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Efficient and selective transformation of biomass-derived furfural with aliphatic alcohols catalyzed by a binary Cu-Ce oxide

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ABSTRACT

The efficient transformation of furfural (FUR) with aliphatic alcohols to achieve the carbon-chain growth has been developed using a binary Cu-Ce oxide as the catalyst. In the presence of molecular oxygen, the tandem oxidative condensation of FUR with *n*-propanol is successfully performed, in which an 85.4% conversion of FUR in 95.3% selectivity of 3-(furan-2-yl-)-2-methylacryaldehyde was obtained. The effects of different Cu/Ce ratios and base additives were investigated in detail. As a result, it is found that the CuO-CeO₂ (1: 9) catalyst is optimal and potassium carbonate is a suitable additive. Next, the recycling of CuO-CeO₂ catalyst was tested and there is no obvious activity loss after being reused five times. Moreover, the oxidative condensation of FUR with various aliphatic alcohols including ethanol, isopropanol, *n*-butanol and *n*-hexanol was studied where the long chain alcoholic molecule hinders the proceeding of reaction. Finally, based on the experimental results and reaction phenomena, a possible mechanism for the oxidative condensation of FUR with *n*-propanol-O₂ is proposed.

1. Introduction

Serious environment problems and the diminishing fossil resources have driven the search for new forms of alternative and renewable energy [1,2]. The efficient use of biomass resources can supply common and sustainable chemical intermediates and liquid fuels [3-5]. Particularly, the selective conversion of a biomass-derived platform compound using a catalytic cascade reaction is beneficial to improve the efficiency and energy consumption in large-scale industrial applications [6]. Furfural (FUR) is one of the most common platform chemicals derived from the lignocellulosic biomass and has an annual production of more than 200,000 tons [7]. FUR can be obtained from C5 carbohydrates and is critical in the valorization of the hemicellulose contained in biomass feedstocks [8]. Numerous studies showed that furfural, as the starting material, could be used to synthesize a variety of commercial products [9], including the hydrogenation, oxidation, reductive amination, decarbonylation, nitration, and condensation reaction of furfural [10]. For example, in the presence of an Au/TiO₂ catalyst with NaCH₃O as the additive, the oxidative esterification of furfural yields high amounts of methyl furoate [11]. Pinna et al. [12-15] found that gold-supported sulfated zirconia was also active for the oxidative esterification, in which the highest conversion of FUR and selectivity of methyl furoate was 94% and 99% under the optimal reaction conditions. In addition, aldol condensation of furfural with acetone was extensively researched because the produced compound is a useful intermediate in the synthesis of the second-generation biofuels [16–20]. Fakhfakh et al. [21] further reported that sodium hydroxide could promote the aldol-condensation reaction of furfural and acetone where the yield of 4-(furan-2-yl)but-3-en-2-one arrived at 50% in ethanol-water solvent. Moreover, Sádaba et al. [22] found that coprecipitated Mg-Zr mixed oxides were an efficient catalyst for the aldol condensation of furfural and acetone. Kikhtyanina et al. [23] reported that a 27% conversion of furfural and a 71% selectivity of 4-(furan-2-yl) but-3-en-2-one were obtained with MOF and zeolite catalysts. Furthermore, Thanh et al. [24] investigated the catalytic performance of nanosized TiO₂ in the aldol condensation, which yielded a 25% conversion of furfural in a 72% of selectivity of 4-(furan-2-yl)but-3-en-2-one as the main product.

Generally, the condensation reaction of furfural and aldehyde can drive two carbon molecules together to produce longer hydrocarbon chains and low volatile liquid transport fuels. Previous reports confirmed that acetone and aldehydes could be produced from the oxidation of secondary and primary alcohols in the presence of molecular oxygen [25]. Therefore, from the standpoint of green and sustainable chemistry, the cascade transformation of alcohol oxidation and aldol condensation in a ternary FUR-alcohol-O₂ (FAO) system may

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be an efficient use of FUR.

In the previous study, our group has reported the oxidative condensation of FUR and aliphatic alcohols in the presence of molecular oxygen using the Au/FH, Pt/FH, and Co_xO_y -N/Kaolin as catalyst [26–29]. In this work, we employ the simple and low cost mixed Cu-Ce oxides as the catalysts to perform the oxidative condensation of FUR with aliphatic alcohols and further hydrogenation reaction. Based on the experimental results, it was found that 85.4% conversion of FUR and 95.3% selectivity to 3-(furan-2-yl)-2-methylacrylaldehyde (1) was obtained in the furfural-*n*-propanol-O₂ (FPO) system in the presence of CuO-CeO₂ and potassium carbonate. Besides, in the catalytic hydrogenation of 1, a 95.8% conversion and 94.7% selectivity of 3-(furan-2-yl)-2-methylpropanol was attained under H₂ atmosphere with similar catalyst system.

2. Experimental sections

2.1. Reagents and instruments

 $(NH_4)_2Ce(NO_3)_{6}$, Cu $(NO_3)_2$ ·3H₂O, Fe $(NO_3)_3$ ·9H₂O, Ni $(NO_3)_2$ ·6H₂O, Zn $(NO_3)_2$ ·6H₂O, and Ca $(NO_3)_2$ ·4H₂O were of analytical grade and purchased from the Aladdin Reagent Co., Ltd. (Shanghai, China). The 3-(furan-2-yl-)-2-methylacryaldehyde as the standard sample was obtained from Alfa Aesar, Thermo Fisher Scientific, Inc. (Ward Hill, MA, U.S.A.). Methanol, ethanol, *n*-propanol, isopropanol, *n*-propanal, *n*-butanol, *n*-hexane, *n*-octane and other solvents were purified by distillation before use. All other chemicals were used without further purification.

The measurement of X-ray diffraction (XRD) was performed by diffractometer with Cu Ka radiation (0.02° resolution) and was collected from 20 to 80° [20]. BET surface areas, pore volumes, and average pore diameters of the prepared samples are obtained from N₂ (77 K) adsorption measurement using a Micromeritics ASAP2020 M system, in which the samples are pretreated under vacuum at 250 °C for 4 h before the measurement. The average pore diameters are calculated according to Barrett-Joyner-Halenda (BJH) model to absorption and desorption data. Scanning electron microscopy (SEM) was used by a JSM-6301F, JEOL to obtain the surface morphology of the catalytic materials. A transmission electron microscope (TEM: JEM-2100, JEOL) was also used to characterize the catalyst. The solid catalyst was analysed by temperature programmed desorption (TPD) using a Micromeritics 2920 Autochem II Chemisorption Analyzer. The samples were first pretreated at 500 °C for 1 h in the presence of Ar with a flow rate of 25 mLmin^{-1} , then cooled to room temperature and ammonia was absorbed with a flow rate of about 25 mLmin^{-1} . During the TPD experiments, the temperature was set at a heating rate of 10 °C - min rising to 900 °C in the presence of He with a flow rate of 60ml-min. Effluent gas was dried by powdered KOH, and the concentrations of ammonia were recorded by a thermal conductivity detector.

The quantitative analyses of the products are performed on a GC apparatus with FID detector. The capillary column is HP-5, 30 m \times 0.25 mm \times 1.0 µm. In addition, the qualitative analysis for the product is carried out on the Agilent 6890/5973 Gas Chromatograph-Mass Spectrometer (GC–MS) instrument.

2.2. The preparation of catalyst

The CuO-CeO₂ catalyst was prepared as follows. The aqueous

solution was mixed with copper nitrate and $(NH_4)_2Ce(NO_3)_3$ (1:9) by dissolving 1 mmol of $Cu(NO_3)_2$; $3H_2O$ and 9 mmol of $(NH_4)_2Ce(NO_3)_3$ in 30 mL de-ionized water. Then, 2 g of urea were added into the solution and the mixture was heated to 100 °C in oil bath pot with vigorous stirring for 8 h. A dark brown precipitate was obtained, separated by filtration and washed with of de-ionized water at 70 °C. The cake was dried in a vacuum oven at 100 °C over night. After grinding the solid precursor to powder, the material was calcined in a muffle furnace at 650 °C for 4 h in air. The final powder was designated as the CuO-CeO₂ catalyst and characterized by XRD, SEM, TEM, and NH₃-TPD techniques. The surface area and pore structure of catalyst are detected by BET method. In addition, Fe₂O₃-CeO₂, NiO-CeO₂, CaO-CeO₂, and ZnO-CeO₂catalysts were synthesized for comparison using the same method.

The characterizations of catalysts including XRD patterns, BET detection, TEM images and TPD measurement were presented in the supporting information, respectively.

2.3. General procedure for the oxidative condensation of furfural and aliphatic alcohols

In a typical oxidative condensation-hydrogenation reaction of furfural with *n*-pronanol, 15 mL solution of *n*-propanol is thoroughly mixed with 0.05 g CuO-CeO₂ catalyst, 0.05 g K₂CO₃, and 0.2 g furfural. The mixture was charged into a 120 mL autoclave equipped with the magnetic stirring and automatic temperature control. After reactor is sealed, the solution was then stirred for 4 h at 140 °C under 0.3 MPa of O₂ for the oxidative condensation process. After the reaction, the autoclave was cooled to room temperature and a certain amount of solution was diluted with CH₃CN solvent and analyzed by GC and GC–MS after the excess gas is purged.

3. Results and discussion

3.1. The oxidative condensation of furfural with n-propanol using different catalytic systems

To investigate the activities of different catalysts, a series of catalysts were used in the FPO system where the reaction process is shown in Scheme 1. As shown in Table 1, five types of metal (Cu, Ni, Fe, Ca, and Zn) supported on cerium oxide were tested under the same experimental conditions. In the presence of CuO-CeO₂ catalyst, 85.4% conversion of FUR and 95.3% selectivity of 1 were obtained when K₂CO₃ was used as the additive (entry 1). However, the conversion of FUR fell to 58.2%, 44.1%, 30.9%, 22.6% and the selectivity of 1 was 60.9%, 73.7%, 55.1%, 62.8%, respectively, when Fe₂O₃-CeO₂, NiO-CeO₂, CaO-CeO₂, and ZnO-CeO₂ catalysts were employed instead of the CuO-CeO2 catalyst. Based on the above experimental results, it is concluded that copper oxide plays a crucial role on the oxidative condensation of FUR with n-propanol in the presence of molecular oxygen which leads to the CuO-CeO₂ exhibiting a higher catalytic activity than other mixed oxides. Furthermore, when a single CuO or CeO₂ was used as the catalyst (entries 6 and 7), the conversion of FUR was decreased to 47.8% or 48.2%, and the selectivity of 1 was 89.5% or 57.9%, respectively. In addition, in the presence of physically-mixed CuO and CeO₂, the conversion of FUR and selectivity of 1 were respectively 51.2% and 74.5% under similar reaction conditions. Therefore, the cooperation effect between copper oxide and cerium oxide favored the tandem oxidative condensation reaction in FPO



Scheme 1. The reaction of FUR with *n*-propanol in the presence of oxygen.

Table 1

Oxidative condensation of FUR with *n*-propanol-O₂ using different catalytic systems.^a

Entry	Catalytic system	Conversion (%) ^b	Product distribution (%) ^b		
_			1	2	Others ^c
1	$CuO-CeO_2 + K_2CO_3$	85.4	95.3	4.7	-
2	Fe_2O_3 - $CeO_2 + K_2CO_3$	58.2	60.9	8.5	30.5
3	$NiO-CeO_2 + K_2CO_3$	44.1	73.7	13.2	13.1
4	$CaO-CeO_2 + K_2CO_3$	30.9	55.1	17.2	27.7
5	$ZnO-CeO_2 + K_2CO_3$	22.6	62.8	18.9	18.3
6	$CuO + K_2CO_3$	47.8	89.5	10.5	0
7	$CeO_2 + K_2CO_3$	48.2	57.9	32.1	10.0
8	CuO	51.2	74.5	8.5	17.0
	$+ \text{CeO}_2 + \text{K}_2\text{CO}_3$				
9	CuO-CeO ₂	25.0	2.1	16.1	81.8 ^d
10	K ₂ CO ₃	8.7	98.3	1.7	-

system. In addition, it needs to be mentioned that the selectivity of **1** could be improved with the participation of copper oxide on the catalytic reaction. In order to reveal the action of K_2CO_3 , the control experiments were performed using only CuO-CeO₂ or K_2CO_3 as promoter. As a result, it is found that a mere 25.0% conversion of FUR and 2.1% selectivity of **1** was obtained in the absence of K_2CO_3 (entry 9); meanwhile, only 8.7% conversion of FUR and 98.3% selectivity of **1** was acquired in the absence of CuO-CeO₂ catalyst (entry 10).

According to the results of GC–MS, the main by-product is compound **2**, furfuryl alcohol and 2- (dipropoxymethyl)furan where the compound **2** is obtianed from the oxidative esterification route. While, the furfuryl alcohol is generated *via* the reduction of FUR by *n*propanol, and the 2- (dipropoxymethyl)furan is produced *via* the acetalization of FUR with *n*-propanol in the absence of K_2CO_3 . These data showed that both the CuO-CeO₂ and K_2CO_3 are necessary to the proceeding of this tandem reaction. Moreover, based on catalytic data of Table 1 and characterization of different catalysts, it can be concluded that the conversion of FUR is mainly attributed to the component of mixed oxide catalyst; while, the selectivity of compound 1 should be closely related to the surface area and amount of weak acid sites of those catalysts.

3.2. The effect of different Cu/Ce ratios on the oxidative condensation

The effects of different ratios on the oxidative condensation of FUR with *n*-propanol-O₂ was investigated. As shown in Table 2, it is found that the catalytic activity of CuO-CeO₂ was gradually decreased along with the elevation of the amount of CuO component in mixed oxides. Therein, a 70.5% and 67.6% conversion of FUR was respectively obtained when CuO-CeO₂ (1:3) and CuO-CeO₂ (1:1) was employed as catalyst. Especially, in case of CuO-CeO₂ (9:1) catalyst, only 49.8% conversion of FUR in 91.2% selectivity of 1 was attained, which is near to that of using pure CuO as the catalyst (entry 6 in Table 1).

 Table 2

 The effect of different ratios of Cu and Ce on the oxidative condensation with CuO-CeO2.

Entry	Catalyst	Conversion (%) ^b	Product distribution (%) $^{\rm b}$		
			1	2	
1	CuO-CeO ₂ (1:9)	85.4	95.3	4.7	
2	CuO-CeO ₂ (1:3)	70.5	88.1	11.9	
3	CuO-CeO ₂ (1:1)	67.6	91.5	8.5	
4	CuO-CeO ₂ (3:1)	63.2	89.2	10.8	
5	CuO-CeO ₂ (9:1)	49.8	91.2	9.8	

 a Reaction conditions: 0.2 g of FUR, CuO-CeO_2 catalyst 0.05 g and 0.05 g K_2CO_3 in 15 mL $n\mbox{-}propanol,$ under 0.3 MPa of O_2, at 140 $^\circ$ C for 4 h.

^b The result was obtained using GC with the internal standard technique where 1, 3dichlorobenzene is chosen as the internal standard.

In order to further reveal the nature of copper oxide and cerium oxide in CuO-CeO2 catalyst, the catalyst including different Cu/Ce ratios was characterized by different techniques. The SEM images of CeO₂, CuO-CeO₂ (1:9), CuO-CeO₂ (1:1), CuO-CeO₂ (9:1) and CuO were shown in Fig. 1. It is found that the pure CeO_2 material appears as the loose and even nanobulk (Fig. 1a), while pure CuO material is the flower-like spherical composed of numerous tight nanoflake parts (Fig. 1e). Moreover, along with the increase of the amount of CuO. the surface morphology of CuO-CeO₂ was also gradually changed. Therein, the morphology of $CuO-CeO_2$ (1:9) is very similar with that of CeO₂, and a few CuO supports on the surface of CeO₂; while, the morphology of CuO-CeO₂ (9:1) is so much like that of CuO, and few CeO₂ should be doped on the nanoflake CuO material. Correspondingly, the difference of morphology leads to the distinction of BET surface, in which the BET surface of CuO, CeO2 and CuO-CeO2 (1:9) is 4.3, 27.4 and 46.4 $m^2 g^{-1}$, respectively (shown in supporting information).

3.3. The effect of various additives on the oxidative condensation

Considering the importance of K₂CO₃ as the additive in the reaction, the effects of different basic additives including carbonates, hydroxides, and ammonium salts were further investigated. The results are shown in Table 3. It can be seen that, when Na₂CO₃ or Cs₂CO₃ were used as additive, the conversion of FUR was 25.0% or 50.8%, and the selectivity of 1 was 85.6% or 88.5%, respectively (entries 1 and 2). Otherwise, with NaOH as the basic additive, a 95.0% conversion of FUR in a 72.3% selectivity of 1 was attained in the presence of CuO-CeO₂ catalyst (entry 3), in which the decrease of selectivity can be attributed to the strong basicity of NaOH leading to the occurrence of more sidereactions. Furthermore, when K3PO4 or Na2SiO3 was employed as additive, only 28.6% and 15.8% conversion of FUR was obtained where the selectivity of 1 was 95.3% and 79.3%, respectively (entries 4 and 5). On the other hand, a large amount of the Schiff bases were produced when ammonium salts were used as the additives in this reaction system (entries 6 and 7). In addition, seen from the data displayed in Table 3, it is found that the strong basic additives are more efficient than weak basic ones during the oxidative condensation of FUR with *n*-propanol. However, the suitable basicity is more selective for the generation of compound 1; meanwhile, the existence of carbonate or phosphate ions is also helpful to the increase of selectivity. Consequently, K₂CO₃ was considered as the best basic additive in the FPO system, not only because of its promotion effect of the CuO-CeO₂ catalyst, but also because it is environmentally friendly and cost effective.

In the following, the effects of reaction time and reaction temperature have been also studied for the oxidative condensation of FUR with *n*-propanol (the data are shown in supporting information). As a result, the optimal temperature is 140 °C and the suitable reaction time is 4 h.

3.4. The investigation on the recycling of catalyst

The recycling experiment was carried out to investigate the stability and reuse of CuO-CeO₂ catalyst. After the catalytic reaction, the catalyst was separated, and washed with anhydrous ethanol, and then dried at 80 °C for 12 h before being reused in the next run. As shown in Fig. 2, the conversion of FUR still kept *ca*. 80% and the selectivity of **1** was as high as 92% even after the CuO-CeO₂ catalyst being recycled five times. These results showed that the CuO-CeO₂ catalyst was efficient and kept stable in FPO system, which indicates that this oxidative condensation is the heterogeneous catalytic process.

3.5. The oxidative condensation reactions of FUR with various aliphatic alcohols

In the following experiments, various alcohols were used to study the oxidative condensation reaction of FUR in the presence of dioxygen.

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Fig. 1. SEM images of different catalysts [a. CeO2; b-CuO-CeO2 (1:9); c. CuO-CeO2 (1:1); d. CuO-CeO2 (9:1); e. CuO].

Table 3
Effects of various additives on the oxidative condensation of FUR with <i>n</i> -propanol. ^a

entry	additive	Conversion (%) ^b	Production distribution (%) $^{\rm b}$			
			1	2	Others ^c	
1	Na ₂ CO ₃	25.0	85.6	14.4	-	
2	Cs ₂ CO ₃	50.8	88.5	11.5	-	
3	NaOH	95.0	72.3	3.7	24.0	
4	K ₃ PO ₄	28.6	95.3	4.7	-	
5	Na ₂ SiO ₃	15.8	79.3	20.7	-	
6	C_2H_7N	24.9	9.8	-	90.2 ^d	
7	$C_4H_{11}N$	8.7	8.2	-	91.8 ^c	

 a Reaction conditions: 0.2 g of FUR, CuO-CeO_2 catalyst 0.05 g and 0.05 g additive in 15 mL n propanol, under 0.3 MPa of O_2, at 140 $^\circ$ C for 4 h.

^b The result was obtained using GC with the internal standard technique where 1, 3dichlorobenzene is chosen as the internal standard.

^c The selectivity of others is generally referred to the selectivity of furfuryl alcohol.

 $^{\rm d}$ The main product is the corresponding Schiff base in the reaction system.



Fig. 2. The recycling of the CuO-CeO₂ catalyst in the FPO system.

As shown in Fig. 3, an 83.2% conversion of FUR and 92.1% selectivity of 1 were obtained in ethanol, which trended similar to that in the *n*-propanol. Otherwise, when isopropanol was used as reaction medium, the conversion of and the selectivity of 4-(furan-2-yl)but-3-en-2-one are respectively 20.3% and 52.1% in the oxidative condensation, which is probably result of the steric hindrance during the catalytic reaction. Moreover, the yield of the desired product from oxidative condensation is decreased when the carbon chain length in alcoholic molecule is increased. Therein, only 32.2% or 34.3% conversion of FUR was attained when *n*-butanol or *n*-hexanol was used in FAO system, which can be attributed to the slow rate of hydrogen transferring between FUR and long chain alcoholic molecule.



Fig. 3. The oxidative condensation of FUR with various aliphatic alcohols using CuO-CeO₂ + K₂CO₃ catalytic system. [Reaction conditions: 0.2 g of FUR, 0.05 g CuO-CeO₂ catalyst and 0.05 g K₂CO₃ in 15 mL alcohol, under 0.3 MPa of O₂, at 140 °C for 4 h; Compound **X** is the product from the oxidative condensation process that can be 3-(furan-2-yl-)-2-R-acrylaldehyde (R = H, methyl, ethyl and butyl) or 4-(furan-2-yl)but-3-en-2-one].

Table 4

The results of control experiments for studying the catalytic reaction mechanism.^a

Entry	Catalyst	Reactants	Conversion (%) ^b	Selectivity (%) ^b		
				1	2	Others ^c
1	CuO- $CeO_2 + K_2CO_3$	FUR + n- propanal	93.2	46.4	-	53.6
2	CuO-CeO ₂	FUR + n- propanal	18.2	91.7	-	8.3
3	K ₂ CO ₃	FUR + n- propanal	92.3	45.1	-	54.9
4 ^d	CuO- $CeO_2 + K_2CO_3$	FUR + n- propanol	26.9	45.6	4.20	50.2
5 ^d	CuO-CeO ₂	FUR + n- propanol	21.2	1.7	-	98.3 ^e
6	CuO- $CeO_2 + K_2CO_3$	FUR + n- propanol ^f	42.2	8.5	-	91.5
7	$CuO-CeO_2 + K_2CO_3$	FUR + n- propanal ^f	89.5	98.3	1.7	-

 a Reaction conditions: 0.2 g of FUR, CuO-CeO_2 catalyst 0.05 g and 0.05 g K_2CO_3 in 15 mL n-propanol or propanal, under 0.3 MPa of O_2, at 140 $^\circ C$ for 4 h.

^b The results were obtained by GC with the internal standard technique where 1, 3dichlorobenzene is chosen as the internal standard.

^c The selectivity of others is generally referred to the selectivity of furfuryl alcohol.

^d The reaction was performed under a N₂ atmosphere.

e This datum is the selectivity of 2-(dipropoxymethyl) furan.

^f The ratio of FUR to *n*-propanol (or *n*-propanal) is 10: 1 (mol: mol), and the value of conversion refers to that of *n*-propanol or *n*-propanal.

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Scheme 2. Possible reaction mechanism for oxidative condensation in FPO system.

3.6. The reaction mechanism for the oxidative condensation of FUR with npropanol

The results of control experiments are provided in Table 4. The interaction of FUR and n-propanal was first detected where numerous products were obtained from different processes including FUR-propanal condensation, n-propanal self condensation and FUR-FUR disproportionation process, etc. Therefore, only 46.4% selectivity of 1 was got although the conversion of FUR arrived at 93.2%. Furthermore, an 18.2% conversion and 97.1% selectivity for 1 was obtained in the presence of single CuO-CeO2, and a 92.3% conversion in 45.1% selectivity of 1 was attained in the presence of K₂CO₃. In addition, a 26.9% conversion and 45.6% selectivity of 1 was obtained using CuO-CeO₂ and K₂CO₃ as catalyst in FPO system under N₂ atmosphere. It should be noted that, in the obtained products, furfuryl alcohol selectivity reaches 50.2% which exhibits that the hydrogen transferring occurs between FUR and *n*-propanol. These results show that CuO-CeO₂ and K₂CO₃ both contributed to the hydrogen transfer between FUR and n-propanol. However, the acetalization process is dominant in FPO system under N₂ atmosphere when only CuO-CeO₂ was employed. These confirm that K₂CO₃ should act as weak bases in the reaction involving proton extraction. Besides, the reaction of FUR with npropanol or *n*-propanal in the ratio of 10: 1 was performed, in which a 42.2% conversion of n-propanol and very little 1 was acquired in FPO system; however, the conversion of *n*-propanal and selectivity of 1 still arrived at 89.5% and 98.3% under the similar conditions, respectively. This shows that highly selective production of 1 can be achieved when the reaction is carried out between a large number of FUR and little npropanal.

From the above results of the control experiments, we presented the possible mechanism for the oxidative condensation process (Scheme 2). The hydrogen transfer process occurs between FUR and *n*-propanol where a little propanal and furfuryl alcohol are generated with assistance of K₂CO₃ component. Next, the condensation is performed between the left FUR and the propanal. Therein, the furfuryl alcohol can be oxidized to FUR in the presence of molecular oxygen with the solid CuO-CeO₂ catalyst. Meanwhile, there could be another catalytic route in this mixed system; firstly, a little n-propanol was first oxidized by molecular oxygen to produce little propanal; in the following, the rapid condensation process happens between FUR and the in situ generated propanal in the solution. Therefore, in the oxidative condensation reaction, the CuO-CeO2 catalyst is responsible for the catalytic selective oxidation of n-propanol and furfuryl alcohol. While, the role of K_2CO_3 should be impelling the hydrogen transferring between FUR and n-propanol and promoting the condensation process to generate compound 1.

4. Conclusions

In summary, a highly efficient and selective oxidative condensation furfural with aliphatic alcohols and further hydrogenation has been achieved in the presence of CuO-CeO₂ catalyst. In the oxidative condensation reaction, an 85.4% conversion of FUR and 95.3% selectivity of **1** was obtained when CuO-CeO₂ and K₂CO₃ was employed as the catalysts. The optimal reaction time and temperature was are 4 h and 140 °C. The activity of catalyst has no obvious loss after being recycled five times. This will provide a promising approach for efficient valorization of biomass-derived hemicelluloses in biomass transformation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2017.04.057.

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