

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

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Complete List of Authors:	Xia, Qineng; East China University of Science and Technology, Research Institute of Industrial Catalysis Xia, Yinjiang; East China University of Science and Technology, Research Institute of Industrial Catalysis Xi, Jinxu; East China University of Science and Technology, ; East China University of Science and Technology, Research Institute of Industrial Catalysis Liu, Xiaohui; East China University of Science and Technology, Wang, Yanqin; East China University of Science and Technology, Chemistry



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ARTICLE

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

Qineng Xia, Yinjiang Xia, Jinxu Xi, Xiaohui Liu and Yanqin Wang*

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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/NbOPO₄ 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 acidic additive and sum yield of 1-octanol and octane. With the addition of TfOH, a highest yield of 1-octanol (62.7%) was obtained from one-pot conversion of biomass-derived FFA over Pd/NbOPO₄.

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 resources 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 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}

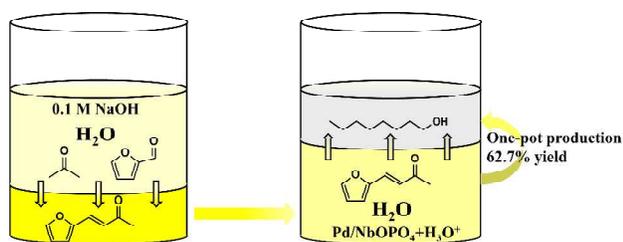
1-Octanol is a particularly attractive industry product widely used in detergents, surfactants and fragrances production as well as chemical synthesis.²⁸ It also serves as an important solvent in biomass conversion.²⁹ Currently, 1-octanol is mainly produced from petroleum-based process.²⁸ Recently, Julis and Leitner³⁰ 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 under 120 °C and 120 bar H₂ 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] under 150 °C and 120 bar H₂ pressure.³⁰ The strategy of synthesis 1-octanol from biomass-derived platforms with 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 catalyst.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 properly modified to prevent 1-octanol finally going to n-octane, the one-pot efficient production of 1-octanol from FFA could be envisaged. In literature, NbOPO₄ has been extensively studied as a water-tolerant solid acid and has been applied in dehydration,^{32–34} hydrolysis^{35,36} and esterification³⁷. It also possesses strong hydrophilic character due to its large metal size.³⁸ Therefore, if water was used as a solvent for the production of 1-octanol from FFA using hydrophilic Pd/NbOPO₄ as 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 water phase once it was generated owing to their immiscibility, while hydrophilic Pd/NbOPO₄ would stay in aqueous phase throughout the reaction, which will separate with 1-octanol.

Key Lab for Advanced Materials, Research Institute of Industrial Catalysis, East China University of Science and Technology, # 130, Meilong Road, Shanghai, 200237, P. R. China. E-mail: wangyanqin@ecust.edu.cn

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Scheme 1 one-pot production of 1-octanol from biomass-derived FFA over Pd/NbOPO₄ in water.

Herein, we describe an energy-efficient catalytic system for the one-pot production of 1-octanol from biomass-derived FFA, using hydrophilic Pd/NbOPO₄ as 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 secondary C-O bond compare to 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, a highest yield of 1-octanol (62.7%) was obtained from one-pot conversion of biomass-derived FFA over a hydrophilic Pd/NbOPO₄ catalyst.

Experimental section

Chemicals

Pt(NO₃)₂·xH₂O and Pd(NO₃)₂·xH₂O were purchased from Heraeus Materials Technology Shanghai Ltd. (Shanghai, China). RuCl₃·3H₂O was purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). γ-Al₂O₃ 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 NbOPO₄ used here was prepared by a hydrothermal method at pH = 2 according to our previous reports³³. M/NbOPO₄ (M = Pt, Pd, Ru) catalysts were prepared by incipient wetness impregnation of NbOPO₄ with aqueous solution of Pt(NO₃)₂, Pd(NO₃)₂, and RuCl₃, 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/NbOPO₄ was reduced at 300 °C under the flow of 10% H₂/Ar mixture gas before use.

Catalyst characterizations

The N₂ adsorption/desorption isotherm of NbOPO₄, X-ray diffraction (XRD) pattern, X-ray photoelectron spectroscopy (XPS) pattern and transmission electron microscopy (TEM) image of Pd/NbOPO₄ are provided in supporting information.

The NH₃-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 N₂ (45 ml·min⁻¹) for 1 h at 500 °C, and then cooled to 50 °C. NH₃ was adsorbed onto the samples by exposure to flowing 10% NH₃ in N₂ gas mixture (50 ml·min⁻¹) for 45 min at 50 °C. Residual and physical adsorbed NH₃ was removed by purging the samples with flowing N₂ (45 ml·min⁻¹) at 90 °C for 1 h. Desorption of NH₃ was performed by heating the samples at a rate of 10 °C·min⁻¹ under flowing N₂ (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/NbOPO₄ and 4 g of water were put into the autoclave. The reaction was hydrogenated at room temperature and 2.5 MPa H₂ pressure for 3h 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 liquid phase were extracted by 4 mL of cyclohexane and both organic phase and aqueous phase were analyzed by GC (Agilent 7890) equipped with an HP-5 column and an FID detector using 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/NbOPO₄ catalyst, and found 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 aqueous phase over Pd/NbOPO₄ to investigate the practicability of 1-octanol production. The catalytic reaction was carried out at room temperature and 2.5MPa for 3h 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 time is shown in Figure 1, and the main reaction pathway according to the reaction time plot is proposed in Scheme 2. For the first 3 h hydrogenated at room temperature, FFA was completely converted to saturated intermediates with 87.1% yield of tetrahydrofurfural alcohol (THFA, 4-(2-tetra-

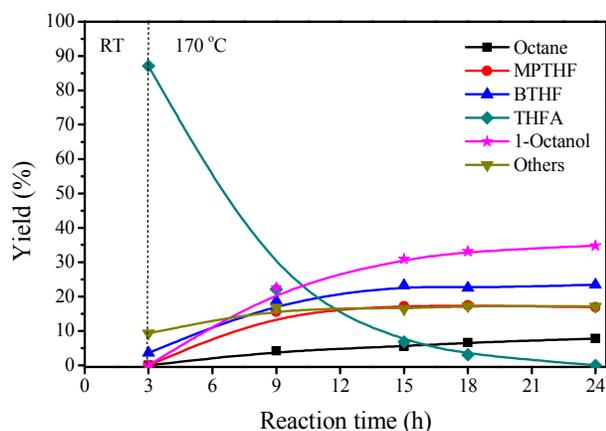
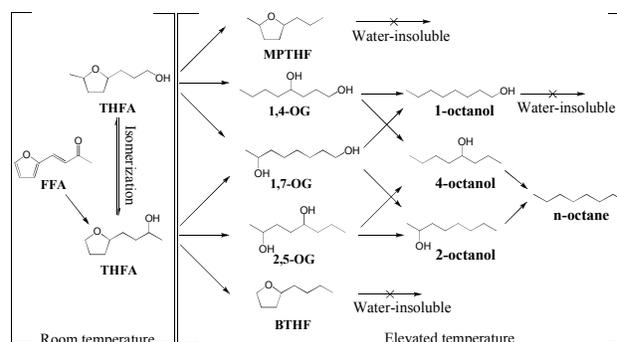


Figure 1 the product distribution of one-pot conversion of FFA at different reaction time. The reaction was hydrogenated at room temperature and 2.5 MPa for 3 h first and then reacted at 170 °C for a certain period of time.

hydrofuryl)-2-butanol and its isomer 3-(5-methyl-2-tetrahydrofuryl)-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 hold 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 amount of other products such as 1,4-octylene glycol (1,4-OG), 1,7-OG, 2,5-OG, 2-octanol, 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 reaction for 18 h, with very little amount of THFA remained. 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, MPTHF were relatively stable in water medium



Scheme 2 Proposed reaction pathway of the one-pot FFA conversion over Pd/NbOPO₄ 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.

under these conditions. It was because 1-octanol, BTHF and MPTHF all separated spontaneously from water, while the hydrophilic catalyst Pd/NbOPO₄ remained in 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 condition but cyclohexane was used as a solvent, revealing that the solvent could impose a significant influence on the product distribution.

Effects of reaction conditions

The effects of reaction temperature and initial H₂ pressure were systematically investigated to optimize the reaction condition and improve the selectivity of 1-octanol. Table 1 shows the product distribution achieved over Pd/NbOPO₄ under different reaction conditions. FFA was hydrogenated at room temperature for 3h 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

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

Entry	T (°C)	P (MPa)	Yield ^[b] [%]					
			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 3h first and then reacted at elevated temperature for another 18 h.

^[b] >99% conversion was observed in all cases. MPTHF, BTHF, THFA are abbreviations for 2-methyl-5-propyltetrahydrofuran, 2-butyltetrahydrofuran, 4-(2-tetrahydrofuryl)-2-butanol. ^[c] “THFA” include 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]

Entry	Catalyst ^[b]	Yield [%]					
		Octane	1-Octanol	MPTHF	BTHF	THFA	Others
1	Pd/NbOPO ₄	10.8	39.9	16.8	23.6	0	8.9
2	Pd/ γ -Al ₂ O 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 ₂ O 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.

an negligible 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 H₂, leading to a faster hydrogenolysis rate.⁴⁰ Comparing to reaction temperature, the H₂ pressure has minor effects on the final product distributions (Entries 4,6,7). However, an increase in the initial H₂ pressure from 2.5 to 6 MPa leads to a slight increase in the yield of octane, indicating that high H₂ pressure favors hydrodeoxygenation.

Catalytic performance of various catalysts

Under the optimized reaction condition, we investigated a series of Pd catalysts with different hydrophilic oxygen-containing supports, namely Pd/NbOPO₄, Pd/ γ -Al₂O₃, Pd/H-Beta and Pd/Nb₂O₅, as their catalytic performance and NH₃-TPD profile of the supports summarized in Table 2 and Figure 2 respectively. The yields of 1-octanol were strongly related to the acid properties of the supports. In contrast to the reaction results over Pd/NbOPO₄ (entry 1), FFA only underwent hydrogenation reaction over Pd/ γ -Al₂O₃, giving rise to 97% yield of hydrogenated intermediates (THFA), without any C-O bond cleavage products (entry 2), owing to the weak acidity of γ -Al₂O₃ 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/NbOPO₄, this is in well accordance with their relative quantity of acid sites (see Figure 2). However, the over-hydrogenolysis over Pd/H-Beta was much more significant with 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/Nb₂O₅ had an outstanding performance for hydrodeoxygenation of FFA in cyclohexane medium, thanks to the significant promotion effect of NbO_x on the cleavage of 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-

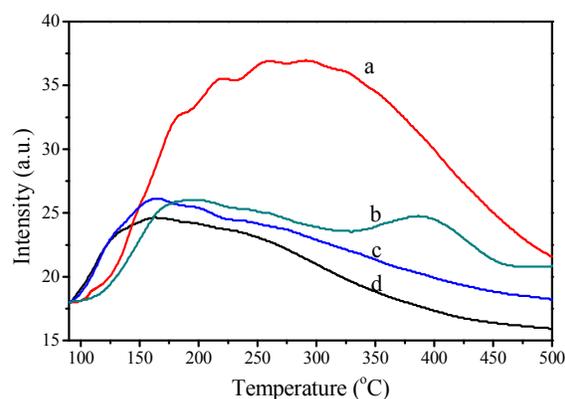


Figure 2 NH₃-TPD profiles of different supports. a) NbOPO₄; b) H-Beta; c) γ -Al₂O₃; d) Nb₂O₅.

hydrogenolysis (entry 4), indicating 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 acid sites of these two niobium-based catalysts (Figure 2).

Other noble-metal (Pt, Ru) loaded NbOPO₄ were also investigated under the optimized reaction condition (entries 5,6). Only 23.8% yield of 1-octanol was produced over Pt/NbOPO₄ catalyst, with MPTHF being the primary product (31.6%). This was probably due to the over high activity of hydrogenolysis over Pt/NbOPO₄ and thus the hydrogenolysis rate of 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/NbOPO₄, although the intermediates (THFA) had been completely converted. These completely different results indicate that the metals were not just play a role as hydrogenation catalysts, but also surely have the synergistic effect with the supports to influence the selectivity of the final products.

Catalytic performance of Pd/NbOPO₄ 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 Pd/NbOPO₄ catalyst in order to

Table 3 Reaction results of the one-pot conversion of FFA over Pd/NbOPO₄ in the presence of various acidic additives.^[a]

Entry	Additive	pKa	Yield ^[b] [%]				
			Octane	1-Octanol	MPTHF	BTHF	Others ^[c]
1	H ₃ PO ₄	2.12	8.9	50.5	9.1	27.2	4.3
2	H ₂ SO 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/NbOPO₄, a certain amount of liquid acid (2 mmol of [H] in all cases), 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 3h first and then reacted at 190 °C for another 18 h.

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 reaction. As expected, the yields of 1-octanol and octane were highly related to the acid strength of the liquid acids added in (Table 3 and Figure 3). Indeed, 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 was also increased. With strong mineral acids H₂SO₄, 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, could actually play a role as a biphasic catalyst. The lowest yield (37.7%) of 1-octanol was got with weak acetic acid (HAc) as 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 secondary car-

benium ion structure than primary carbenium ion structure in water. However, stronger acidity would also lead to the increase of over hydrogenolysis, though not so significant.

The recyclability of the catalytic system

The recyclability of the catalytic system comprised of the hydrophilic Pd/NbOPO₄ catalyst and acidic additive TfOH was then investigated under the optimal reaction condition. After each reaction cycle, the products were extracted by cyclohexane and the aqueous phase together with the Pd/NbOPO₄ catalyst and acidic additive was directly used for the next run. TfOH water 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 Figure 4. The conversion of FFA remained 100% and there was no significant change in the product distribution, with only a slightly 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 condition 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.

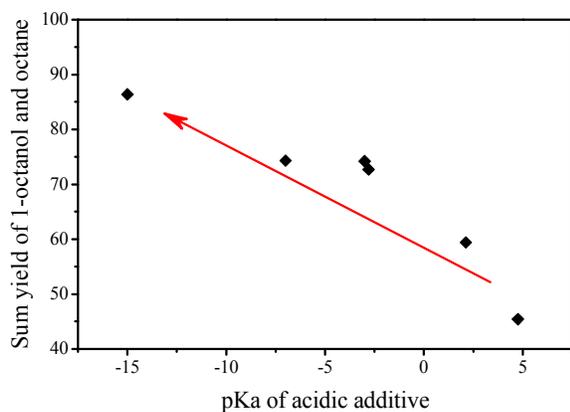


Figure 3 Correlation between the acid strength of acidic additive and sum yield of 1-octanol and octane.

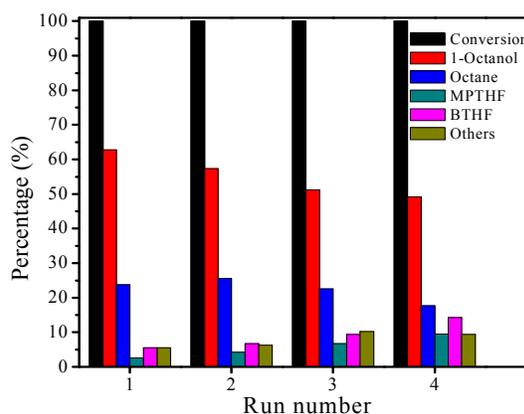


Figure 4 Reuse of Pd/NbOPO₄ together with TfOH for the one-pot production of 1-octanol from FFA. The reaction was hydrogenated at room temperature and 2.5 MPa for 3h first and then reacted at 190 °C for another 18 h.

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/NbOPO₄ catalyst together with an acidic additive. Up to 62.7% yield of 1-octanol was obtained under the optimal condition over Pd/NbOPO₄ together with TfOH as 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 alcohols production from biomass-derived oxygenates in water.

Acknowledgements

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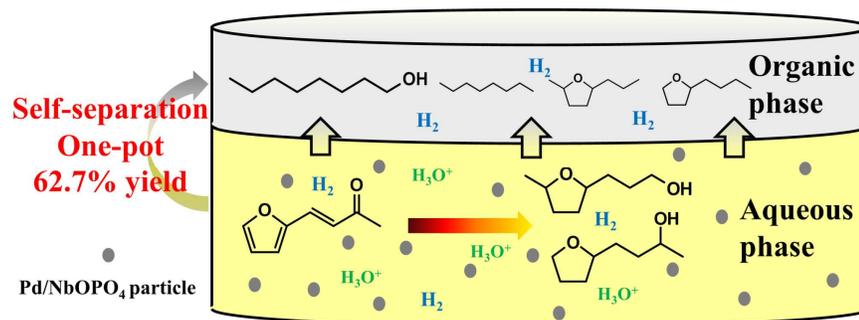
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Energy-efficient production of 1-octanol from biomass-derived furfural-acetone in water

Qineng Xia, Yinjiang Xia, Jinxu Xi, Xiaohui Liu, and Yanqin Wang*



An energy-efficient catalytic system for the one-pot production of 1-octanol from biomass-derived furfural-acetone (FFA) was developed, using a hydrophilic Pd/NbOPO₄ catalyst together with an acidic additive in water, which creating an intentional “phase problem” to prevent the over hydrogenolysis of 1-octanol into n-octane.