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Communication

A Tunable Process: Catalytic Transformation of Renewable Furfural with Aliphatic Alcohols in the Presence of Molecular Oxygen

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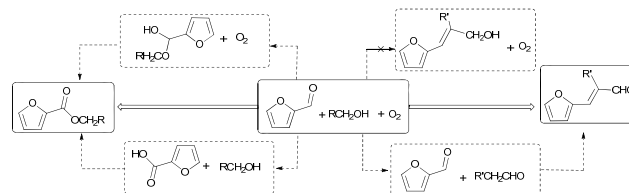
A tunable transformation of renewable furfural with aliphatic alcohols in the presence of O₂ is developed. Based on nano Au catalyst and potassium carbonate, a 91.8% yield of methyl 2-furoate in 98.7% selectivity is obtained via the oxidative esterification in furfural-methanol-O₂ system; while, a 91.4% yield of 3-(furan-2-yl)-2-methylacrylaldehyde in 97.2% selectivity is attained via the oxidative condensation in furfural-n-propanol-O₂ system.

Renewable biomass resources are promising alternatives for the sustainable supply of chemical intermediates and liquid fuels.¹ The selective transformation of biomass or bio-based platform compound via catalytic cascade reaction is beneficial to improve the efficiency and cut energy consumption in a large-scale and sustainable industrial production.² Furfural (FUR) is one of the most common platform chemicals derived from lignocellulosic biomass, with an annual production volume of more than 200 000 tonnes.³ FUR can be obtained from C5 carbohydrates and its further application play a critical role in the valorization of the hemicellulose contained in biomass feedstock.⁴

Actually, utilization of furfural as the starting material could synthesize a variety of chemicals including numerous commercial products,⁵ in which furfural can be efficiently converted by hydrogenation, oxidation, reductive amination, decarbonylation, nitration, condensations, etc.⁶ In particular, the efficient aldol condensation of furfural with acetone has been proposed as an intermediate step to synthesize second generation biofuels obtained from lignocellulosic biomass.⁷ As a matter of course, the condensation reaction of furfural and aldehyde is also feasible to impel two carbon molecules together and produce longer hydrocarbon chains and low volatile liquid transport fuels. Herein, it is well known that the acetone and aldehyde can be produced from the oxidation of secondary and primary alcohols in the presence of molecular oxygen.⁸ Therefore, from the viewpoints of green and sustainable chemistry, the cascade transformation of alcohol oxidation and aldol condensation in ternary FUR-alcohol-O₂ (FAO) system will be very promising to efficient utilization of FUR. However, it is inevitable that more reaction routes can happen in FAO system. For example, the oxidative esterification of furfural has also been reported to produce alkyl furoates which can be often applied as flavour and fragrance components in the fine chemical industry.⁹⁻¹⁰ It is shown that furfural can be converted to methyl furoate by the oxidative esterification with methanol in the presence of Au/TiO₂ catalyst and NaCH₃O as

additive.⁹ Moreover, Pinna et. al.¹⁰ found that gold-supported sulfated zirconia was also active for the oxidative esterification.

In FAO system, the main reaction routes are given in Scheme 1. It is shown that the first reaction may be semi acetal process of FUR with alcohol, oxidation of FUR with oxygen or oxidation of alcohol with oxygen, while the condensation of FUR with alcohol hardly happens. It is obvious that the oxidation-condensation reaction and the oxidative esterification are two competitive cascade processes, which process is dominant will depend on the reaction micro-environment and regulation of catalyst.



Scheme 1. the main reaction routes and products in FAO system

In this communication, we propose a tunable catalytic reaction of furfural and aliphatic alcohols in the presence of a nano Au catalyst and alkali metal carbonate, where the oxidation-condensation or oxidative esterification can be successfully performed based on the variety of alcohol in FAO system. It was found that the oxidative esterification reaction occurs in FUR-methanol-O₂ (FMO) system; however, the efficient and selective oxidation-condensation process is achieved in FUR-n-propanol-O₂ (FPO) system. For instance, a 91.8% yield of methyl 2-furoate in 98.7% selectivity was obtained in FMO system, while a 91.4% yield of 3-(furan-2-yl)-2-methylacrylaldehyde in 97.2% selectivity was attained in FPO system under suitable conditions.

Initially, the reactions of FUR with methanol-O₂ (Eq. 1) and FUR with n-propanol-O₂ (Eq. 2) were carried out with different catalyst under same conditions, respectively. The experimental results are summarized in Table 1.

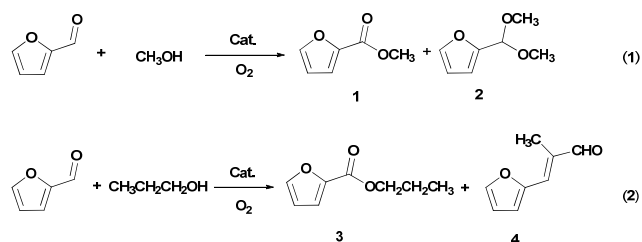


Table 1. The catalytic transformation of furfural with Methanol-O₂ and propanol-O₂ catalyzed by nano Au catalysts^[a]

Entry	Catalytic system	FUR-methanol-O ₂ system			FUR-n-propanol-O ₂ system		
		Conversion (%) ^[b]	Selectivity (%) ^[b]		Conversion (%) ^[b]	Selectivity (%) ^[b]	
			1	2		3	4
1	Au/FH	54	11	89	24	99	1
2	Au/FH+K ₂ CO ₃	93	99	1	94	3	97
3	K ₂ CO ₃	18	4	96	6.1	2	98
4	FH + K ₂ CO ₃	20	1	99	34	2	98
5	Au/H+K ₂ CO ₃	48	93	7	85	1	99
6	Au/Fe ₃ O ₄ +K ₂ CO ₃	41	82	18	86	3	97
7	Au/CeO ₂ +K ₂ CO ₃	55	82	18	88	3	97
8	no catalyst	15	0	100	<1	-	-

[a] Reaction conditions: 0.2 g FUR, 0.05g nano Au (5.0 wt.% loading) catalyst, 0.05 g K₂CO₃, in 15 mL of methanol or n-propanol, under 0.3 MPa of O₂, reaction time 4 h, temperature 140 °C. [b] The results are obtained with internal standard technique by GC; the compound **1** is methyl furoate; the compound **2** is 2-(dimethoxymethyl)furan; the compound **3** is propyl furan-2-carboxylate; the compound **4** is 3-(furan-2-yl)-2-methylacrylaldehyde.

In the presence of single Au/FH catalyst (the preparation method is shown in supported in formation, FH refers to Fe_xO_y-Hydroxyapatite), a 54% conversion and 89% selectivity for **2** was obtained in FMO system; while, a 24% conversion and 99% selectivity for **3** was attained in FPO system (entry 1). With the addition of K₂CO₃, the oxidative esterification of FUR are obviously improved in FMO system and a 93% conversion and 99% selectivity for **1** was obtained; meanwhile, the highly selective oxidation-condensation process was achieved in FPO system in which a 94% conversion and 97% selectivity for **4** was attained at 140 °C for 4 h (entry 2). Moreover, the control experiment showed that, in the presence of only K₂CO₃ or FH-K₂CO₃, an 18% or 20% conversion and more than 96% selectivity for **2** was respectively obtained in FMO system which indicates that Au catalyst is responsible for the reaction orientation and K₂CO₃ play a acceleration role in FMO system; while, a 6.1% or 34% conversion and 98% selectivity for **4** was attained in FMO system (entries 3 and 4), which exhibits that K₂CO₃ provides a significant effect on product selectivity and the nano Au catalyst promotes the oxidation of n-propanol to generate propanal in FPO system. Furthermore, the catalytic performances of the Au/H-K₂CO₃, Au/Fe₃O₄-K₂CO₃ and Au/CeO₂-K₂CO₃ catalysts were also investigated. As a result, it was found that the conversions of FUR are 48%, 41% and 55% in FMO system, respectively. Correspondingly, the conversions of FUR are respectively 85%, 86% and 88% in FPO system (entries 5-7). Also, the blank experiment was carried in FAO system which showed that only semi acetal or no reaction happens in the absence of any catalyst (entry 8). These results indicated that the cooperation effect of iron oxide and hydroxyapatite in Au/FH catalyst has more significant influence in FAO system. Moreover, the high activity of Au/FH catalyst should be contributed to its large surface area and pore volume (Table 1s, ESI), small and average Au nanoparticles (Figure 2s, ESI) and numerous weak acid sites (Figure 3s, ESI), which are obtained from the BET, XRD, TEM and TPD measurements.

In order to further reveal the influence of base as the additive, several typical bases including Na₂CO₃, KHCO₃, Li₂CO₃, Cs₂CO₃ and NaOH are chosen and used in the reaction of FUR with alcohols. As shown in Table 2, when Na₂CO₃ was used instead of K₂CO₃, a 52% conversion and 37% selectivity of **1** was obtained in FMO system, while 25% conversion and 74% selectivity of **4** was attained in FPO system (entry 1). Moreover,

29% and 81% conversions were respectively obtained in FMO and FPO systems using KHCO₃ as the base additive (entry 2). Furthermore, when Li₂CO₃ and Cs₂CO₃ was added, the conversion of FUR was 93% and 95% in FMO system, while the conversion of FUR was 38% and 76% in FPO system, respectively (entries 3-4). In the case of NaHCO₃, a 52% conversion in 39% selectivity of **1** was obtained in FMO system; while, a 64% conversion in 77% selectivity of **4** was attained in FPO system (entry 5). When NaOH was used as the additive, 68% and 74% conversions were obtained in FMO and FPO systems, respectively (entry 6). On the other hand, using H₃PO₄ as the acidic additive, the selectivity of **1** in FMO system is very low and the main product is the compound **2**. Meanwhile, in FPO system, the selectivity of **4** is very low and the dominate product is 2-(dipropoxymethyl)furan which is generated from acetal process. Considering the efficiency and economy, potassium carbonate is the best base additive in both FMO and FPO systems in the presence of Au/FH catalyst.

Table 2. The effects of various bases and acid additive in FAO system^[a]

Entry	The additive	In FMO system		In FPO system	
		Conv. (%) ^[b]	Select. (%) ^[b]	Conv. (%) ^[b]	Select. (%) ^[b]
1	Na ₂ CO ₃	52	37	25	74
2	KHCO ₃	29	88	81	90
3	Li ₂ CO ₃	93	91	38	-
4	Cs ₂ CO ₃	95	94	76	88
5	NaHCO ₃	52	39	64	77
6	NaOH	68	97	74	58
7	H ₃ PO ₄	74	1	56	5

[a] Reaction conditions: 0.2 g FUR, 0.05g Au/FH (5 wt.% Au loading) catalyst, 0.05 g the additive, in 15 mL of methanol or n-propanol, under 0.3 MPa of O₂, reaction time 4 h, temperature 140 °C. [b] The results are obtained with internal standard technique by GC; the select. in FMO system refers the selectivity of **1**; the select. in FPO system refers the selectivity of **4**.

As we know, carbonates are often used as weak bases in numerous organic reactions involving proton extraction. In general, a stoichiometric excess of carbonate is necessary to promote a high substrate conversion except the Au-catalyzed reaction.¹¹ Herein, the effect of amount of K₂CO₃ in FPO system was further investigated and the results are presented in Figure 1. It can be seen that the conversion of FUR and the selectivity of **4** was gradually increased with K₂CO₃ being added from 0.01 to 0.05 g in the presence of Au/FH catalyst. Then, the conversion was almost kept unchanged with the addition of more K₂CO₃;

while, the selectivity of **4** was decreased a little, which can be attributed to the occurrence of self-condensation of a little propanal according to the result of GC/MS detection.

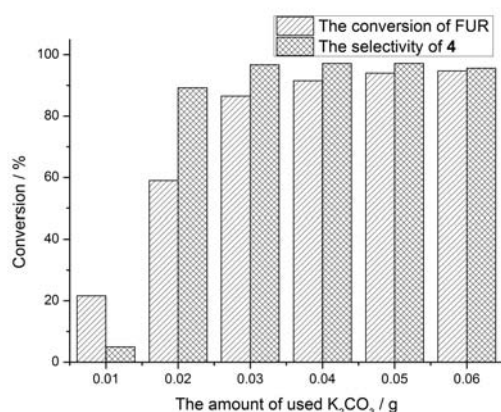


Figure 1. The effect of amount of K_2CO_3 in FPO system [Reaction conditions: 0.2 g FUR, 0.05g Au/FH (5 wt.% Au loading) catalyst, in 15 mL n-propanol, under 0.3 MPa of O_2 , for 4 h, at 140 °C]

Furthermore, the recycling of Au/FH catalyst has been examined in FAO system. 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 Figure 2, it was seen that the yield of **1** in FMO system and the yield of **4** in FPO system still kept about 90 % even after the Au/FH catalyst being recycled five times. These results showed that Au/FH catalyst was efficient and kept stable in both the FMO system and FPO system.

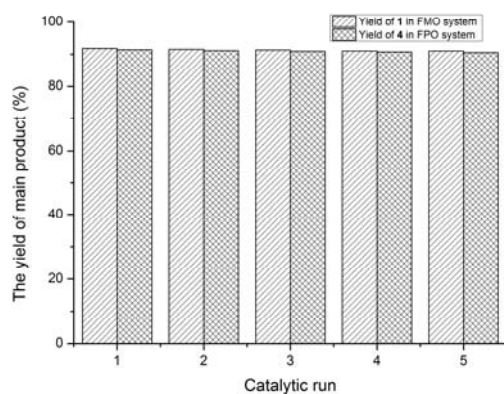


Figure 2. The recycling of the Au/FH catalyst in FAO system [Reaction conditions: 0.2 g FUR, 0.05 g Au/FH (5 wt.% Au loading) catalyst, in 15 mL methanol or n-propanol, under 0.3 MPa of O_2 , for 4 h, at 140 °C]

The reaction mechanism is also studied based on the control experiments and catalytic principle of the reaction. The results are shown in Table 3. First, the reaction of furanic acid with methanol was carried out and no esterification happens in the presence of Au/FH catalyst and K_2CO_3 (entry 1). Second, the reaction of FUR and methanol under nitrogen atmosphere showed that the acetalization is the main route, in which a 46% conversion in 99% selectivity of **2** was obtained (entry 2). These indicate that the oxidative esterification is achieved *via* the semi-

acetalization and further oxidation of hydroxyl group of intermediate in FMO system (see upper-left route in Scheme 1). In the reaction, the function of support and K_2CO_3 is promoting the semi-acetalization of FUR with methanol, while the Au/FH catalyst efficiently impels the selective oxidation of generated semi-acetal intermediate.

Table 3. The results of control experiments to study the mechanism ^[a]

Entry	Catalyst	Reactant	Conv. (%) ^[b]	Product distribution ^[b]
1	Au/FH+ K_2CO_3	Furanic acid +CH ₃ OH	No reaction	-
2 ^[c]	Au/FH+ K_2CO_3	FUR+CH ₃ OH	46%	99% for 2
3 ^[d]	Au/FH+ K_2CO_3	FUR+propanol	39%	78% for 3
4	Au/FH+ K_2CO_3	FUR+propanal	94%	48% for 4
5	Au/FH	FUR+propanal	21%	96% for 4
6	K_2CO_3	FUR+propanal	92%	45% for 4
7 ^[c]	Au/FH+ K_2CO_3	FUR+propanol	42%	99% for acetal
8 ^[d]	Au/FH+ K_2CO_3	FUR+propanal	99%	97% for 4

[a] Reaction conditions: Furanic acid or FUR 0.2 g, Au/FH catalyst (5 wt.% Au loading) 0.1g, 0.05 g additive, in 15 mL of methanol, n-propanol or propanal under 0.3 MPa of O_2 , reaction time 4 h, temperature 140 °C.

[b] The results are obtained by GC with internal standard technique; [c] the reaction was performed under N_2 atmosphere, and the main product is 2-(dipropoxymethyl)furan. [d] the ratio of FUR and alcohol (aldehyde) is 10:1 (mol : mol) and the conversion of alcohol or aldehyde is presented.

On the other hand, the reaction of FUR with propanol in the ratio of 10 : 1 was performed, in which a 39% conversion of n-propanol and 78% selectivity for **3** was attained (entry 3). Also, the reaction of FUR with propanal was detected where various products obtained from different processes including FUR-propanal condensation, self condensation of propanal and FUR-FUR disproportionation process, etc.. Therefore, only 48% selectivity of **4** was attained although the conversion of FUR arrived at 94% (entry 4). Otherwise, a 21% conversion and 96% selectivity for **4** was obtained in the presence of single Au catalyst (entry 5), and a 92% conversion in 45% selectivity of **4** was attained in the presence of only K_2CO_3 (entry 6). In addition, a 42% conversion and 99% selectivity for 2-(dipropoxymethyl) furan was obtained when the reaction of FUR with n-propanol is performed under nitrogen atmosphere (entry 7). Particularly, the reaction of FUR and propanal in the ratio of 10 : 1 was also performed, in which a 99% conversion of propanal and 99% selectivity for **4** was attained in the presence of Au catalyst and K_2CO_3 (entry 8). This exhibits that highly selective production of **4** is achieved when the reaction was carried out between a large number of FUR and little propanal. So, it can be concluded that the first step is the oxidation of little propanol to propanal, and next step is the rapid condensation happening between FUR and very little *in situ* generated propanal in FPO system (see lower-right route in Scheme 1). Correspondingly, in this reaction, the Au/FH catalyst is responsible for the selective oxidation of propanal; while, the role of K_2CO_3 is promoting the next condensation process.

Conclusions

In summary, a tunable and efficient transformation of FUR, aliphatic alcohols with molecular oxygen has been achieved. In the presence of the Au/FH catalyst and potassium carbonate, a

oxidative esterification process occurs in FMO system, in which a 91.8% yield of methyl 2-furoate in 98.7% selectivity is obtained at 140 °C for 4 h under 0.3 MPa O₂; while, a highly selective oxidative condensation process arises in FPO system where a 91.4% yield of 3-(furan-2-yl)-2-methylacrylaldehyde in 97.2% selectivity is attained under same conditions. This will provide a promising approach for the efficient valorization of hemicellulose in the biomass transformation.

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Notes and references

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- † Electronic Supplementary Information (ESI) available: [Experiment such as catalyst preparation and characterization, the GC and GC-MS spectra of the product and several results for optimization of conditions]. See DOI: 10.1039/b000000x/
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