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A regulatable oxidative valorization of furfural with aliphatic alcohols catalyzed by functionalized metal-organic frameworks-supported Au nanoparticles



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ABSTRACT

The oxidative upgrading of furfural (FUR) and aliphatic alcohols is an important way to produce desirable precursor of jet fuel or value-added furanic compound. Therein, developing a highly active catalytic system with switchable product selectivity still remains a challenge. In this work, we report a novel strategy on regulating the oxidative condensation and oxidative esterification of FUR with aliphatic alcohol in the presence of molecular oxygen. Firstly, Au@UiO-66 is prepared using different methods and employed as the catalyst for the oxidative valorization of FUR with methanol. It is found that the impregnationreduction- H_2 (I-H) method is the best where a 100% selectivity of methyl-2-furoate with a complete conversion was obtained using Au@UiO-66 as catalyst. Then, a series of metal-organic frameworks (MOFs) supported Au nanoparticles (Au@UiO-66-X) such as Au@UiO-66, Au@UiO-66-NH₂, Au@UiO-66-NO₂, Au@UiO-66-COOH and Au@UiO-66-NH₃Cl have been prepared with I-H method and employed for oxidative valorization of furfural with ethanol. Experimental results showed that, in "FUR-ethanol-O₂" system, the Au@UiO-66-X can efficiently regulate the oxidative condensation and oxidative esterification as two competitive reaction pathways. With Au@UiO-66-COOH as the catalyst, the oxidative condensation process is dominant in which 84.1% selectivity of furan-2-acrolein is attained; Meanwhile, the Au@UiO-66 is beneficial to the occurrence of oxidative esterification and generation of ethyl-2-furoate. At last, based on the catalyst characterization and the numerous control experiments, a possible catalytic reaction mechanism for conversion of FUR is proposed.

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1. Introduction

Catalytic transformation of biomass-derived platforms into fine chemicals represents a promising and sustainable way for the replacement the unfriendly exhaustible fossil fuels [1,2]. Furfural (FUR), as a famous biomass-based platform chemical, has great potential applications in the present chemical industry. It can be not only used as a feedstock for producing high grade gasoline, diesel, or jet fuel, but also can be transformed into oxygen-containing solvents and chemical products such as furfural alcohol, tetrahydrofuran and alkyl furoates, etc.. Particularly, alkyl furoates, widely found in flavor and fragrance component in the fine chemicals, can be synthesized *via* the oxidative esterification of FUR with aliphatic alcohol in the presence of molecular oxygen [3,4]. Up to now, several reports have demonstrated that the supported gold nanoparticles exhibited excellent performance for promoting the oxidative esterification of FUR to produce methyl-2-furoate in methanol [5]. For example, Menegazzo et al. have studied nano gold catalysts on different oxide supports for oxidative esterification of FUR with methanol [6–8]. Moreover, our group has extensively investigated the catalytic oxidative transformation of FUR with different aliphatic alcohols in the presence of molecular oxygen [9–11]. Therein, when the aliphatic alcohol molecule contains α -H, the oxidative condensation of FUR with alcohol occurs as a competitive process of oxidative esterification reaction which impels two carbon molecules together for producing longer hydrocarbon chains. The possible reaction routes in the "FUR-alcohol-O2" system are summarized in Scheme 1. For the oxidative esterification, FUR can firstly react with alcohol to generate hemiacetal and then be further oxidized to alkyl furoate (Route (i)). Also, the FUR can be firstly oxidized to furoic acid and then react with alcohol to produce alkyl furoate (Route (ii)). For the oxidative condensation,



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Scheme 1. The possible reaction routes in the oxidative transformation of FUR with aliphatic alcohol.

the alcohol can be firstly oxidized to the corresponding aldehyde and then react with FUR to produce furan-based acrolein *via* the adol condensation reaction (Route (iii)). Also, the hydrogen transferring process is firstly performed between FUR and alcohol, and then *in situ* generated aldehyde reacts with FUR to produce furan-based acrolein, in which the furfuryl alcohol can be oxidized to FUR by O₂ to realize the whole cycle (Route (iv)). Based on the previous investigations [9,10], the Route (i) is dominant in the oxidative esterification process. While, both the Route (iii) and Route (iv) can occur simultaneously in the oxidative condensation process. Considering the complication and diversity of routes, the efficient regulation of product selectivity is a curial point and still keeps a challenge at present.

In the supported metal catalysts, the support surface properties could affect the size and the distribution of metal nanoparticles as well as the catalytic performances [7,12]. Especially, in a tandem reaction, the morphological and physical-chemical properties of support, such as acidic and basic sites, adsorption capacities are not only helpful to accelerate the reaction process but also may regulate the product selectivity during reaction [13,14]. On the other hand, Metal-organic frameworks (MOFs) have been emerging as attractive materials in catalytic field due to their outstanding designability [15–17]. Distinct from traditional inorganic porous materials, the active sites of MOFs-based catalysts can either originate from the immobilizing metal nanoparticles or from metal linkers, sometimes from the functional groups on the organic ligands as well [18–20]. Therefore, the catalytic abilities of MOFs can be tuned through adjusting the ligand's structure, selecting metal linkers and functionalizing the organic ligand [21-25]. In the large family of MOFs, Zr-based MOFs (UiO-66) have been widely applied in the catalytic field. It is a class of zirconiumbased MOFs with molecular formula $[Zr_6O_4(OH)_4(BDC)_6]_{\infty}$ (BDC = 1,4-benzenedicarboxylate). In the crystal of UiO-66, each Zr oxide secondary building unit, Zr₆O₄(OH)₄(-CO₂)₁₂, is linked to 12 BDC units to form a porous, three dimensional framework containing large octahedral (7.2 Å) and small tetrahedral (6.8 Å) pores. UiO-66 possess very high surface area and display unprecedented the thermal and chemical stability. Furthermore, its linker, BDC, is easily functionalized with various chemical groups. (crystal structure in supporting information) [26,27].

UiO-66 encapsulated Au nanoparticles (NPs) showed good catalytic performances in the different types of reactions, such as oxidation, reduction, tandem reaction, and photocatalysis. The highly activities of the Au@UiO-66 can be ascribed to its small size, the uniform distribution of the particles, the confinement effect and the synergetic effect between Au NPs and MOFs [28–30]. Concerning the UiO-66 support, the Zr(IV) centers can supply Lewis acidic sites. Besides, the organic linker in UiO-66 has been tailored to be functionalized with different groups such as $-SO_3H$ and $-NH_2$, etc., in which the Bronsted acidic and basic sites could be introduced [31–33]. The researches exhibited that highly dispersed Au@UiO-66-NH₂ catalyst can promote the selective tandem catalytic reactions [34].

As aforementioned, the oxidative transformations of FUR with aliphatic alcohol are the tandem reactions. Among them, some steps such as acetalization, hydrogen transferring, aldol condensation and oxidation are sensitive to the acidic and basic sites [4,35]. Intrigued with these, we attempted to employ the Au@UiO-66 and functionalized Au@UiO-66-X as the catalysts to explore the oxidative transformation of FUR, aiming to find a regulatable catalytic system for tuning the competitive reaction between the oxidative esterification and condensation. Firstly, we screened out and optimize the synthesis method of Au@UiO-66 catalyst. It is found that the as-obtained Au@UiO-66 via impregnation-reduction method can efficiently catalyze the oxidative esterification of FUR with methanol with dioxygen as the terminal oxidant where a 100% selectivity of methyl-2-furoate at a complete conversion of FUR is obtained. In addition, experimental results show that the functionalized Au@UiO-66 with -COOH, -NH₂, -NO₂, and -NH₃Cl can further regulate the reaction pathway between the oxidative esterification and the oxidative condensation in the "FUR-ethanol-O₂" system. When the Au@UiO-66-COOH is employed as catalyst, 84.1% selectivity of furan-2-acrolein produced via oxidative condensation is attained under mild conditions.

2. Experimental section

2.1. Chemicals

All solvents were analytical grade and were used without further purification. Terephthalic acid (H₂BDC), 2-aminoterephthalic acid (H₂BDC-NH₂), 2-nitroterephthalic acid (H₂BDC-NO₂), 1,2,4benzenetricarboxylic acid (H₂BDC-COOH), ZrCl₄, ZrOCl₂·8H₂O, ZrO (NO₃)₂·xH₂O, K₂CO₃, FUR and HAuCl₄·4H₂O were purchased from Sigma-Aldrich.

2.2. The preparation of nano gold catalysts

2.2.1. The in situ synthesis of the functionalized MOFs

The UiO-66 was prepared with the adjustable method according to the literature [27]. The ZrCl₄ (0.053 g, 0.227 mmol) and H₂BDC (0.034 g, 0.227 mmol) were dissolved in 16 mL *N*, *N*-dimethyl-formamide (DMF) at room temperature. Then, the mixture was sealed and placed in a preheated oven at 120 °C for 24 h. After being cooled in air to room temperature, the resulting solid product was filtered and washed with DMF and ethanol for six times.

At last, the sample was dried in a vacuum oven at 100 $^\circ\!C$ for 12 h to afford pure UiO-66.

The UiO-66-NH₂ was synthesized with a modified method [36]. ZrCl₄ (0.0203 g, 0.087 mmol) and 2-aminoterephthalate acid (0.0118 g, 0.065 mmol) were dissolved in 15 mL DMF. The mixture was stirred in a glass vial for 10 min, and the resulting solution was transferred into a 20 mL teflon-lined stainless steel autoclave and heated at 120 °C for 24 h. After being cooled to room temperature naturally, the precipitate was collected by centrifugation at 4000 rpm for 10 min, and further washed with ethanol for three times, and dried under vacuum at 100 °C for 12 h to afford pure UiO-66-NH₂.

The UiO-66-NO₂, UiO-66-COOH and UiO-66-NH₃Cl were synthesized according to the literatures [37,38].

2.2.2. Synthesis of Au@UiO-66-X catalysts (X = –H, –NH₂, –NO₂, – COOH)

For the synthesis of Au@UiO-66, the impregnation-reduction- H_2 (**I-H**), the impregnation-reduction-NaBH₄ (**I-S**), deposition–pre cipitation-carbonization (**D-C**), deposition–precipitation- H_2 (**D-H**) and colloid-immobilization (**C-I**) methods were used, respectively [39–43]. The experimental procedures were given as followings.

In a typical procedure of **I-H** method, 100 mg of activated UiO-66 was immersed in 1 mL solution of HAuCl₄ (0.01 g/mL), and then 2 mL of deionized water was added under N₂ atmosphere. After being sonicated for 6 h at room temperature, the mixture was placed in a vacuum oven and dried at 100 °C for 12 h. Finally, the dried precursor of the catalyst was treated in a fixed-bed stainless steel reactor with an inner diameter of 6 mm under H₂ with a total flow rate of 50 mL min⁻¹ and maintained at 250 °C for 2 h to obtain 4.7 wt% Au@UiO-66 catalyst.

In a typical procedure of **I-S** method, 100 mg of UiO-66 and 1 mL solution of HAuCl₄ (0.01 g/mL) were mixed in a three-neck flask and 2 mL of deionized water was added. The reaction mixture was ultrasonicated for 6 h. Then, the reaction mixture was heated to 105 °C, and 5 mL fresh solution of NaBH₄ (20 mg/mL) was added dropwise and the mixture was refluxed for 5 h. Next, the resulting solid was filtered and further washed with deionized water for several times. After being dried under vacuum at 100 °C for 12 h, 4.7 wt% Au@UiO-66 catalyst was prepared.

In a typical procedure of **D-C** method, the solution of HAuCl₄ (1 mL, 0.01 g/mL) was charged into a beaker where the pH value was adjusted to 9 with 0.1 M NaOH under vigorous agitation. Then, 100 mg of UiO-66 was added to the above solution under the stirring, and the pH value of the suspension was re-adjusted to 9 using 0.1 M NaOH. Then, the as-obtained suspension was heated to 65 °C and kept for 1 h. After the precipitate was filtered, the solid was washed with deionized water for three times and dried at 60 °C overnight, the resulting Au@UiO-66 precursor was calcined at 300 °C for 3 h to prepare the final catalyst.

The procedure of **D-H** method was similar with **D-C** except that the as-prepared catalyst precursor was further treated in a fixedbed stainless steel reactor with an inner diameter of 6 mm under H₂ with a total flow rate of 50 mL min⁻¹ and maintained at 250 °C for 2 h to obtain Au@UiO-66 catalyst. Herein, the reduction temperature of Au particles has been confirmed by the H₂-TPR result of catalyst precursor (shown in Fig. S3 of supporting information).

In a typical procedure of **C-I** method, 10 mg HAuCl₄ was dissolved in 100 mL distilled water, and 2 mL 0.3 wt% PVP aqueous solution was added (PVP/Au = 1.2/1.0 in weight ratio). After stirring at room temperature for 1.0 h, 2.5 mL 0.1 moL/L NaBH₄ aqueous solution was promptly added into the mixture, and Au(III) species were immediately reduced to metallic Au species, and Au colloids were formed (0.24 mmol/L). After further being stirred at room temperature for 1.0 h, 0.1 g UiO-66 was added into the Au colloid solutions. The suspension was further stirred overnight at room temperature so that Au colloids can be completely deposited on the UiO-66. The solid was collected by centrifugation (8000 r/ min, 5 min), and washed using distilled water for three times, and then dried under vacuum at room temperature overnight, and finally calcined at 300 °C in air for 2.0 h to obtained the Au@UiO-66 catalyst.

In addition, the Au@UiO-66-NH₂, Au@UiO-66-NO₂, Au@UiO-66-COOH and UiO-66-NH₃Cl catalysts were synthesized with **I-H** method, respectively.

2.3. Characterization of the catalysts

X-ray single-crystal diffraction data were collected on a Rigaku SCX-mini diffractometer at 293(2) K with Mo KR radiation ($\lambda = 0$. 71073 Å) by ω scan mode. The powder X-ray diffraction patterns (XRD) were recorded on Rigaku D/Max 2400 diffractometer with Cu/Ka radiation. Fourier transform infrared spectra (FT-IR) were recorded using Bruker EQUINOX55 infrared spectrometer. The gold contents of all the samples were quantitatively determined by the inductively coupled plasma optical emission spectrometry (ICP-OES: Varian 700-ES). High resolution scanning electron microscopy (HRSEM) was performed in a JSM 6490LV JEOL microscope at 25 kV. Transmission electron microscopy (TEM) was performed in a Phillips CM200 at 200 kV. X-ray photoelectron spectroscopy (XPS) was carried out in a 5700 model Physical Electronics apparatus. Temperature programmed reduction (TPR) analysis were carried out using a Micromeritics ChemiSorb 2720 Pulse Chemisorption System, 50 mg of each catalyst was pre-treated in 5% H_2/N_2 (100 mL/min) at 70 °C for 1 h, and then TPR was performed over the sample with the temperature increasing from 70 °C to 700 °C at a speed of 10 °C /min.

2.4. Catalytic reaction

Catalytic experiments were carried out in a 120 mL autoclave equipped with a magnetic stirrer and automatic temperature control. After the FUR, Au catalyst, K₂CO₃ and the alcohol were added, the reactor was sealed, and purged with pure O₂ for three times to remove the air. Then, the pressure of oxygen was charged to 0.3 MPa and the reaction mixture was heated to 140 °C and kept for 4 h. When the reaction was finished, the solution was diluted with acetonitrile after the reactor was cooled to room temperature. The products were qualitatively detected by an Agilent 7890A/5975C gas chromatography-mass spectrometry (GC–MS). The conversion of FUR and selectivity of the product were quantitatively obtained by GC instrument with the FID detector.

2.5. Recycling test

After first cycle was completed, the catalyst was filtered through the high speed centrifugation (8000 r/min, 5 min), and washed with ethanol ($3 \times 30 \text{ mL}$) and then dried at $80 \degree$ C in the vacuum oven overnight, and then was directly used for the next catalytic cycle. After being recycled five times, the catalyst was respectively characterized by XRD, HRSEM, TEM and other techniques.

3. Results and discussion

3.1. Oxidative esterification of FUR with methanol in the presence of molecular oxygen

Firstly, the catalytic performances of Au@UiO-66 catalysts with different preparation methods were investigated in the "FUR-methanol- O_2 " system (Scheme 2). In order to find a suitable load-



Scheme 2. Oxidative transformation of FUR with methanol with the Au@UiO-66 catalyst.

ing approach, we synthesized Au@UiO-66 catalysts using five different methods (impregnation-reduction-H₂: designated as I-H; impregnation-reduction-NaBH₄: designated as I-S; deposition-pre cipitation-carbonization: designated as D-C; deposition-precipita tion-H₂: designated as **D-H**; colloid-immobilization: designated as **C-I**). The possible products is mainly methyl-2-furoate (1) and 2-(dimethoxymethyl)furan (2), and obtained results are presented in Table 1. It is found that all the Au@UiO-66 catalysts from different methods can promote the oxidative esterification of FUR with methanol although the catalytic efficiencies are distinguishing during reaction. The optimal preparation methods should be the I-H method and C-I method in which more than 90% conversions of FUR were attained (Entries 1 and 5, Table 1). Particularly, the Au@UiO-66 catalyst prepared with I-H method can catalyze full conversion of FUR and the selectivity of formation of 1 up to 100% (Entry 1, Table 1). However, the Au@UiO-66 catalysts prepared with **D-C** and **D-H** methods exhibited relatively low activities; especially, only a 21.8% conversion of FUR and 91.5% selectivity of **1** was obtained using the Au@UiO-66 prepared with **D-H** method. In addition, the carbon balances for all catalytic processes have been measured and calculated (The particular calculation is supplied in the supporting information). Indicated from the data in Table 1, all the carbon mass balance can keep more than 95.2% in the oxidative esterification of FUR with methanol.

Table 1

Influences of preparation methods on Au@UiO-66 catalyzed transformation of FUR with methanol. $^{\rm a}$

-							
	Entry	Preparation method	Conversion (%) ^b	Select	ivity	/ (%) ^b	Carbon mass
				1	2	Others ^c	balance (%)
	1	I-H	100	100	-	-	98.9
	2	I-S	62.1	100	-	-	95.2
	3	D-C	69.2	93.6	-	6.4	98.2
	4	D-H	21.8	91.5	-	8.5	97.4
	5	C-I	92.1	100	-	-	99.0

 a Reaction conditions: FUR (0.1 g), catalyst (25 mg), K_2CO_3 (25 mg), in 15 mL methanol, under 0.3 MPa of $O_2,$ at 140 °C, for 4 h.

^b The results are obtained by GC with internal standard technique.

^c Other products generally refer to furfuryl alcohol as by-product.

Table 2 The blank and control experiment results in the oxidative esterification of FUR with methanol- O_2 .^a

Entry	Catalytic system	Conversion (%) ^b	Selectivity (%) ^b		
			1	2	Others
1	None (baseline)	15.1	-	100	-
2	K_2CO_3	12.6	6.0	-	94.0 ^c
3	UiO-66	90.2	-	100	-
4	UiO-66 + K ₂ CO ₃	15.5	6.6	-	93.4 ^c
5	Au@UiO-66	91.5	11.3	88.7	-
6	Au@UiO-66 + K ₂ CO ₃	100	100	-	-

 a Reaction conditions: FUR (0.1 g), catalyst (25 mg), K_2CO_3 (25 mg), in 15 mL methanol, under 0.3 MPa of $O_2,$ at 140 $^\circ C,$ for 4 h.

^b The results are obtained by GC with internal standard technique.

^c Other products generally refer to furfuryl alcohol as by-product.

Some blank and control experiments were performed to identify the active species for the oxidative esterification of FUR with methanol, and the results are provided in Table 2. As we know, the dominate route is the oxidation of hemiacetal into compound 1 rather than reoxidation of the acetal into compound 1 due to high stability of the acetal in the oxidative esterification for FUR with methanol [5]. The data of entries 1, 2 and 4 in Table 2, demonstrated potassium carbonate can probably inhibit the transformation from hemiacetal to acetal. The UiO-66 support may promote the formation of hemiacetal and acetal during reaction (Entry 3, Table 2). Therein, the Au nanoparticles are responsible for accelerating the oxidation of hemiacetal to the ester in reaction. On the other hand, the transfer hydrogenation process can occur between FUR and methanol in the presence of UiO-66 and K₂CO₃ that leads to substantial conversion of furfural into furfuryl alcohol (Entires 2 and 4, Table 2). Some previous works also demonstrated that the basic active sites can promote it greatly [44–46]. Thus, the synergistic effect among the additive. Au nanoparticles and support is necessary to the oxidative esterification of FUR with methanol to generate the compound **1** (Entry 6, Table 2).

The influence of Au loading is further studied in the oxidative esterification of FUR in which the reaction was performed in methanol at 100 °C with Au loading from 1.17 to 9.40 wt% in Au@UiO-66 catalysts (Table 3). It is found that, when the loading of Au ranges from 1.17 to 9.40 wt%, the selectivity of the compound **1** remained nearly unchanged (100%) while the conversion of FUR increased gradually (Entries 1–3, Table 3). With a 4.70 wt% loading of Au, the highest conversion of FUR and 100% selectivity of **1** are obtained under suitable conditions. The worse performance of the catalyst was observed with Au loading above 4.70 wt% (Entries 4–5, Table 3).

The Au contents in the Au@UiO-66 catalysts were determined by ICP-OES. As shown in Table 3, the experimental values are in good agreement with the theoretical values.

Moreover, the effects of the additive, reaction temperature and reaction time were investigated in detail and the results are displayed in Figs. 1 and 2. It is found that the conversion of FUR was increased along with the elevation of temperature and prolonging of time. The full conversion of FUR and 100% selectivity of **1** were obtained at 110 °C for 4 h. Unlike the previous reported Au-catalyzed processes where strong basic CH₃ONa was usually

Table 3

Influence of Au loading level on the oxidation esterification of FUR with methanol- $\mathrm{O_2}^{\mathrm{.a}}$

Entry	Au Load (%)		Conversion (%) ^b	Select	(%) ^b	
	Theoretical	ICP-OES		1	2	Others ^c
1	1.17	1.16	29.7	100	-	-
2	2.35	2.17	56.5	100	-	-
3	4.70	4.55	79.1	100	-	-
4	6.58	6.27	75.3	100	-	-
5	9.40	9.15	67.3	100	-	-

 $^a\,$ Reaction conditions: FUR (0.1 g), catalyst (25 mg), K_2CO_3 (25 mg), methanol (15 mL), O_2 (0.3 MPa), 100 °C and 4 h.

^b The results are obtained by GC analysis with the internal standard technique.

^c Other product generally refers to furfuryl alcohol as by-product.



Fig. 1. Influences of time (a) and temperature (b) on the oxidative esterification of FUR with methanol (Reaction conditions: 0.1 g FUR, 25 mg catalyst, 25 mg K₂CO₃, in 15 mL methanol, under 0.3 MPa of O₂).

used to achieve better results [46], in this case, weak basic K_2CO_3 showed the perfect promotion in the oxidative esterification of FUR with Au@UiO-66 catalyst (Fig. 2).

Furthermore, the recycling experiment of catalyst showed that the reused Au@UiO-66 exhibited similar activity with the fresh one in the oxidative esterification. It was shown in Fig. 3, the conversion of FUR decreased slightly and the selectivity of methyl-2furoate kept unchanged after the Au@UiO-66 catalyst being recycled for five times (Fig. 3).

3.2. Oxidative transformation of FUR with ethanol using Au@UiO-66-X as catalysts

The reaction equation for the transformation of FUR with ethanol in the presence of molecular is given as Scheme 3. In the "FURethanol- O_2 " system, the oxidative esterification and oxidative condensation are competitive processes, in which the reaction products include furan-2-acrolein (3), ethyl-2-furoate (4), 2-(diethoxymethyl) furan (5) and furfuryl alcohol (6). Recently, our





Fig. 2. Influences of additive on the oxidative esterification of FUR with methanol (Reaction conditions: 0.1 g FUR, 25 mg catalyst, 25 mg additive, in 15 mL methanol, under 0.3 MPa of O₂, at 110 °C, for 4 h).



Fig. 3. The recycling experimental results of Au@UiO-66 in the oxidative esterification of FUR with methanol (Reaction conditions: 0.1 g FUR, 25 mg catalyst, 25 mg K_2CO_3 , in 15 mL methanol, under 0.3 MPa of O_2 , at 110 °C, for 4 h).



Scheme 3. Oxidation transformation of FUR with ethanol catalyzed by Au@UiO-66-X catalysts (X = H, NH₂, NO₂, COOH and NH₃Cl).

ble 4
xidation transformation of FUR with ethanol catalyzing by Au@UiO-66-X (X = H, NH ₂ , NO ₂ , COOH and NH ₃ Cl), Pt@UiO-66-X and Au@CeO ₂ . ^a

Entry	Catalysts	Conversion (%) ^b	Selectivity	r (%) ^b		Carbon mass balance (%)	
			3	4	5	6	
1	Au@UiO-66	44.1	40.2	40.0	-	19.8	92.8
2	Au@UiO-66-NO2	42.5	89.3	4.9	-	5.8	90.6
3	Au@UiO-66-COOH	66.7	84.1	15.9	-	-	94.7
4	Au@UiO-66-NH ₂	46.4	73.9	-	-	26.1	90.3
5	Au@UiO-66-NH ₃ Cl ^c	77.2	95.3	1.7	-	3.0	95.6
6	Au@CeO2 ^d	6.8	0	70.7	29.3	0	97.1
7	Au@CeO ₂	61.5	86.7	13.3	0	0	92.6

^a Reaction conditions: FUR (0.1 g), catalyst (25 mg), K₂CO₃ (25 mg), ethanol (15 mL), O₂ (0.3 M Pa), 140 °C and 4 h.

^b The results are obtained by GC analysis with the internal standard technique.

^c Synthesis of UiO-66-NH₃Cl: 1.2 N HCl was mixed with UiO-66-NH₂ and the mixture was stirred overnight. Then the solid was washed with deionized water for 3 times and dried at 100 $^{\circ}$ C in the vacuum oven for one night.

^d Catalyst (100 mg) and FUR (300 µL) were dissolved in 150 mL ethanol. The reactor was with oxygen (6 bar) and stirred at 1000 rpm. The progress of the reaction was determined after 90 min.

Table 5

Effects of the additives in "FUR-ethanol-O2 system" with the Au@UiO-66 catalyst.^a

Entry	Additives	Conversion (%) ^b	Selectivity (%)	b		
			3	4	5	6
1	K ₂ CO ₃	44.1	40.2	40.0	-	19.8
2	NaOH	88.3	93.6	3.1	0	3.3
3	CaO	90.5	84.3	2.3	6.3	7.1
4	Na ₂ CO ₃	67.3	83.2	10.6	0	6.2
5	$(NH_4)_2SO_4$	31.2	3.2	0	94.6	2.2
6	Na ₂ SO ₃	67.0	0	0	100	0
7	NaAc	20.2	100	0	0	-
8	KAc	20.3	37.2	62.8	0	0
9	$Mn(Ac)_2$	38.2	3.3	4.1	88.7	3.9
10	K ₃ PO ₄	27.4	20.9	70.9	0	8.2

^a Reaction conditions: FUR (0.1 g), catalyst (25 mg), in 15 mL ethanol, under 0.3 MPa of O₂, at 140 °C, for 4 h.

^b The results are obtained by GC with internal standard technique.

Au@UiO-66-COOH or Au@UiO-66-NH₃Cl catalysts are employed, 66.7% or 77.2% conversion of FUR and 84.1% or 95.3% selectivity of **3** were obtained, respectively (Entries 3 and 5, Table 4). Especially, no oxidative esterification product was observed in "furfural-ethanol-O₂" system with the Au@UiO-66-NH₂ catalyst (Entry 4, Table 4). These phenomena indicated that product selectivity can be regulated through the introduction of functional group in UiO-66 support. As comparison with Au@CeO₂, Au@UiO-66-X show better catalytic performance (Entries 6 and 7, Table 4). So, the Au@UiO-66-X catalysts have outstanding advantage for the regulation on the oxidative transformation of FUR with ethanol, in which both oxidative condensation and oxidative esterification can be successfully performed through adjusting the structure of UiO-66 support. It should be mentioned that the carbon mass balance are more than 90% for all the oxidation processes (Table 4).

In order to further improve the yield and selectivity of **4**, the influences of several additives were investigated in "FURethanol-O₂" system with the Au@UiO-66 catalyst, and the results are summarized in the Table 5. As a result, it is found that oxidative condensation process was predominant when strong base such as NaOH or CaO was added (Entries 2 and 3, Table 5). Using (NH₄)₂-SO₄, Na₂SO₃ and Mn(OAc)₂ as additives, the direct acetalization occured which restricts the oxidative esterification and oxidative condensation processes (Entries 5, 6 and 9, Table 5). On the other hand, the KAc and K_3PO_4 additives were helpful to promote oxidative esterification process (Entries 8 and 10, Table 5).

In the following, the effect of reaction time and temperature were investigated in detail using Au@UiO-66-COOH + K₂CO₃ and Au@UiO-66 + K₃PO₄ catalytic system, respectively (Figs. 4 and 5). According to experimental results, it is found that, when the reaction was performed at 140 °C for 4 h, the conversion (66.7%) of FUR and the selectivity (84.1%) of **3** were up to the maximum with Au@UiO-66-COOH + K₂CO₃ catalytic system (Fig. 4). Along with the prolonging of reaction time and increase of temperature, the conversion of FUR was gradually elevated and the selectivity of **4** was decreased using the Au@UiO-66 + K₃PO₄ catalytic system, where the conversion of FUR can reach the highest after two hours (Fig. 5).

In Fig. 6, the recycling experiment results showed that both Au@UiO-66-COOH in oxidative condensation process and Au@UiO-66 in oxidative esterification process keep stable and can provide high catalytic activities after being reused for five times.



Fig. 4. Influences of reaction time (a) and temperature (b) on the oxidative condensation process of FUR with ethanol using Au@UiO-66-COOH + K₂CO₃ catalytic system.



Fig. 5. Influences of reaction time (a) and temperature (b) on the catalytic oxidation esterification process of FUR with ethanol Au@UiO-66 + K₃PO₄ catalytic system.



Fig. 6. The cyclic performance of the catalysts in the transformation of FUR with ethanol: (a) Au@UiO-66-COOH for oxidative condensation process; (b) Au@UiO-66 for oxidative esterification process.

3.3. Characterization of gold catalysts

3.3.1. Au@UiO-66 catalysts

Typical morphologies of the Au@UiO-66 catalysts synthesized with different methods were given in Figs. 7 and 8. The HRSEM and TEM images of Au@UiO-66 synthesized with **I-H** method

exhibited that the Au particles were embedded in the crystal and were homogeneously distributed throughout the crystal of UiO-66. The size of Au nanoparticles was about 3-5 nm (Figs. 7(a) and 8(a)). From the HRSEM and TEM images of the Au@UiO-66 prepared using **I-S**, **D-C** and **D-H** methods, the bigger Au nanoparticles and uneven disperse were observed (Figs. 7(b)–(d) and 8(b)–(d)).



Fig. 7. HRSEM images of Au@UiO-66 catalysts synthesized with different methods: (a) I-H; (b) I-S; (c) D-C; (d) D-H; (e) C-I. (f) used Au@UiO-66 catalyst synthesized with I-H method.



Fig. 8. TEM images of Au@UiO-66 catalysts synthesized with different methods: (a) I-H; (b) I-S; (c) D-C; (d) D-H; (e) C-I. (f) used Au@UiO-66 catalyst synthesized with I-H method.

Compared with former one, the Au particles were slightly accumulated over the UiO-66 with a mean particle size of ca. 10-25 nm. For the Au@UiO-66 prepared with **C-I** method, the distribution of Au nanoparticles were uniform and the size of particle was in the range of 2-3 nm which was similar with that obtained from I-H approach (Figs. 7(e) and 8(e)). Notably, the crystal shape of UiO-66 were well preserved during the course of synthesizing the catalysts using I-H and C-I methods, while the other three synthesized methods resulted in destroying the shape of UiO-66. Related to the catalytic results in oxidation reactions, the excellent catalytic performances of Au@UiO-66 synthesized by I-H and C-I methods were ascribed to the small size of Au nanoparticles and the wellpreserved pore structure of UiO-66. The HRSEM and TEM images of used Au@UiO-66 catalyst synthesized by I-H method were also shown in Figs. 7(f) and 8(f). After being recycled for 5 times, no Au particles agglomeration appeared on the surface of UiO-66.

To ascertain the homogeneity of the as-synthesized catalytic materials and identify the active species for oxidation of FUR, the as-synthesized UiO-66 and the Au@UiO-66 with different preparation methods were further compared by powder X-ray powder



Fig. 9. XRD patterns of Au@UiO-66 catalysts synthesized with different methods: (a) simulated pattern of UiO-66; (b) as-synthesized UiO-66; (c) I-H; (d) D-C; (e) I-S; (f) D-H; (g) C-I. (h) used Au@UiO-66 catalyst synthesized with I-H method.

diffraction (XRD). The powder XRD pattern of UiO-66 matches well with the respective simulated powder pattern obtained from the single crystal data (Fig. 9(a) and (b)). After immobilizing Au nanoparticles using **I-H** and **C-I** methods, the structures of UiO-66 were mostly preserved (Fig. 9(c) and (g)). Moreover, some typical diffraction peaks corresponding to Au crystallite have been observed. Fig. 9(d)–(f) present the XRD patterns of Au@UiO-66 catalysts synthesized with other methods and the results show that the crystal structure of UiO-66 were severely destroyed, which was probably due to the addition of the strong base (NaOH) during preparation. While, the characteristic peaks associated with metallic Au can be clearly observed. Obviously, the results from the XRD detections were in good agreement with those of HRSEM and TEM images.

The X-ray photoelectron spectroscopy (XPS) spectra of fresh and reused Au@UiO-66 catalysts using **I-H** method were displayed in Fig. 10 and Fig. S2 (Fig. S2 is given in supporting information). The photoelectron peaks at 83.75 eV (Au4f), 182.86 eV (Zr3d), 284.78 eV (C1s), and 531.83 eV(O1s) were assigned to the main elements on the catalyst surface. In the Au4f XPS spectrum of the Au@UiO-66 catalyst, two main peaks located at 87.4 and 83.8 eV correspond to Au4f_{7/2} and Au4f_{5/2}, respectively (Fig. 10(a) and (b)), indicating that the Au (III) ion were successfully reduced to Au(0) by H₂.

3.3.2. Au@UiO-66-X catalysts

A series of the in situ functional UiO-66-X (X = -H, -COOH, -NH₂, -NO₂ and -NH₃Cl) were used to support Au nanoparticles. Figs. 11 and 13 show the morphology of functional UiO-66 supported Au nanoparticles. It can be seen that the size of Au nanoparticles in Au@UiO-66-X catalyst was bigger than that of Au@UiO-66. Meanwhile, more uneven dispersion of Au particles was observed. Especially, for that of Au@UiO-66-NH₃Cl, the average particle size of the spherical particles was about 30 nm. In the Au@UiO-66-COOH and Au@UiO-66-NH₂, the size of numerous Au particles was in the range of 6-10 nm. Element mapping from SEM measurements shows that the Au content of Au@UiO-66-X (X = -COOH, -NH₂ and -NH₃Cl) was significantly less than that of the Au@UiO-66 and some Au particles aggregation were observed in Au@UiO-66-NO2, Au@UiO-66-NH3Cl and Au@UiO-66-COOH catalysts (Fig. 12). As mentioned in the catalytic performance in "FUR-ethanol-O₂" system, the uniform dispersion and small size of Au particles in Au@UiO-66 catalyst might be responsible for the excellent performance in oxidative esterification process. However, in the oxidative condensation process of FUR with ethanol- O_2 , the Au@UiO-66-COOH shows better catalytic activity. So we con-



Fig. 10. XPS spectra of the fresh and used Au@UiO-66 catalysts were synthesized using I-H method: (a) fresh Au@UiO-66; used Au@UiO-66.

cluded that the oxidation of hemiacetal was the rate-determining step in the process of oxidative esterification, which can be affected greatly by the size and dispersibility of Au particles. While the formation of acetaldehyde may be the rate determining step in oxidative condensation process of FUR.

The crystalline structure of the UiO-66-X (X = -H, -COOH, $-NH_2$, $-NO_2$ and $-NH_3Cl$) does not change before and after the functional groups or Au nanoparticles were introduced, as shown by the XRD patterns (Fig. 14). The well defined and highly intense

peaks demonstrate the existence of MOFs phase. Some Au crystalline phases can be detected in the XRD patterns of UiO-66-X, which confirm the high purity of the synthesized UiO-66, the functional UiO-66 and Au@UiO-66-X catalyst.

3.4. Possible reaction mechanism

In order to reveal the reaction mechanism of catalytic oxidation processes, the numerous control experiments have been per-



Fig. 11. HRSEM images of Au@UiO-66-X catalysts: (a) Au@UiO-66; (b) Au@UiO-66-COOH; (c) Au@UiO-66-NH2; (d) Au@UiO-66-NH2; (e) Au@UiO-66-NH3Cl.



Fig. 12. Au element mapping from HRSEM images of Au@UiO-66-X catalysts: (a) Au@UiO-66; (b) Au@UiO-66-COOH; (c) Au@UiO-66-NH2; (d) UiO-66-NO2; (e) UiO-66-NH3Cl.

formed (Table 6). In methanol, the 2-furoic acid is used to replace FUR with Au@UiO-66 and K₂CO₃ as catalyst and no esterification takes place (Entry 1, Table 6), which shows the intermediate should be hemiacetal rather than 2-furoic acid in the "FURmethanol-O₂" system. When the oxidation of FUR and methanol was performed under N₂ atmosphere, only the compound **2** was produced via the acetalization process where a 33.7% conversion in 99% selectivity was obtained (Entry 2, Table 6). This demonstrated the oxidation process with O_2 is crucial for the generation of compound **1** during reaction. Combined with the data of entries 1, 3, 5 in Table 2, it is concluded that compound 2 should be thermodynamically stable, and the route through the oxidation of hemiacetal to ester should be favorable in the "FUR-methanol-O₂" system (shown in Route i of Scheme 1). Furthermore, similar control experiments have also been performed in the "FURethanol-O₂" system. The reaction route of oxidative esterification process is verified again (Entries 4 and 5, Table 6). Thus, in the oxidation esterification of FUR with aliphatic alcohol, the role of UiO-66 and K₂CO₃ is promoting the hemi-acetalization of FUR with alcohol, while the Au nanoparticles and O₂ can efficiently impel the selective oxidation of in situ generated hemi-acetal intermediate.

On the other hand, in the "FUR-ethanol- O_2 " system, the hydrogen transferring reaction occurs under N_2 atmosphere and the compound **3** and furfuryl alcohol were generated as main products in the presence of Au catalyst and K₂CO₃ (Entries 5 and 6, Table 6), which is consistent with the Route iv of Scheme 1. Combined with entries 1 and 3 of Table 4, it can be concluded that the Au@UiO-66-COOH is very efficient for the oxidation of furfuryl alcohol to FUR that will impel the rapid proceeding of tandem oxidative condensation reaction. Really, the results from the oxidation of furfuryl alcohol in ethanol confirm this deduction (Entries 7 and 8, Table 6). Therein, only 8.0% conversion of furfuryl alcohol was attained



Fig. 14. XRD patterns of Au@UiO-66-X catalysts: (a) UiO-66; (b) Au@UiO-66; (c) UiO-66-NH₂; (d) Au@UiO-66-NH₂; (e) UiO-66-NO₂; (f) Au@UiO-66-NO₂; (g) UiO-66-COOH; (h) Au@UiO-66-COOH.

using Au@UiO-66 as the catalyst, while the conversion of furfuryl alcohol reached 57.5% with Au@UiO-66-COOH as the catalyst under similar conditions. Also, it is found that the Au@UiO-66 favors the production of compound **4**; However, the Au@UiO-66-COOH catalyst is beneficial to the generation of compound **3** where the FUR is obtained as other product in the oxidation of furfuryl alcohol. So, in the oxidative condensation of FUR with ethanol, first step can be hydrogen transferring process between FUR and etha-



Fig. 13. TEM images of Au@UiO-66-X catalysts: (a) Au@UiO-66; (b) Au@UiO-66-COOH; (c) Au@UiO-66-NH₂; (d) UiO-66-NO₂; (e) UiO-66-NH₃Cl.

Tabl	e 6
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The results of control experiments to explore the mechanism.^a

Entry	Catalyst	Reactant	Conversion (%) ^b	Product d	listribution (%) ^b		
				1	2	3	4
1	Au@UiO-66	2-Furoic acid + methanol	-	-	-	-	-
2 ^c	Au@UiO-66	FUR + methanol	33.7	-	100	-	-
3	Au@UiO-66	FUR + methanol	100	100	-	-	-
4	Au@UiO-66	2-Furoic acid + ethanol	-	-	-	-	-
5 [°]	Au@UiO-66	FUR + ethanol	36.2	-	-	44.7	-
6 ^c	Au@UiO-66-COOH	FUR + ethanol	43.9	-	-	47	-
7 ^d	Au@UiO-66	Furfuryl alcohol + ethanol	8.0	-	-	28.5	33.4
8 ^d	Au@UiO-66-COOH	Furfuryl alcohol + ethanol	57.5	-	-	64.2	5.5

^a Reaction conditions: 0.1 g reactant (2-fuoric acid, FUR, furfuryl alcohol), 25 mg catalyst (4.7 wt% Au loading), 25 mg K₂CO₃, in 15 mL of methanol or ethanol, under 0.3 MPa of O₂, at 140 °C, for 4 h.

^b The results are obtained by GC using the internal standard technique.

^c The reaction is performed under N₂ atmosphere, and another product is furfuryl alcohol in the FUR + ethanol.

^d Other product generally refers to FUR as by-product.

nol, and next step is the rapid condensation happening between FUR and very little *in situ* generated acetaldehyde, then simultaneously little furfuryl alcohol is oxidized to generate FUR and enter into the following catalytic cycle. In this reaction, the synergetic effect among UiO-66-COOH and K₂CO₃ should be responsible for the hydrogen transferring process and the subsequent condensation process. Meanwhile, the Au@UiO-66-COOH can promote selective oxidation of furfuryl alcohol to FUR in the presence of molecular oxygen.

4. Conclusions

In conclusion, we developed a novel catalytic system for regulating the oxidative transformation of FUR with aliphatic alcohol in the presence of molecular oxygen. For the "FUR-methanol-O2" system, a 100% selectivity of 1 with full conversion of FUR was obtained using Au@UiO-66 as the catalyst. Moreover, in the "FUR-ethanol-O₂" system, the orientation of oxidative transformation of FUR may be successfully regulated by functionalizing the MOFs support with different functional groups. As a result, about 84.1% selectivity of 3 was attained using Au@UiO-66-COOH as the catalyst, while the main product is compound **4** when the Au@UiO-66 catalyst and K₃PO₄ were used. The results also demonstrated the size and uniform distribution of Au nanoparticles play critical role for oxidative esterification of FUR with aliphatic alcohol. The oxidative condensation of FUR with ethanol is via hydrogen transferring and rapid condensation to produce the target product, where Au@UiO-66-COOH catalyst can efficiently promote the oxidation of the intermediate furfuryl alcohol. It provides a promising approach for the efficient utilization of biomassderived platform compound in chemical industry.

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Appendix A. Supplementary material

Crystal structure of UiO-66, Survey XPS scan, H₂-TPR patterns, GC and GC-MS, ¹H NMR spectrum, Theoretical calculation of carbon balance, etc. Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j. jcat.2018.04.030.

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