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Molecular Catalysis

Selective carbon-chain increasing of renewable furfural utilizing oxidative condensation reaction catalyzed by mono-dispersed palladium oxide



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ARTICLE INFO	A B S T R A C T
Keywords:	A novel carbon-chain increasing valorization of furfural (FUR), a cheap bio-based platform compound, has been
Oxidation	successfully performed via the catalytic oxidative condensation process with mono-dispersed palladium oxide
Furfural	catalyst. For the reaction of furfural, n-propanol and O_2 , the PdO@TiO ₂ exhibited a prominent catalytic activity
Molecular oxygen Palladium	in which a 77.8% conversion of FUR with 89.2% selectivity of 3-(furan-2-yl)-2-methylacrylaldehyde was ob-
Biomass transformation	tained. Based on the XRD, SEM, TEM, HRTEM, XPS, and UV-vis results of catalysts, it was concluded that high
	activity is associated with particle size, uniform distribution of palladium oxide and surface area of the support.
	Moreover, the recycling experiments confirmed that mono-dispersed palladium oxide catalyst was stable, in
	which it still kept a good catalytic performance after being recycled for five times. This provided a new route for

the selective transformation of the hemicellulose-derived platform compounds.

1. Introduction

The excessive development and utilization of fossil energy have caused more and more worldwide problems, such as environmental pollution and the greenhouse effect [1,2]. Thus, exploring a new, green, low-carbon, and recycling energy has gradually become the hot topic on the present chemical industry and engineering research. In all renewable energy substitutes, biomass feedstock has attracted extensive attention from researchers because of its nature of renewable, clean, abundant and sustainable application [3–5]. Therein, a feasible technology to resolve the energy problem is the efficient conversion of biomass feedstocks to the fine chemicals and the high-quality fuels through the catalytic processes.

Furfual (FUR), derived from the hemicelluose of lignocellulose, is a very important bio-based platform compound that can be converted to numerous valuable chemicals by catalytic reduction [6,7], oxidative transformation [8–10], decarboxylation [11] acetalization [12,13] or aldol condensation [14–16], *etc.* For example, Taarning's research group found that the oxidative esterification of FUR was achieved in methanol using the Au/TiO₂ as the solid catalyst, and a 99% yield of methyl fuorate was acquired under the optimized conditions [8]. Gupta et al. [9] conducted aerobic oxidation of FUR to furoic acid using an *N*-heterocyclic carbene as a homogeneous catalyst and obtained a 99% product yield at 40 °C in dimethyl sulfoxide for 4 h. Choudhary's group

[10] performed FUR oxidation in aqueous media with H_2O_2 as terminal oxidant, and a 74.2% yield of succinic acid was obtained at 80 °C. In addition, aldol condensation of FUR and ketones was also studied widely to produce the value-added compounds as the feedstock of biofuel, in which the basic sodium hydroxide [17] and Mg-Zr mixed oxides [18] are often employed as the catalysts.

Furthermore, FUR can also be used to synthesize the carbon-chain growing products by carrying out the oxidative condensation with aliphatic alcohol, which is a very important approach to prepare high quality aviation kerosene [19,20]. During the oxidative condensation, generally used catalysts are Au, Pt, Co, Fe and Cu metals [21-27]. For example, using Au/FH as the catalyst, the condensation reaction of FUR with n-propanol was performed successfully, in which ca. 91.2% yield of main product 3-(furan-2-yl-)-2-methylacrylaldehyde was attained [21]. Moreover, in the FUR-ethanol-O₂ system, a more than 63.7% yield of the target product furan-2-acrolein could be obtained with the Pt/FH as catalyst under the suitable conditions [22]. Besides, it was also presented that metallic Co-based catalyst derived from a two dimensional metal-organic framework could effectively promote selective transformation of FUR with n-propanol under the oxygen atmosphere. Correspondingly, a near to 85.0% yield of 3-(furan-2-yl-)-2-methylacryl aldehyde was acquired [23]. In particular, our group found a novel versatile catalyst of iron, which offered a 70% yield of the main product furan-2-acrolein during the oxidation-condensation reaction of FUR,

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ethanol and molecular oxygen [27]. Although the precious metal catalysts have showed excellent catalytic performance, the less reserve, high price and agglomeration effect under harsh conditions hinder the development and spreading of noble metal catalysts. In particular, most noble metal catalysts usually have high metal loading which may increase the cost and cause aggregation of the particles. Thus, a lot of effort has been made to design and to develop of novel noble catalysts by researchers with improved atomic utilization. Mono-dispersed catalyst, with the atomic utilization of up to 100%, is considered to be a promising catalyst to meet the requirement [28–31].

In this work, a novel PdO@TiO₂ nanomaterial was fabricated, by a facile method, and pioneered application of the catalyst to promote the tandem oxidative condensation of FUR with aliphatic alcohol. Herein, homogenous Pd nanoparticles were evenly anchored on the special 2D TiO₂ support by a simple photochemical reduction method. As a result, the high conversion of FUR and high selectivity of target product were acquired in the reaction of FUR with n-propanol-O₂ with Pd-based catalysts. Moreover, the catalytic reaction mechanism is proposed according to the control experiment results in which Pd(II) species play a crucial role in the catalytic reaction.

2. Experimental

2.1. Reagents and equipment

All reagents and chemicals used were of analytical grade unless otherwise specified. Palladium chloride (PdCl₂, 59.5%) was purchased from Energy Chemical (Shanghai, China), Titanium tetrachloride (TiCl₄), CeO₂, gama-Al₂O₃, Pd/C, ammonia water, ethylene glycol (EG) and absolute ethanol was purchased from Aladdin Chemistry Co. Itd. (Shanghai, China). Deionized water was used from commercial during this study.

The morphology and particle size of catalytic materials were respectively detected by SEM and TEM instruments. In addition, the XRD patterns were carried out using a Rigaku D/max-IIIA diffractometer (Cu-K α , $\lambda = 1.54056$ Å). The IR spectrum was characterized with a Bruker Vertex-70 Spectrometer. The UV-vis spectrum was investigated with Hitachi-3900 UV-vis Spectrophotometer. For the characterization of surface acidity of catalysts, the NH3-TPD technique was also performed. The as-prepared samples were treated at 650 °C for 1 h, and purged with NH₃ gas to saturation and kept at 50 °C for 1 h, and then streamed with Ar for 0.5 h at 120 °C before being cooled to room temperature, and then warmed up to 800 °C with the temperature control program (10 °C /min). The pore structures of catalytic materials were tested by the Micromeritics ASAP2020 M system. Next, the TG results were recorded from 40 °C up to 800 °C with a 10 °C/min heating rate. The oxidation states of Pd in the catalysts were studied by XPS technique. The UV treatment of the catalysts were performed using a Xenon-lamp light source with filter at 365 nm, in which a power density of about 1.94 mW/cm² was used. The quantitative analysis of the products was performed on a Gas Chromatography (GC) with a hydrogen ion flame detector. The molecular structures of products were determined with gas chromatography and mass spectrometry (Agilent 7890/5975C) apparatus.

2.2. Synthetic procedure of different catalytic materials

2.2.1. The preparation of ultrathin TiO_2 nanosheet

The general preparation route of TiO_2 nanosheet is as follows: about 1 mL of $TiCl_4$ solution was slowly added into 30 mL EG, and then the mixture was placed at room temperature for more than 2 h to verify the release of HCl gas; next, 1 mL deionized water (~18 M Ω cm) was appended to the mixture under stirring. The obtained colorless solution was transferred into the stainless-steel autoclave for further hydro-thermal treatment for 6 h at 150 °C. After being cooled to the room temperature, the solid products were attained through the

centrifugation. Finally, the product was dried in a vacuum oven.

2.2.2. Preparation of palladium oxide supported catalysts

The above TiO_2 nanosheet (17.4 mg) was added to a certain amount of water, and then $0.5 \text{ mL } \text{H}_2\text{PdCl}_4$ solution (5 mM, 2.5 µmol Pd) was added with a magnetic stirring. The mixture was then treated under the UV light (365 nm wavelength) for 5 min. After that, the obtained grey catalytic material was further washed by the diluted water. Therein, the product was collected after the release of Cl⁻ was confirmed (The amount of Cl⁻ ions was measured by the Mohr titration method which uses chromate ions as an indicator, which is provided in the supporting information). After being dried on vacuum, the powder was grinded and named as Pd@TiO_2. Then, the solid was further calcined in air at 350 °C for 2 h, and named as PdO@TiO_2 catalyst.

The light yellow PdO@TiO₂ powder was further treated in a stream of H₂ (flowing rate: 10 mL/min) at 120 °C for 2 h. The product was named as r-Pd@TiO₂.

As comparison, the n-TiO₂ material was firstly prepared by simple ammonia precipitation method from TiCl₄. In the following, using n-TiO₂ as the solid support, the PdO/n-TiO₂ catalyst was prepared by reduction loading method, which is similar with above UV treatment on the PdO@TiO₂ synthesis.

2.2.3. General conditions for oxidative condensation of FUR with alcohol

The selective transformation of FUR with alcohol was carried out in the stainless steel reactor. A general testing procedure is presented as follows: 0.200 g of FUR, 0.050 g of PdO@TiO₂ catalyst, 0.050 g of K₂CO₃ and 15 mL of n-propanol were added to a 120 mL autoclave. The atmosphere in the reactor was exchanged by pure oxygen for three times, and then the autoclave was sealed. Before the heating, the pressure of oxygen was controlled to 0.3 MPa for the oxidation process. Next, the temperature was raised to 140 °C, and the time was 4 h. After the oxidative condensation, the mixture was slowly cooled and the excessive gas was discharged. Finally, the solid PdO@TiO₂ catalyst was separated, and the products were detected by gas chromatography - mass spectrometry (GC–MS) instrument.

3. Results and discussion

3.1. Physical properties of catalytic materials

The formation and crystalline structure of the product was confirmed by XRD. As shown in Fig. 1, the diffraction peaks at the 20 values of 14.38°, 24.86°, 27.72°, and 48.31° can be attributed to (001), (110), (002), and (020) facets of TiO₂ phase with the PDF card No. 74-1940, which is consistent with the literature reported.²¹ The diffraction peak at around 7.2° can be attributed to the 2D layered structure of TiO₂



Fig. 1. XRD patterns of different catalytic materials.



Fig. 2. SEM images of TiO₂ (a), the TiO₂-calcined (b), Pd@TiO₂ (c, d) and PdO@TiO₂ (e, f).

nanosheet.²⁸ While, after being calcinated at 350 °C for 2 h, the diffraction peak at around 7.2° disappears which indicates a structure change of TiO₂ nanosheets to the aggregates of TiO₂ nanoparticles. Besides, it is noticeable that after calcination the intensity of the diffraction peaks of PdO@TiO₂ and TiO₂ are increased, which indicates that the crystallinity elevates by heating. Moreover, the diffraction peaks of mono-metallic Pd nanoparticles cannot be seen from the XRD images, which could also confirm the possibility of the existence of mono-dispersed palladium.

The morphologies of catalytic materials have been characterized by SEM and TEM techniques. It was shown from Fig. 2a and b that TiO_2 shows the regularly flower-like nanospheres, in which thickness of the surrounding curved flake was about several nanometers. In addition, it can be seen that there exist numerous pores on the surface of TiO_2 nanosheets, in which the well-distributed pores are helpful to the adsorption of small molecules. After the anchor of mono-metallic Pd, the

morphology of Pd@TiO₂ shows a little change with some aggregation of TiO₂ nanospheres (Fig. 2c and d). Then, after being calcinated in air at 350 °C for 2 h, the morphology of the following product PdO@TiO₂ shows more aggregation. The flower like nanospheres that assembled by TiO₂ nanosheets disappear. TiO₂ shows microsphere morphology which is assembled by lots of nanoparticles (Fig. 2e and f).

The transformation of the TiO₂ support can be further verified by the TEM images of PdO@TiO₂. It can be seen from Fig. 3a and b that the morphology of TiO₂ has been changed to nanoparticles where the structure of 2D nanosheets disappeared. In TiO₂ crystal, the interplanar distances of 0.521 nm and 0.211 nm could be attributed to the (200) and (003) facets of the TiO₂ phase (shown in the HRTEM image of the Fig. 3b). Meanwhile, mono dispersed Pd nanoparticles have been oxidized and aggregated, which can be detected by HRTEM (Fig. 3c and d). In PdO@TiO₂ material, the corresponding interplanar distance of 0.304 nm can be attributed to the (100) facet of the PdO phase.



Fig. 3. TEM (a, b) and HRTEM (c, d) images of PdO@TiO2.



Fig. 4. The XPS spectrum of PdO@TiO2 (a) and its high-resolution survey of Pd 3d region (b).

Table 1	
The physical property of the synthesized different catalysts.	

Catalyst	BET surface	Pore Volume $(cm^3 q^{-1})$	Average pore diameter (Å)			
	$(m^2 g^{-1})$	(chí g)	BJH adsorption	BJH desorption		
TiO ₂ TiO ₂ -calcined Pd@TiO ₂ PdO@TiO ₂	343.6 164.3 181.3 105.2	0.3934 0.3631 0.2411 0.2281	33.82 66.89 40.09 66.11	30.47 65.17 35.95 63.81		

Moreover, the existence of Pd element and the PdO phase have also been verified by performing the XPS characterization and ICP-AES detection. As seen from Fig. 4a, the peaks of Ti, O, Pd, C and Cl elements were respectively detected in the full XPS spectrum of PdO@TiO₂ nanomaterial. In Fig. 4b, there are two states of Pd species on PdO/TiO₂ catalyst with Pd $3d_{5/2}$ binding energy values of 336.30 and 337.85 eV, respectively. The peak of Pd species at 336.30 eV should be related to the species of Pd²⁺ in the form of PdO on the surface of PdO/TiO₂ catalyst, while the peak at 337.85 eV should be related to Pd species with a higher oxidation valence in the form of PdO₂; Moreover, the XPS results of used PdO@TiO₂ catalysts (presented in Fig. S4 of supporting information) showed two states of Pd species on PdO/TiO₂ catalyst still existed, only the relative peak area were different, which indicates that after the heating treatment under the air Pd has been oxidized into PdO and PdO₂ species. Furthermore, the ICP-AES result shows that the loading content of PdO is as low as 1.35 wt.%, and it is similar to that calculated according to the Pd/Ti molar ratio obtained from the XPS characterization result. These further confirm the mono-dispersion of Pd species on the TiO₂ support.

In order to further investigate the solid surface characters of the synthesized catalysts, BET surface measurement has been conducted. Table 1 shows the textural properties of different catalysts measured by



Fig. 5. UV-vis spectra of TiO₂, TiO₂-calcined, Pd@TiO₂ and PdO@TiO₂.

nitrogen physisorption. It can be seen from the table that the surface area of TiO₂ is as high as 343.6 m² g⁻¹. After being calcinated at a high temperature of 350 °C for 2 h, the surface area of TiO₂ decreases to 164.3 m² g⁻¹. This result is consistent with the SEM images. After calcination, the morphology of TiO₂ changed from nanosheets to nanoparticles aggregations, which resulted in the decrease of surface area of the catalyst. Moreover, the surface areas of Pd@TiO₂ and PdO@TiO₂ are 181.3 and 105.2 m² g⁻¹, respectively. The pore volume of TiO₂ is much larger than that of other catalysts which reaches about 0.3934 cm³ g⁻¹. And the average pore diameters of these catalysts are between 3.047–6.689 nm.

On the other hand, TiO_2 is an n-type semiconductor material whose light absorption and the migration of the light-induced electrons and holes are the key factors in achieving palladium atomic immobilization. Fig. 5 shows the UV–vis spectra (DRS) for TiO₂ nanosheets, TiO₂-calcined, Pd@TiO₂ and PdO@TiO₂. All of the samples showed strong photoresponsive in the ultraviolet regions. Moreover, the ultraviolet absorption of the TiO₂ after calcination enhances, which can be interpreted by the high temperature caused aggregation of TiO₂ to larger nanoparticles. The addition of palladium (Pd@TiO₂) promotes a slight increase in UV absorption. The addition of PdO (PdO@TiO₂) weakens the absorption peak in the ultraviolet ranges. However, after the addition of palladium elements, the Pd@TiO₂ and PdO@TiO₂ materials show significant absorption in the visible region, which is different from the UV absorption peak of bare TiO₂.

In addition, the NH_3 -TPD results and TG-DTG curves of different catalysts are provided in the supporting information.

3.2. The oxidative condensation of FUR with aliphatic alcohols

In order to investigate the catalytic performances of various solid palladium catalysts, the selective transformation of FUR and n-propanol was employed as the model reaction. The catalytic equation was provided in the Scheme 1.

The corresponding experimental data were summarized in Table 2. When any catalyst was not added, conversion of FUR was about 22.1% and the main product is 2-(dipropoxymethyl)furan (entry 1). Using Pd@TiO₂ and K₂CO₃ as catalytic system, a 40.4% conversion of FUR in a 16.8% selectivity of **1** was attained (entry 2). In the following, when the catalyst system was changed to the combination of r-Pd@TiO₂ and K₂CO₃, the conversion of FUR and selectivity of **1** was respectively

Table 2

The oxidative	transformation	of F	FUR	and	n-propanol	using	various	palladium
catalysts. ^a								

Entry	Catalytic system	Conv. (%) ^b	Selectivity (%) ^b		
			1	3	2 + 4
1	/	22.1	< 1	0	> 99
2	$Pd@TiO_2 + K_2CO_3$	40.4	16.8	-	83.2
3	r-Pd@TiO ₂ + K ₂ CO ₃	52.3	68.5	12.3	19.2
4	$PdO@TiO_2 + K_2CO_3$	77.8	89.2	10.8	-
5	K ₂ CO ₃	19.6	95.0	-	-
6	PdO@TiO2	32.4	3.0	-	97
7	$TiO_2 + K_2CO_3$	39.9	16.4	-	83.6
8	$Pd/C + K_2CO_3$	50.9	71.2	3.1	25.7
9	$PdO/n-TiO_2 + K_2CO_3$	47.6	69.7	5.4	24.9

 $^a\,$ Reaction conditions: 0.2 g of FUR, 0.05 g of catalyst and 0.05 g of K_2CO_3, in 15 mL n-propanol solvent, with 0.3 MPa of O_2 pressure, at 140 °C, for 4 h.

 $^{\rm b}$ The conversion and selectivity of product were attained by GC using the internal standard method.

52.3% and 68.5% at similar reaction conditions (entry 3). Surprisingly, a 77.8% FUR conversion with 89.2% selectivity of 1 was acquired when PdO@TiO2 and K2CO3 was employed as the catalyst (entry 4), and this result is comparable to that obtained using supported Pt catalyst [20]. These showed that PdO@TiO2 is more efficient than r-Pd@TiO2 and Pd@TiO₂ as the catalyst on the oxidative condensation process. Then, to explore the action of K2CO3 on the transformation of FUR and npropanol, a certain amount of K₂CO₃ was tested during the reaction, and it was found that the conversion of FUR and the selectivity of 1 is 19.6% and 95%, respectively, which indicates the significant effect of K₂CO₃ is elevating the selectivity of product via promoting the occurrence of condensation reaction (entry 5). Therefore, it can be concluded that production of compound 2 and 4 is closely related to the acidic sites on the catalyst surface. Meanwhile, the by-product 3 is generated via the further oxidation of 2 by molecular oxygen in the presence of a suitable metallic Pd catalyst.

Moreover, in the presence of single $PdO@TiO_2$ catalyst, the conversion of FUR was 32.4% and the selectivity of 4 reached 97% (Entry 6). On the other hand, conversion of FUR and the selectivity of 1 were 39.9% and 16.4% when the coupled TiO_2 and K_2CO_3 were used during reaction (entry 7). As comparison, the Pd/C and PdO/n-TiO₂ were respectively detected as the solid catalysts to accelerate the oxidative transformation of FUR and n-propanol. Therein, a 50.9% or 47.6% conversion of FUR with a 71.2% or 69.7% selectivity of 1 was respectively acquired (entries 8 and 9). Thus, it was clearly exhibited that the PdO@TiO₂ and K_2CO_3 have the important synergy in the selective oxidative transformation of FUR and n-propanol under the oxygen at mosphere.

Considering the promotion effect of K_2CO_3 as additive for the generation of compound 1 during oxidation reaction, actions of various basic additives such as the Cs_2CO_3 , Na_2CO_3 , $CaCO_3$, Na_2SiO_3 , K_3PO_4 , NaOH, NaOEt, KHCO_3 and NaOAc were also further studied. As indicated on Fig. 6, about 55.0% conversion of FUR with a 90.3% selectivity of 1 was attained using Cs_2CO_3 as the promotor. When the Na₂CO₃ was added, the conversion of FUR was 12.7% at the similar conditions. It is assumed that strong electron structure effect of the sodium element decreased reaction efficiency during the whole oxidation process. Furthermore, when $CaCO_3$, Na_2SiO_3 or K_3PO_4 was added, a 27.2%, 28.5% or 24.2% conversion of FUR with 82.9%, 12.5% and



Scheme 1. The oxidative transformation of FUR and n-propanol under the oxygen atmosphere.



Fig. 6. The effect of different basic additives on the oxidation reaction (Reaction conditions: 0.2 g of FUR, 0.05 g catalyst and 0.05 g of additive, in 15 mL n-propanol, under a 0.3 MPa of O₂ pressure, at 140 °C, for 4 h).

Table 3		
Oxidative transformation	of FUR in different aliphatic alcoho	ols.ª

Entry	Aliphatic alcohol	Conv. (%) ^b	Product distribution (%) ^b			
	uiconor		Oxidative condensation	Oxidative esterification	Others	
1	ethanol	88.4	85.7	14.3	-	
2	i-propanol	62.4	83.1	16.9	-	
3	n-butanol	52.8	65.0	10.3	24.7	
4	n-pentanol	50.4	48.2	17.2	27.7	
5	n-hexanol	35.6	50.3	24.0	25.7	

 a Reaction conditions: 0.2 g FUR, 0.05 g PdO@TiO_2 solid catalyst and 0.050 g of K_2CO_3 , in 15 mL of alcohol, with 0.3 MPa of O_2 pressure, at 140 $^\circ$ C temperature, for 4 h.

^b The conversion and selectivity of product were attained by GC using the internal standard method.



Fig. 7. Effect of reaction temperature on the oxidative condensation process (Reaction conditions: 0.2 g of FUR, 0.05 g catalyst and 0.05 g of K_2CO_3 , in 15 mL n-propanol, under a 0.3 MPa of O_2 pressure, for 4 h).



Fig. 8. The recycling of the PdO@TiO₂ catalyst on the oxidative condensation process (Reaction conditions: 0.2 g of FUR, 0.05 g catalyst and 0.05 g of K₂CO₃, in 15 mL n-propanol, under 0.3 MPa of O₂, at 140 °C, for 4 h).

74.3% selectivity of **1** were obtained. With NaOH as the additive, the conversion of FUR is 55% and selectivity of **1** arrives at 86.4%. Those results showed that suitable basicity of the additive is advantageous to the proceeding of oxidative condensation reaction. Next, a 34.7%, 35.8% or 30.9% conversion of FUR in a high selectivity of **1** was respectively attained using EtONa, KHCO₃ or NaOAc as the additive. Relied on the promotion effect and the commercial value, the K_2CO_3 was selected as the optimal additive.

To further reveal the effects of solvent, the selective oxidative transformation of FUR and different aliphatic alcohols were carried out under the O_2 atmosphere. As presented in Table 3, the generated main product is furan-2-acrolein in the ethanol solvent, where the conversion of FUR and the product selectivity was 88.4% and 85.7%, respectively. Then, in case of *i*-propanol, the obtained main product is 4-(furan-2-yl) but-3-en-2-one, and the conversion of FUR and the selectivity of product were respectively 62.4% and 82.1% after the oxidation reaction, in which low conversion is attributed to the effect of steric hindrance. Besides, it was found that the yield of oxidative condensation product is gradually declined along with the increase of carbon chain length of

Table 4

Alcoholvsis	of di	ifferent	reactants	with	the	PSS	as	cataly	vst.ª

Entry	Reactant	Catalytic system	Conv. (%) ^b	Selectivity of 1 (%) $^{\rm b}$
1	FUR + n-propanol	$PdO@TiO_2 + K_2CO_3$	77.8	89.2
2	FUR + n-propanal	$PdO@TiO_2 + K_2CO_3$	75.9	87.7
3 ^c	FUR + n-propanol	$PdO@TiO_2 + K_2CO_3$	61.5	62.7
4 ^d	FUR + n-propanol	$PdO@TiO_2 + K_2CO_3$	75.2	90.1
5	Furfuryl alcohol + n-propanol	$PdO@TiO_2 + K_2CO_3$	17.7	91.0
6	FUR + n-propanol	K ₂ CO ₃	19.6	95.0
7	Furfuryl alcohol in CH ₂ Cl ₂	PdO@TiO ₂	12.8	32.9 for FUR

^a Reaction conditions: 0.2 g FUR, 0.05 g PdO@TiO₂ catalyst and 0.050 g of K₂CO₃, in 15 mL of n-propanol or CH₂Cl₂ as solvent, with 0.3 MPa of O₂ pressure, at 140 °C temperature, for 4 h.

^b The conversion and selectivity of product were attained by GC using the internal standard method.

^c The reaction was performed under N₂ atmosphere.

 d The reaction was first performed under N₂ atmosphere, and then performed under O₂ atmosphere for 4 h.



3-(furan-2-yl)-2-methylacrylaldehyde

Scheme 2. Proposed mechanism for transformation of FUR with n-propanol in the presence of O2.

alcohol. Also, for n-butanol, pentanol and hexanol, the selectivity of alkyl ester is increased with the growth of carbon chain length. Particularly, a 35.6% conversion of FUR in 50.3% selectivity of 2-(furan-2-ylmethylene)hexanal and 24.0% of hexyl ester was acquired when the n-hexanol was used, which is probably contributed to relatively slow rate of H-transfer between FUR and long chain alcohol molecule.

Owing to the oxidative condensation being endothermic, the reaction temperature should play a significant role during the oxidation reaction. Therefore, the influence of reaction temperature has also been performed at the ranges of 100 °C to 180 °C. As indicated in Fig. 7, the FUR conversion increases slowly with the gradual increase of the reaction temperature, while the selectivity of **1** remains at a high level at the temperature from 100 to 140 °C, after that it begins to be obviously decreased. It is considered that there was further condensation being occurred between compound **1** and n-propanol under the O₂ atmosphere.

In addition, the recycling of PdO@TiO₂ catalyst was investigated to examine the stability on oxidative condensation. After the first catalytic run, the palladium catalyst is filtered, and cleaned by the ethanol, and treated at 100 °C for 12 h to be dried before next reaction. As presented in Fig. 8, it was exhibited that the FUR conversion is still larger than 70% and the selectivity of **1** is almost unchanged even after PdO@TiO₂ being reused for four times. These results showed that this catalyst should be recyclable on the selective oxidative transformation of FUR, n-propanol and O₂.

The control experiments were carried out and obtained data are provided in Table 4. It could be indicated that $PdO@TiO_2$ helps to accelerate transformation of n-propanol to generate propanal, and the basic additive can promote the condensation reaction of FUR with *in situ* produced propanal. This entirely suits to the efficient production of compound **1** with the $PdO@TiO_2 + K_2CO_3$ catalytic system.

Correspondingly, as the propanal was employed as solvent, the FUR conversion of could be declined a little, which should be attributed to the happening of propanal self-condensation process (Entries 1 and 2). Moreover, a 61.2% conversion of FUR in 62.7% selectivity of 1 was attained and a near half of FUR was converted to furfuryl alcohol under the atmosphere of nitrogen, which exhibits that the PdO@TiO₂ + K_2CO_3 catalyst system can mediate the hydrogen transfer between FUR and n-propanol (Entry 3). In addition, combined with the datum of entries 5–7 in Table 4, it is concluded that the oxidation of furfuryl alcohol to FUR can also be achieved in the presence of molecular oxygen.

Based on the above experimental results and the catalytic reaction theory, a simple reaction mechanism is proposed for the oxidative transformation of FUR in n-propanol solvent (given in Scheme 2). Firstly, a very few molecular n-propanol was oxidized by oxygen to generate a very few propanal as intermediate; next, the fast condensation reaction occurred between FUR and the in situ produce molecular propanal in the reactor (presented in Scheme 2a). Besides, there is another possible catalytic route in this process. At first, a hydrogen transfer reaction happened between n-propanol and FUR, where a 1: 1 M ratio of furfuryl alcohol and propanal was attained. In the following, the condensation process was achieved between the remained FUR and the obtained propanal; Moreover, furfuryl alcohol was further converted to FUR through the selective oxidation with dioxygen (presented in Scheme 2b). Therein, for this catalytic process, the used PdO@TiO2 helps to the proceeding of n-propanol oxidation and furfuryl alcohol oxidation; while, the added K₂CO₃ is promoting the second condensation step to generate compound 1 as a main product.

4. Conclusion

In summary, we have developed a novel carbon-chain increasing transformation of FUR based on the selective oxidative condensation with the mono-dispersed PdO catalyst. With this catalytic approach, a 77.8% conversion of FUR with 89.2% selectivity of 3-(furan-2-yl)-2-methyl acrylaldehyde was obtained in the presence of molecular oxygen. It will provide a new route for the selective transformation of the hemicellulose-derived platform compounds.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.110545.

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