



# 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 impregnation-reduction-H<sub>2</sub> (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-NH<sub>2</sub>, Au@UiO-66-NO<sub>2</sub>, Au@UiO-66-COOH and Au@UiO-66-NH<sub>3</sub>Cl have been prepared with I-H method and employed for oxidative valorization of furfural with ethanol. Experimental results showed that, in “FUR-ethanol-O<sub>2</sub>” 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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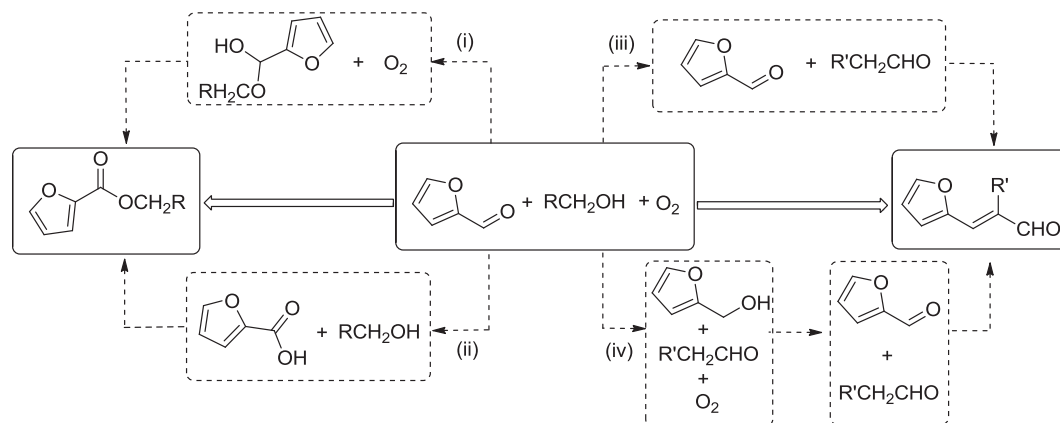
## 1. Introduction

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, sev-

eral 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  $\alpha$ -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-O<sub>2</sub>” 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 aldol 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  $O_2$  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 zirconium-based 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,  $Zr_6O_4(OH)_4(-CO_2)_{12}$ , 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- $NH_2$  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  $-COOH$ ,  $-NH_2$ ,  $-NO_2$ , and  $-NH_3Cl$  can further regulate the reaction pathway between the oxidative esterification and the oxidative condensation in the “FUR-ethanol- $O_2$ ” 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 ( $H_2BDC$ ), 2-aminoterephthalic acid ( $H_2BDC-NH_2$ ), 2-nitroterephthalic acid ( $H_2BDC-NO_2$ ), 1,2,4-benzenetricarboxylic acid ( $H_2BDC-COOH$ ),  $ZrCl_4$ ,  $ZrOCl_2 \cdot 8H_2O$ ,  $ZrO(NO_3)_2 \cdot xH_2O$ ,  $K_2CO_3$ , FUR and  $HAuCl_4 \cdot 4H_2O$  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  $ZrCl_4$  (0.053 g, 0.227 mmol) and  $H_2BDC$  (0.034 g, 0.227 mmol) were dissolved in 16 mL *N,N*-dimethylformamide (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.

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