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Energy-efficient production of 1-octanol from biomass-derived furfural-acetone in water†

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An energy-efficient catalytic system for the one-pot production of 1-octanol from biomass-derived furfural-acetone (FFA) under mild conditions in water was developed, by sequential hydrogenation/hydrogenolysis over a hydrophilic Pd/$NbOPO_4$ catalyst. A strategy of creating an intentional "phase problem" has been employed to prevent the over-hydrogenolysis of 1-octanol into *n*-octane and therefore increased the selectivity to 1-octanol. The effects of reaction conditions as well as a variety of noble-metal loaded bifunctional catalysts have been systematically investigated to maximize the yield of 1-octanol. Moreover, the addition of liquid acids to the catalytic system further enhanced the selectivity towards the formation of 1-octanol. There is a strong correlation between the acid strength of an acidic additive and the sum yield of 1-octanol and octane. With the addition of TfOH, the highest yield of 1-octanol (62.7%) was obtained from one-pot conversion of biomass-derived FFA over Pd/$NbOPO_4$.

Introduction

Biomass has been considered as a promising alternative to petroleum resources and extensive efforts have been made worldwide to convert renewable biomass into fuels and value-added chemicals.[1–4] Lignocellulose is the most abundant biomass resource on earth which consists of cellulose, hemicellulose and lignin.[5] In lignocellulose conversion, 5-hydroxymethylfurfural (HMF) and furfural are two extremely important biomass platform chemicals, which are typically produced by acid-catalyzed dehydration of fructose and xylose respectively.[6–10] So far, a great number of strategies and approaches have been put forward to convert furfural compounds into the downstream value-added products, such as methylfurans,[11–14] long-chain alkanes,[15–17] diols[18–20] and acids.[21,22] In recent studies, furfural-acetone (FFA, C8) was produced by the aldol condensation of furfural with acetone and was used as a platform molecule for gasoline-fuel synthesis.[15,16,23–25] It is noted that acetone is also available from renewable biomass through acetone–butanol fermentation and can be regarded as a biomass-derived chemical.[26,27]

1-Octanol is a particularly attractive industrial product widely used in detergents, surfactants and fragrance production as well as chemical synthesis.[28] It also serves as an important solvent in biomass conversion.[29] Currently, 1-octanol is mainly produced from the petroleum-based process.[28] Recently, Julis and Leitner[30] reported for the first time that 1-octanol could be synthesized from furfural and acetone. They first converted furfural to FFA by aldol condensation in the presence of excess acetone. After evaporation of acetone, neat FFA was then hydrogenated into 4-(2-tetrahydrofuryl)-2-butanol (THFA) over Ru/C at 120 °C and 120 bar H_2 pressure. Finally, 1-octanol and dioctyl ether were obtained by selective deoxygenation and ring opening over Ru/C in [EMIM][NTf2] with acidic additive [BSO3BIM][NTf2] at 150 °C and 120 bar H_2 pressure.[30] The strategy for the synthesis of 1-octanol from biomass-derived platforms with a retrosynthetic analysis concept was creative. However, the process could be further improved if a more eco-friendly solvent and a more efficient catalytic system was employed.

More recently, we reported that *n*-octane can be produced directly from FFA with yields higher than 90% under mild conditions in cyclohexane over multifunctional niobium phosphate supported Pd catalysts.[31] The proposed reaction pathway showed that 1-octanol had been produced before it was finally converted into *n*-octane. From this point of view, if the catalyst or the reaction condition was appropriately modified to prevent 1-octanol from finally converting to *n*-octane, the one-pot efficient production of 1-octanol from FFA could be envisaged. In the literature, $NbOPO_4$ has been extensively studied as a water-tolerant solid acid and has been applied in dehydration,[32–34] hydrolysis[35,36] and esterification.[37] It also possesses a strong hydrophilic character due to its large metal size.[38] Therefore, if water was used as a solvent for the

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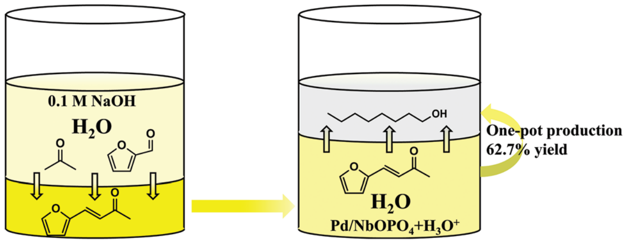


Scheme 1 One-pot production of 1-octanol from biomass-derived FFA over $Pd/NbOPO_4$ in water.

production of 1-octanol from FFA using hydrophilic $Pd/NbOPO_4$ as a catalyst, it would actually cause a man-made "phase problem" to prevent the over-hydrogenolysis of 1-octanol, because 1-octanol would separate spontaneously from the water phase once it was generated owing to its immiscibility, while hydrophilic $Pd/NbOPO_4$ would stay in the aqueous phase throughout the reaction, which will separate with 1-octanol.

Herein, we describe an energy-efficient catalytic system for the one-pot production of 1-octanol from biomass-derived FFA, using hydrophilic $Pd/NbOPO_4$ as a catalyst and water as a solvent, as shown in Scheme 1. The over-hydrogenolysis of 1-octanol to *n*-octane can be largely avoided and 1-octanol can be easily separated from water after being produced, which makes this catalytic system much more energy-efficient for the industrial production. Moreover, strong acidity is found to be in favor of the cleavage of the secondary C–O bond compare to the primary C–O bond, which can be attributed to the greater stability of secondary carbenium ion structures than primary carbenium ion structures in water.[39] Therefore, liquid acids were added to further increase the system acidity, which enhance the selectivity of secondary C–O bond cleavage, leading to the primary alcohol formation. With the addition of TfOH, the highest yield of 1-octanol (62.7%) was obtained from one-pot conversion of biomass-derived FFA over a hydrophilic $Pd/NbOPO_4$ catalyst.

Experimental section

Chemicals

$Pt(NO_3)_2 \cdot xH_2O$ and $Pd(NO_3)_2 \cdot xH_2O$ were purchased from Heraeus Materials Technology Shanghai Ltd (Shanghai, China). $RuCl_3 \cdot 3H_2O$ was purchased from Aladdin Reagent Co., Ltd (Shanghai, China). γ-Al_2O_3 and H-Beta were purchased from Nankai University Catalyst Co., Ltd (Tianjin, China). All other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All purchased chemicals were of analytical grade and used without further purification.

Catalyst preparation

Hydrophilic $NbOPO_4$ used here was prepared by a hydrothermal method at pH = 2 according to our previous reports.[33] $M/NbOPO_4$ (M = Pt, Pd, and Ru) catalysts were prepared by incipient wetness impregnation of $NbOPO_4$ with aqueous solution of $Pt(NO_3)_2$, $Pd(NO_3)_2$, and $RuCl_3$, respectively. After impregnation, the catalysts were dried at 100 °C for 12 h, followed by calcination in air at 500 °C for 3 h with a rate of 2 °C min^{-1}. Pd/H-Beta was also prepared by the same procedure. Metal loading was 5 wt% in all cases. Pd and Pt catalysts were used without pre-reduction and reduced *in situ* during the reaction. $Ru/NbOPO_4$ was reduced at 300 °C under the flow of 10% H_2/Ar gas mixture before use.

Catalyst characterization

The N_2 adsorption/desorption isotherm of $NbOPO_4$, the X-ray diffraction (XRD) pattern, the X-ray photoelectron spectroscopy (XPS) pattern and the transmission electron microscopy (TEM) image of $Pd/NbOPO_4$ are provided in the ESI.†

The NH_3-TPD was carried out in an apparatus (PX200, Tianjin Golden Eagle Technology Co. Ltd) equipped with a thermal conductivity detector (TCD). The samples (100 mg) were loaded into a U-shaped quartz tube. Prior to TPD measurements, the samples were pretreated in flowing N_2 (45 ml min^{-1}) for 1 h at 500 °C, and then cooled to 50 °C. NH_3 was adsorbed onto the samples by exposure to flowing 10% NH_3 in a N_2 gas mixture (50 ml min^{-1}) for 45 min at 50 °C. Residual and physical adsorbed NH_3 was removed by purging the samples with flowing N_2 (45 ml min^{-1}) at 90 °C for 1 h. Desorption of NH_3 was performed by heating the samples at a rate of 10 °C min^{-1} under flowing N_2 (45 ml min^{-1}) from 90 °C to 550 °C.

Catalytic reaction and product analysis

The one-pot production of 1-octanol from FFA was carried out in a 50 mL Teflon-lined stainless-steel autoclave. Typically, 0.2 g of FFA, 0.1 g of $Pd/NbOPO_4$ and 4 g of water were put into the autoclave. The reaction was hydrogenated at room temperature and 2.5 MPa H_2 pressure for 3 h first to saturate FFA and then reacted at elevated temperature (*e.g.*, 190 °C) for another 18 h. After the reaction, the reactor was quenched in an ice/water bath. The products in the liquid phase were extracted by 4 mL of cyclohexane and both organic and aqueous phases were analyzed by GC (Agilent 7890) equipped with a HP-5 column and an FID detector using the internal standard method. The yields of products were calculated by using the equation: yield [%] = (mol of carbon in product)/(mol of carbon in reactant) × 100%.

Results and discussion

Reaction pathway and practicability study

We have investigated the reaction pathway of one-pot conversion of FFA to *n*-octane in cyclohexane over multifunctional $Pd/NbOPO_4$ catalysts, and found that 1-octanol had been generated before it was finally converted into *n*-octane.[31] So first of all, we studied the reaction profile of one-pot FFA conversion in the aqueous phase over $Pd/NbOPO_4$ to investigate the practicability of 1-octanol production. The catalytic reaction was carried out at room temperature and 2.5 MPa for 3 h first to saturate FFA before being heated up to 170 °C. FFA is just slightly soluble in water, so directly heating up to a high temperature without pre-hydrogenation of the highly unsaturated FFA would cause severe cokes. The product distribution of one-pot conversion of FFA with different reaction times is shown in Fig. 1, and the main reaction pathway according to the reaction time plot is proposed in Scheme 2. For the first 3 h being hydrogenated at room temperature, FFA was completely converted to saturated intermediates with 87.1% yield of tetrahydrofurfural alcohol (THFA, 4-(2-tetra-hydrofuryl)-2-butanol and its isomer 3-(5-methyl-2-tetra-hydrofuryl)-1-propanol), indicating that the hydrogenation of FFA is relatively easy, thus makes it possible for coupling the THFA hydrodeoxygenation step with the FFA hydrogenation step into a one-pot reaction. Then the reaction temperature was raised to 170 °C and held for 6 h, the amount of THFA was drastically decreased, giving a medium yield of 1-octanol (22.6%), with 15.6% yield of 2-methyl-5-propyltetrahydrofuran (MPTHF), 18.7% yield of 2-butyltetrahydrofuran (BTHF) and 4.2% yield of octane. Small amounts of other products such as 1,4-octylene glycol (1,4-OG), 1,7-OG, 2,5-OG, 2-octanol, and 4-octanol were also detected. Further reaction for another 6 h at 170 °C showed a mild increase in the yield of 1-octanol to 30.9%, and this yield was further slightly increased to 33.1% when the reaction continued for 18 h, with very little amounts of THFA remaining. As expected, extension of the reaction time to 24 h did not make much difference to that of 18 h, revealing that 1-octanol, BTHF, and MPTHF were relatively stable in aqueous medium under these conditions. It was because 1-octanol, BTHF and MPTHF all separated spontaneously from water, while the hydrophilic catalyst Pd/NbOPO$_4$ remained in the aqueous phase throughout the reaction, which caused an intentional "phase problem" to prevent further conversion of water-insoluble compounds. This was remarkably different from our previous work,[31] in which all the oxygen-containing compounds were ultimately converted to octane under the same conditions except that cyclohexane was used as a solvent, revealing that the solvent could impose a significant influence on the product distribution.

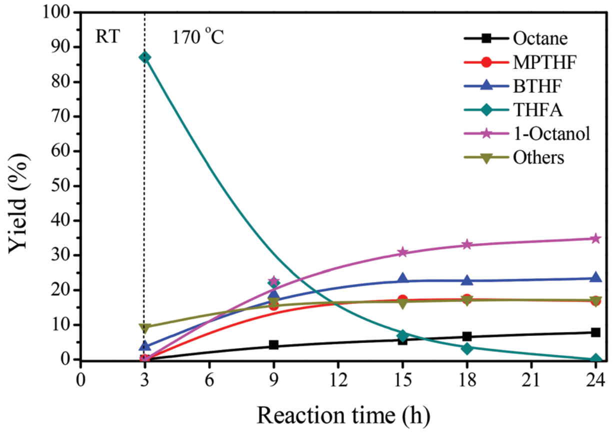
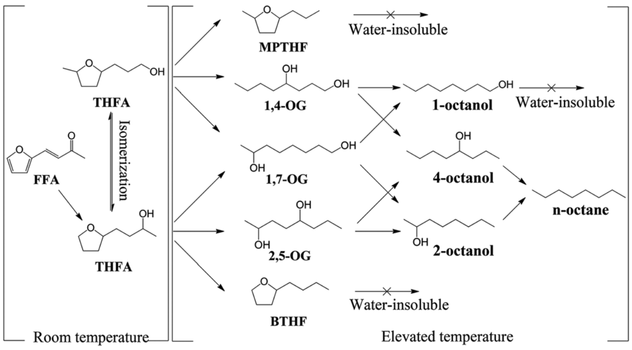


Fig. 1 The product distribution of one-pot conversion of FFA at different reaction times. The reaction was hydrogenated at room temperature and 2.5 MPa for 3 h first and then reacted at 170 °C for a certain period of time.



Scheme 2 Proposed reaction pathway of the one-pot FFA conversion over Pd/NbOPO$_4$ in water. The reaction was hydrogenated at room temperature and 2.5 MPa for 3 h first and then reacted at 170 °C for a certain period of time.

Effects of reaction conditions

The effects of reaction temperature and initial H$_2$ pressure were systematically investigated to optimize the reaction conditions and improve the selectivity of 1-octanol. Table 1 shows the product distribution achieved over Pd/NbOPO$_4$ under different reaction conditions. FFA was hydrogenated at room temperature for 3 h first and its final conversion was 100% in all cases. Entries 1–5 show that it is possible to increase the yield of 1-octanol by optimizing the reaction temperature, which has a significant effect on the final product distribution. In particular, when the reaction temperature was raised from 160 to 200 °C, the yields of THFA, MPTHF and other by-products (mainly 2-octanol and 4-octanol) decreased monotonously whereas the yield of octane increased monotonously, leading to the yield of 1-octanol peaking at 190 °C, first rising from 29.8% to 39.9% and then falling to 36.6%. This is probably because high temperature would promote the mass transfer of the reactants and H$_2$, leading to a faster hydrogenolysis rate.[40] Compared to reaction temperature, the H$_2$ pressure has minor effects on the final product distributions (entries 4, 6, and 7). However, an increase in the initial H$_2$ pressure from 2.5 to 6 MPa leads to a slight increase in the yield of octane, indicating that high H$_2$ pressure favors hydrodeoxygenation.

Catalytic performance of various catalysts

Under the optimized reaction conditions, we investigated a series of Pd catalysts with different hydrophilic oxygen-containing supports, namely Pd/NbOPO$_4$, Pd/γ-Al$_2$O$_3$, Pd/H-Beta and Pd/Nb$_2$O$_5$, as their catalytic performance and NH$_3$-TPD profile of the supports are summarized in Table 2 and Fig. 2 respectively. The yields of 1-octanol were strongly related to the

Table 1 Reaction results of the one-pot conversion of FFA at different temperatures and pressures[a]

			Yield[b] [%]					
Entry	T (°C)	P (MPa)	1-Octanol	MPTHF	BTHF	THFA[c]	Octane	Others[d]
1	160	2.5	29.8	19.1	21.9	6.4	3.1	19.7
2	170	2.5	33.1	17.4	22.5	3.1	6.6	17.3
3	180	2.5	36.7	16.2	26.1	0	7.8	13.2
4	190	2.5	39.9	16.8	23.6	0	10.8	8.9
5	200	2.5	36.6	15.6	27.1	0	13.8	6.9
6	190	4	36.4	18.9	24.6	0	13.5	6.6
7	190	6	38.5	18.2	23.0	0	13.5	6.8

[a] The reaction was hydrogenated at room temperature for 3 h first and then reacted at elevated temperature for another 18 h. [b] >99% conversion was observed in all cases. MPTHF, BTHF, and THFA are abbreviations for 2-methyl-5-propyltetrahydrofuran, 2-butyltetrahydrofuran, and 4-(2-tetrahydrofuryl)-2-butanol. [c] "THFA" includes 4-(2-tetrahydrofuryl)-2-butanol and its isomer (5-methyl-2-tetrahydrofuranpropanol). [d] Unless otherwise specified, "others" include 2-octanol, 4-octanol, dioctyl ether, 2,5-octylene glycol, 1,7-octylene glycol and other un-defined products.

Table 2 Reaction results of the one-pot conversion of FFA over different catalysts[a]

		Yield [%]					
Entry	Catalyst[b]	Octane	1-Octanol	MPTHF	BTHF	THFA	Others
1	$Pd/NbOPO_4$	10.8	39.9	16.8	23.6	0	8.9
2	$Pd/\gamma\text{-}Al_2O_3$	0	0	0	0	97.0	3.0
3	Pd/H-Beta	35.5	33.4	0.9	2.4	0	21.8
4	Pd/Nb_2O_5	2.0	26.8	10.9	57.6	0	2.7
5	$Pt/NbOPO_4$	11.4	23.8	31.6	23.8	0	9.4
6	$Ru/NbOPO_4$	8.0	2.5	13.3	40.7	0	35.5[c]

[a] The reaction was hydrogenated at room temperature and 2.5 MPa for 3 h first and then reacted at 190 °C for another 18 h. [b] All metal loading was 5 wt%. [c] The by-products were mainly heptane and 2-methyl-5-ethyltetrahydrofuran.

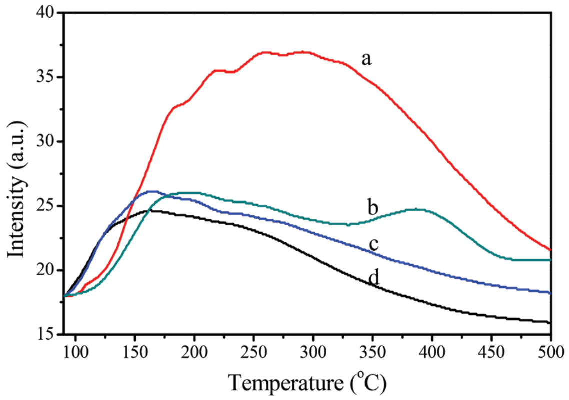


Fig. 2 NH_3-TPD profiles of different supports. (a) $NbOPO_4$, (b) H-Beta, (c) $\gamma\text{-}Al_2O_3$, and (d) Nb_2O_5.

acidic properties of the supports. In contrast to the reaction results over $Pd/NbOPO_4$ (entry 1), FFA only underwent hydrogenation reaction over $Pd/\gamma\text{-}Al_2O_3$, giving rise to 97% yield of hydrogenated intermediates (THFA), without any C–O bond cleavage products (entry 2), owing to the weak acidity of $\gamma\text{-}Al_2O_3$ support. Over catalysts with the more acidic H-Beta as support, 33.4% yield of 1-octanol was obtained respectively (entry 3), slightly lower than the yield over $Pd/NbOPO_4$, this is in good accordance with their relative quantity of acidic sites (see Fig. 2). However, the over-hydrogenolysis over Pd/H-Beta was much more significant with a much higher octane yield obtained (entry 3), probably because the zeolite was not hydrophilic enough to avoid the over-hydrogenolysis of 1-octanol. In our recent work,[31] Pd/Nb_2O_5 had an outstanding performance for hydrodeoxygenation of FFA in cyclohexane medium, thanks to the significant promotional effect of NbO_x on the cleavage of the C–O bond. However, in this catalytic system, only 26.8% yield of 1-octanol was produced with BTHF being the dominant product, though the intermediates (THFA) were quantitatively converted and there was no significant over-hydrogenolysis (entry 4), indicating that the C–O cleavage was constantly active but the selectivity towards 1-octanol formation was inferior. This is also consistent with the strength and quantity of the acidic sites of these two niobium-based catalysts (Fig. 2).

Other noble-metal (Pt, Ru) loaded $NbOPO_4$ was also investigated under the optimized reaction conditions (entries 5 and 6). Only 23.8% yield of 1-octanol was produced over the $Pt/NbOPO_4$ catalyst, with MPTHF being the primary product (31.6%). This was probably due to the very high activity of hydrogenolysis over $Pt/NbOPO_4$ and thus the hydrogenolysis rate of the primary hydroxyl group of THFA was relatively fast, leading to the formation of MPTHF. Surprisingly, only a very little amount of 1-octanol (2.5%) was obtained over Ru/$NbOPO_4$, although the intermediates (THFA) had been completely converted. These completely different results indicate that the metals do not just play a role as hydrogenation catalysts, but also surely have the synergistic effect with the support to influence the selectivity of the final products.

Catalytic performance of Pd/$NbOPO_4$ with different acidic additives

In view of the strong correlation between the 1-octanol yield and the acidity of the catalysts, liquid acids were added into the reaction solution along with the Pd/$NbOPO_4$ catalyst in order to further increase the system acidity. As the products would spontaneously separate from the aqueous solution, adding homogeneous acids to the aqueous solution will not cause any separation problems and the aqueous phase along with the homogeneous acids can be recycled after the reaction. As expected, the yields of 1-octanol and octane were highly related to the acid strength of the liquid acids added (Table 3 and Fig. 3). Indeed, the addition of a superacid, trifluoromethanesulfonic acid (TfOH) gave the highest yield (62.7%) of 1-octanol from one-pot conversion of FFA, although the over-hydrogenolysis of 1-octanol to octane also increased. With strong mineral acids such as H_2SO_4 and HCl as additives, about 55% yield of 1-octanol was obtained, along with about 19% yield of octane. These results indicate that the strong acids could promote the over-hydrogenolysis of 1-octanol at the same time. Interestingly, in the presence of *p*-toluenesulfonic acid (*p*-TSA), 29.8% yield of octane was produced, although *p*-TSA was not the strongest acid. This is probably owing to the molecular structure of *p*-TSA, which has a large organic phenmethyl group and an inorganic sulfonic acid group, that could actually play a role as a biphasic catalyst. The lowest yield (37.7%) of 1-octanol was obtained with a weak acetic acid (HAc) as an additive. These results show that stronger acidity can increase the selectivity to secondary C–O bond cleavage leading to the formation of primary alcohol, which can be attributed to the higher stability of the secondary carbenium ion structure than the primary carbenium ion structure in water. However, stronger acidity would also lead to the increase of over-hydrogenolysis, though not so significant.

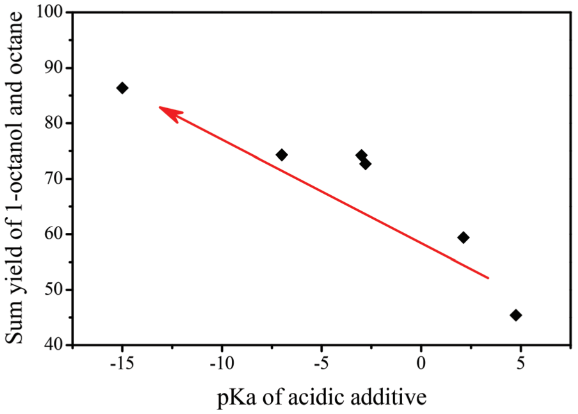


Fig. 3 Correlation between the acid strength of an acidic additive and the sum yield of 1-octanol and octane.

The recyclability of the catalytic system

The recyclability of the catalytic system comprised of the hydrophilic Pd/$NbOPO_4$ catalyst and the acidic additive TfOH was then investigated under the optimal reaction conditions. After each reaction cycle, the products were extracted by cyclohexane and the aqueous phase together with the Pd/$NbOPO_4$ catalyst and the acidic additive was directly used for the next run. TfOH aqueous solution with the same concentration was added to compensate the loss of aqueous solution in the prior run. The product distributions obtained from each cycle are shown in Fig. 4. The conversion of FFA remained 100% and there was no significant change in the product distribution, with only a slight decline in the yield of 1-octanol (from 62.7% to 49.1%) after four successive runs, indicating that the catalytic system was relatively stable and recyclable under the reaction conditions in this work. The ICP analysis of the reaction solution showed that the concentration of Pd was below the detection limit, further confirming the high stability of the catalyst.

Table 3 Reaction results of the one-pot conversion of FFA over Pd/$NbOPO_4$ in the presence of various acidic additives[a]

			Yield [%]				
Entry	Additive	pK_a	Octane	1–Octanol	MPTHF	BTHF	Others
1	H_3PO_4	2.12	8.9	50.5	9.1	27.2	4.3
2	H_2SO_4	−3	18.4	55.8	7.7	13.9	4.2
3	HCl	−7	19.5	54.8	5.5	15.2	5.0
4	HAc	4.76	7.7	37.7	15.1	34.3	5.2
5	*p*-TSA	−2.8	29.8	42.9	2.0	17.9	7.4
6	TfOH	−15	23.7	62.7	2.6	5.5	5.5

[a] Reaction conditions: 0.2 g of FFA, 0.1 g of Pd/$NbOPO_4$, a certain amount of liquid acid (2 mmol of [H] in all cases), and 4 g of water were put into a 50 mL Teflon-lined autoclave. The reaction was hydrogenated at room temperature and 2.5 MPa for 3 h first and then reacted at 190 °C for another 18 h.

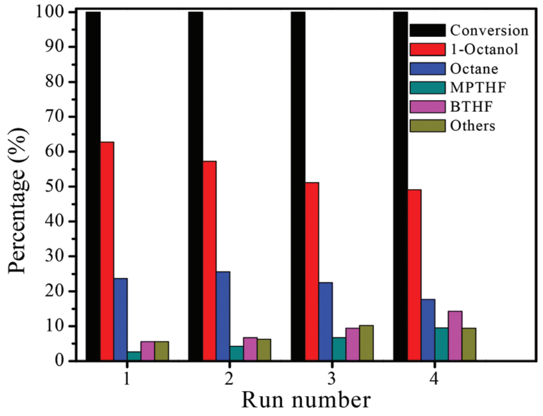


Fig. 4 Reuse of Pd/$NbOPO_4$ together with TfOH for the one-pot production of 1-octanol from FFA. The reaction was hydrogenated at room temperature and 2.5 MPa for 3 h first and then reacted at 190 °C for another 18 h.

Conclusions

In summary, we have demonstrated an energy-efficient catalytic system for the one-pot production of 1-octanol from biomass-derived FFA in water, by sequential hydrogenation/hydrogenolysis using a hydrophilic Pd/$NbOPO_4$ catalyst together with an acidic additive. Up to 62.7% yield of 1-octanol was obtained under the optimal conditions over Pd/$NbOPO_4$ together with TfOH as an acidic additive. The approach of creating an intentional "phase problem" by using a hydrophilic catalyst in water is proved to be able to prevent the over-hydrogenolysis of 1-octanol, as 1-octanol would separate spontaneously from water once generated during the reaction due to their immiscibility, which makes this catalytic system much more energy-efficient for the industrial production. This approach provides a new strategy to enhance the selectivity of the target products by phase separation, for reactions whose reactants are solvent-soluble but target products are solvent-insoluble, particularly for medium- and long-chain primary alcohol production from biomass-derived oxygenates in water.

Acknowledgements

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