over non-sulfide catalysts have also been attempted.⁹ However, the C-C bond cracking was significant and the processes showed low activities towards triglycerides conversion.

Hydrodeoxygenation of triglycerides over metal supported on acidic zeolites (H-beta, H-ZSM-5) as bi-functional catalysts was shown to produce diesel-range alkanes as high-grade transportation fuels.¹⁰ However, the rapid carbon deposition in zeolitic cavity, leading to catalyst deactivation is a major perceived problem. Recently, Nb₂O₅-modified Pd/SiO₂ was reported to be active for the total hydrodeoxygenation of fatty acid and triglycerides, but the detailed mechanism remains to be studied.¹¹

Herein, we report that a simple methodology for the direct hydrodeoxygenation of vegetable oils over Pd/NbOPO₄ catalyst under mild conditions (180 °C, 30 bar). Total conversions with near quantitative yields for alkane formation from triglycerides can be obtained over this efficient catalyst. The low reaction temperature preserves C-C bond cleavage, giving >96% corresponding n-alkane selectivity from fatty acid and propane from glycerol moieties. Catalyst characterization suggests that the glassy nature of NbOPO₄ phase can lose its lattice oxygen in H₂ readily at mild temperature to expose strong Lewis acid Nb⁵⁺ sites hence generating oxygen deficient phase with a high propensity for the adsorption of [O] from triglyceride. In combination with active hydrogen spilled from Pd surface, a highly efficient cooperative catalysis for direct hydrodeoxygenation reaction of triglyceride can be achieved.

In this work, we first employed pure glyceryl trioctanoate as a model compound of vegetable oil to investigate the influence of various reaction conditions for direct hydrodeoxygenation, and the results are summarized in Table 1. It is shown that the hydrodeoxygenation of the triglyceride can be completed as low as 160 °C owing to high catalytic performance of Pd/NbOPO₄ (entry 1). The liquid product contained 91.4% and 5.0% yields of octane and heptane, respectively (carbon yield was defined as mass of carbon in octane (heptane)/mass of carbon in fatty-acid part), with lower than 0.5% yield of methane in the gas phase but it required a long reaction time of 48 h to achieve this result.

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Table 1 Hydrodeoxygenation of glyceryl trioctanoate over bifunctional catalysts under various reaction conditions.^a

Entry	Catalysts	Temp. (°C)	Press. (bar)	Carbon yield (%)		
				Octane	Heptane	C ₇₋₈ alkanes
1	Pd/NbOPO ₄ ^b	160	30	91.4	5.0	96.4
2	Pd/NbOPO ₄	180	30	89.9	5.9	95.8
3	Pd/NbOPO ₄	200	30	87.3	7.7	95.0
4	Pd/NbOPO ₄	180	20	83.6	8.5	92.1
5	Pd/NbOPO ₄	180	10	15.5	3.0	18.5
6	Pd/NbOPO ₄ ^c	180	30	46.6	4.3	50.9
7	Pt/NbOPO ₄	180	30	87.5	6.8	94.3
8	Pd/H-Beta	180	30	55.4	5.8	61.2

^a 0.6 g of glyceryl trioctanoate, 0.2 g of catalyst and 30 mL of cyclohexane were put into a 300-mL autoclave, the reactions were held for 24 h in all cases except for entry 1; the metal loading was 5 wt% in all cases except for entry 6. ^b Reaction time was 48 h. ^c Pd loading was 3 wt%.

An increase of temperature from 160 to 200 °C at 30 bar led to a slightly decrease of octane from 91.4% to 87.3% but an increase of heptane from 5.0% to 7.7% (entries 1-3), which indicated that high reaction temperature favors C-C bond cleavage. The variation of H₂ pressure showed that a decrease of H₂ pressure from 30 to 20 bar at 180 °C gave a slightly decrease in octane formation, but further decrease of the H₂ pressure to 10 bar caused a significant drop of octane yield to 15.5% (entries 2, 4, 5). This clearly suggests that high H₂ pressure is required to overcome a slow mass transfer of the gaseous reactant (H₂ solubility is generally limited at lower pressure). A decrease of Pd loading to 3 wt% also led to a great decline of octane yield as well as the total liquid alkane yield (entry 6). Replacing Pd with Pt was also effective for this reaction (entry 7), indicating that both noble metals can play the role of [H] supplier from readily facilitated H₂ adsorption and dissociation. Notice that Pd/H-Beta can only give a moderate liquid alkane yield but with noticeable deactivation (entry 8). Thus, these results clearly indicate that NbOPO₄ phase is active and selective for the hydrodeoxygenation of triglycerides.

Glyceryl trioleate and stearic acid were also used as substrates under the same conditions of 180 °C, 30 bar H₂ over 5 wt% Pd/NbOPO₄ and the results are presented in Figure 1a. Notably, high (>97%) carbon yields of total liquid alkanes are obtained from the both substrates, indicating that both catalytic reactions are taken place extremely selectively over the Pd/NbOPO₄ catalyst. For the stearic acid conversion, 91.5% yield C₁₈-alkane and 6.1% yield of C₁₇-alkane were obtained in liquid phase with a negligible amount of methane (0.33%) generated by the C-C bond cleavage. This again indicates the cleavage was suppressed under the reaction conditions. Finally, direct hydrodeoxygenation of vegetable oils, palm oil and soybean oil (see Table S1 for detailed composition) were attempted. As shown in Figure 1b, 83.9 wt% and 85.1 wt% of diesel-range alkanes were obtained from the two oils, respectively. Taken the masses of oxygen and glycerol into account, the vegetable oils were quantitatively converted into liquid alkanes (see SI for calculation). Owing to the high catalytic activity at low reaction temperature the C-C bond cleavage side reaction was largely avoided and only a small degree of n-1 alkanes generated (< 6%). Moreover, propane was detected as the main gaseous products (4 wt% and 3.6 wt% from palm oil and soybean oil respectively, which were equivalent to

Figure 1a: Product distributions obtained from hydrodeoxygenation of glyceryl trioleate and stearic acid over Pd/NbOPO₄; **1b:** Product distributions obtained from hydrodeoxygenation of palm oil and soybean oil. 0.6 g of substrate, 0.2 g of 5 wt% Pd/NbOPO₄ and 30 mL of cyclohexane into a 300-mL Teflon-lined stainless steel Parr reactor at 180 °C and 30 bar for 24 h under magnetic stirring of 300 rpm for all four compounds.

Figure 2a: Reuse of Pd/NbOPO₄ catalyst for the hydrodeoxygenation of glyceryl trioctanoate; **2b:** The time plot of glyceryl trioctanoate hydrodeoxygenation.

about 80% carbon yields with respect to their glycerol conversions). Thus, both the fatty-acid and glycerol components were hydrodeoxygenated into the corresponding alkanes.

The recyclability of the Pd/NbOPO₄ catalyst was then investigated with glyceryl trioctanoate as the feedstock under the optimal reaction conditions (180 °C, 30 bar). After the first run, the catalyst was separated from liquid phase by centrifugation, dried and re-used directly for second run without any treatment. A slight activity loss was found and the yield of octane dropped from 89.9% to 75.6% in the second run (Figure 2a). This is attributed to the loss of superfine portion of catalyst powder during its recovery. Then, after the second run, corresponding fresh catalyst was then added to compensate the loss in the catalyst weight for subsequent runs. It can be seen from Figure 2a that the catalytic performance is fully regenerated and the yields for the alkanes maintain at the same values as the first run, revealing the high stability and recyclability of Pd/NbOPO₄. This could be due to two reasons: First, under such mild temperature (180 °C), no significant aggregation of Pd particles was taken place. Secondly, there was no leaching of the catalyst to the non-aqueous medium (cyclohexane). According to our ICP analysis no concentration of Pd, P or Nb in solution was detected above their detection limits.

Figure 2b shows the product distributions in catalytic hydrodeoxygenation of glyceryl trioctanoate as a function of reaction time. Notice that the fatty acid derived alkane (octane) increases steadily during the reaction time course. After 2 h, appreciable amounts of octanol and octanoic acid as well as propyl-octyl ether were detected, followed by the detections of propyl octanoate, octyloctanoate and dioctyl ether at later time. With the further process of reaction, the amounts of these intermediates decreased to zero at beyond 17 h, giving octane as an exclusive product in liquid

phase. Clearly from the product-time profile, the ester bond of the glyceryl trioctanoate was readily cleaved, generating alcohols and acids and cross-reaction intermediates before they were hydrodeoxygenated to octane and propane, as summarized in Scheme S1.

Figure 3a: TPR of Pd/NbOPO₄ shows reduction of PdO and H₂ absorption at -15 °C and reduction of bulk NbOPO₄ at 20 °C, respectively (black line). The unstable drifting background is due to the changes in H₂ flow, while water molecules evolution is held at low temperature until above 50 °C (blue line). Hydrogen evolution from Pd hydride decomposition is taken place at 60 °C. **3b:** k³-EXAFS curves vs radial distance of Pd/NbOPO₄ before (black line) and after (red line) reduction: a substantial peak shift to shorter distance at 1.41 Å is noted.

One important question is why this catalyst can catalyze the hydrodeoxygenation reaction so efficiently and readily at mild temperature. Catalyst characterization was therefore conducted (Figure S1-S9 for the results of XRD, N₂ adsorption/desorption, TEM, Pd dispersion measurements and pyridine-FTIR, NMR, EXAFS, XPS, respectively). Temperature programmed reduction in H₂ shown in Figure 3a depicts two large peaks of hydrogen consumption (negative peak) at -15 °C and 20 °C, respectively, and one positive peak for hydrogen evolution at about 60 °C. The first peak is assigned to sub-ambient reduction temperature of nanosize PdO to Pd, followed by rapid H₂ activation/uptake (known to take place without much activation barrier on clean Pd surface). The second peak is attributed to the reduction of bulk NbOPO₄ by hydrogen and the third peak to the decomposition of Pd hydride to hydrogen. Although catalytic reduction of oxide phase in presence of Pd is long known to be facilitated at low temperature, the ambient temperature reduction of bulk NbOPO₄ is incredible. This reflects extensive contact between Pd and NbOPO₄, fast and readily oxygen transfer from latter material by spilled hydrogen even at 20 °C to form niobium oxygen deficient phase.

The relative low melting and glassy nature Nb-O-PO₄ has long been documented.¹² As a typical sol-gel material it offers an extensive interface at high surface area by hosting small noble metal nanoparticles, as reflected by our material characterization and TEM image (Figure S1-4). There are different oxygens and linkages of NbO₆ octahedra to phosphate group in this glassy structure. To characterize the Nb-O environment before and after reduction, EXAFS study was employed. Figure 3b shows the k³-EXAFS curves versus radial distance of fresh Pd/NbOPO₄ (black line). According to the best fit to the EXAFS data, three Nb-O distances can be identified namely 1.80 Å (Coordination No., CN = 1.1), 1.98 Å (CN = 4.0) and 2.52 Å (CN = 1.0), see Table S2. These values within experimental errors are complementary to earlier EXAFS, diffraction, ³¹P and ⁹³Nb NMR, Raman scattering and O_{1s} XPS results of the Nb-O-P glass.¹²⁻¹³ In this structural network, distorted NbO₆ octahedra possess a corner of a short Nb-O bond of 1.74 Å, four bonds Nb-O-

Nb of ~1.97 Å and a longer bond of ~2.36 Å. The distortion is attributed to the intrinsic difference in bonding valency of Nb (six) and P (five). The over-bonding by substitution of P to Nb of Nb-O-P bridge leads to longer Nb-O bond. Whereas, the deficit of bond valence when Nb is substituted by P creates shorter Nb-O bond.¹³ Notice that a substantial peak shift to even shorter bond of 1.4-1.5 Å at the expanse of longer bond in CN is observed in reduced sample (Figure 3b and Table S2). The removal of oxygen from this glassy structure of Nb-O-P during catalytic reduction further distorts the structure, rendering it similar to those tetrahedra NbO₄ on alumina which possesses shortest Nb=O bond.¹⁴ Thus, the open structure with missing oxygen in surface tetrahedra can allow the high valence Nb cations accessible for oxygenated substrates which may also be attracted by protons on Nb-O(H)-Nb. To characterize the surface acid sites on reduced Pd/NbOPO₄, NMR active probe, trimethylphosphine (TMP), was employed as it can reflect various micro-environments by corresponding chemical shift in ³¹P NMR spectrum. ³¹P nucleus with 100% natural abundance and a chemical shift range over 430 ppm has been shown to be sensitive and reliable technique capable of providing abundant information on the acid type, acid strength, and strength distribution in various solid acids.¹⁵ TMP molecules bound to Lewis acid sites give rise to ³¹P resonances in the range from -20 to -60 ppm. While adsorbing on Brønsted acid sites, TMP molecules are subsequently protonated to form TMPH⁺, bringing the ³¹P resonances in the range of 0 to -5 ppm.¹⁶ The ³¹P MAS NMR spectra of TMP adsorbed on reduced Pd/NbOPO₄ indeed possess both surface Lewis and Brønsted acid sites at -26.1 ppm and -3.9 ppm, respectively (Figures S6). Importantly, the Lewis acidity of reduced NbOPO₄ value measured is found to be much stronger than most solid acid catalysts and is comparable to those of sulfated/BF₃-modified metal oxides (SO₄²⁻/ZrO₂,¹⁷ SO₄²⁻/TiO₂,¹⁸ BF₃/Al₂O₃¹⁹) which are known to give super-acidity (see SI). We therefore anticipate that a synergistic catalytic effect between strong Lewis acidity and excellent H activity from Pd is responsible for the high activity of Pd/NbOPO₄ catalyst for hydrodeoxygenation reaction. It is however, hydrodeoxygenation of oxygenated substrates over many reducible solid oxygen defects is known,²⁰ we wondered what special features of this catalyst that can tackle the generally stable ester bond under such mild conditions.

In order to shed light to this query, we then performed the density functional theory (DFT) simulation with the Van der Waals (VDW) correction of the reaction processes at Nb₂O₅(001) surface. This low index Nb₂O₅(001) surface is commonly used in literature because it contains a well-defined crystalline surface in order to shed light on catalytic properties of Nb-O.²⁰ Besides, the Nb₂O₅ (001) contains exposed NbO₆ and NbO₄ (oxygen deficient) units, which are close to our postulated oxygen vacant surface for the catalysis. For simplicity, we chose ethyl butyrate as a model substrate. First, we considered two adsorption forms (Figure 4): carbonyl oxygen adsorption (O_a adsorption, IS1) and ether oxygen adsorption (O_b adsorption, IS2). In the calculated structure (IS1), O_a bond to Lewis acid, Nb cation with an adsorption energy of 1.12 eV, the C₁-O_b bond is activated and increased by 0.014 Å (from 1.458 Å to 1.472 Å) while the C₂-O_b bond is shortened by 0.032 Å (from 1.364 Å to 1.332 Å), indicating that C₂-O_b bond is not likely to break. Considering the C₁-O_b bond breakage is associated with a high energy barrier of 1.96 eV, we believe that O_a adsorption is not

readily to take place during reaction. For O_b adsorption structure (IS2), O_b interacts with surface niobium cation with adsorption energy of 1.16 eV. At the same time, C_1-O_b bond is increased by 0.022 Å (from 1.458 Å to 1.480 Å) and C_2-O_b bond is increased by 0.036 Å (from 1.364 Å to 1.400 Å), both are thus activated. For the two intermediate structure formed by breaking the above two bonds (rate limiting), the calculated activation energy of TS2 (break C_1-O_b) is 2.34 eV, while an **extremely low energy of 0.84 eV** for TS3 (break C_2-O_b) is noted. Even though intermediate structure IM1 is 0.2 eV more stable than IM2, the reaction could still occur much easier by breaking C_2-O_b bond. In particular, we believe the strong [O] affinity from the super-acidity of Nb cation as discussed, together with contributions from electron withdrawing nature of carbonyl and with inherent stress release trend of regenerated Nb-[O]-Nb assist the C_2-O_b bond cleavage.¹² These make the catalyst material unique for the activation and breaking of C-O bond of ester at such low energy. Although no calculation is yet conducted, the presence of Brønsted acid site in close vicinity may also assist adsorption of carbonyl oxygen O_a to enable further O_b interaction with surface niobium cation for TS3 (break C_2-O_b). We also calculated the subsequent hydrogenation processes which are not rate limiting (see Scheme S2). By performing climbing image nudged elastic band (CI-NEB) calculations, we located the transition state for the diffusion of the adsorbed hydrogen atom to bond with the O atom of the Nb-O-C linkage of ethoxy to form adsorbed ethanol specie, with an energy barrier of 0.38 eV. The second hydrogen atom also favored bonding to O_{2C} beside the Nb-O bond of adsorbed butyrate, and diffused onto the O atom of the Nb-O-C linkage of adsorbed butyrate to form butyric acid specie, the energy barrier is 0.77 eV. The third hydrogen atom adsorbed and helped to break the C-O bond of ethanol with energy barrier of 0.29 eV, which resulted in the formation and desorption of ethane, leaved H atom adsorbed on surface O_{2C} . Further hydrogenation produced ethane and butane as final products.

Figure 4: Calculated structures of model molecule adsorption and C-O bond breakage processes. Nb atoms are shown in light blue, O in red, C in black, and H in white.

In summary, we report a very simple but high-selective catalytic process for direct hydrodeoxygenation of vegetable oils into diesel-range alkanes under mild conditions over Pd/NbOPO₄. The mass yields of diesel-range alkanes from palm oil and soybean oil can approach to quantitative values. The C-C bond cleavage is largely suppressed, owing to high catalytic activity of Pd/NbOPO₄ catalyst at low temperature. Characterization and theoretical studies show that hydrodeoxygenation of triglycerides by hydrogenolysis of the

ester bonds is much facilitated over this catalyst, which is originated from the synergistic effect of hydrogen activity from Pd and superior Lewis acidity with unique structure of reduced NbOPO₄ in H₂.

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