Accepted Manuscript

Title: Au-Catalyzed Oxidative Condensation of Renewable Furfural and Ethanol to Produce Furan-2-acrolein in the Presence of Molecular Oxygen



Author: Xinli Tong Zonghui Liu Jianli Hu Shengyun Liao

PII:	S0926-860X(15)30253-2
DOI:	http://dx.doi.org/doi:10.1016/j.apcata.2015.11.025
Reference:	APCATA 15652
To appear in:	Applied Catalysis A: General
Received date:	12-8-2015
Revised date:	20-10-2015
Accepted date:	14-11-2015

Please cite this article as: Xinli Tong, Zonghui Liu, Jianli Hu, Shengyun Liao, Au-Catalyzed Oxidative Condensation of Renewable Furfural and Ethanol to Produce Furan-2-acrolein in the Presence of Molecular Oxygen, Applied Catalysis A, General http://dx.doi.org/10.1016/j.apcata.2015.11.025

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Au-Catalyzed Oxidative Condensation of Renewable Furfural and Ethanol

to Produce Furan-2-acrolein in the Presence of Molecular Oxygen

Xinli Tong* tongxinli@tju.edu.cn or tongxli@sohu.com, Zonghui Liu, Jianli Hu*

jianlihu@hotmail.com, Shengyun Liao

Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemistry

and Chemical Engineering, Tianjin University of Technology, Tianjin 300384, P. R. China

*Corresponding author. Tel.: +86-22-60214259; Fax: +86-22-60214259.

Graphical Abstract



The efficient aerobic oxidative condensation of renewable furfural and ethanol in the presence of a nano Au catalyst and potassium carbonate has been developed and a 70.6% yield of furan-2-acrolein is obtained.

Highlights

- A catalytic system is developed for the volarization of renewable furfural.
- Oxidative condensation of furfural with ethanol to furan-2-acrolein is achieved.
- The catalyst system is composed of Au nanoparticle and potassium carbonate.
- A 94.1% furfural conversion in 75.0% selectivity of furan-2-acrolein is obtained.

Abstract

A specialty chemical compound, furan-2-acrolein, can be produced from renewable feedstock *via* furfural. An efficient catalytic process related to oxidative condensation of furfural and ethanol using supported Au catalyst has been developed. A series of solid catalysts including Au/Al₂O₃, Au/CeO₂, Au/Fe₃O₄, Au/HTc (hydrotalcite calcined) and Au/Nb₂O₅ are prepared and their catalytic activities in oxidative condensation of furfural with ethanol are compared. Moreover, the influence of the presence of base promoters, such as K₂CO₃, on Au catalyst performance is investigated. The physical properties of these catalysts are characterized by XRD, TEM, SEM, UV-vis and BET techniques. The impact of reaction variables on catalyst performance is measured. It has been found that, in the presence of Au/Al₂O₃ and potassium carbonate, 94.1% conversion of furfural and 75.0% selectivity to furan-2-acrolein are obtained under the conditions of 140 °C, 0.3 MPa of O₂ and reaction time of 4 hours.

Keywords: Furfural; Ethanol; Gold; Furan-2-acrolein; Biomass conversion.

1. Introduction

Nowadays, growing concerns about depletion of petroleum reserve and climate change have been a driving force for the exploration of alternative resources for energy and chemical production. Therein, the applications of photosynthesis, wind-based, geothermal, and biomass-based energy source appear to be promising in the future. Particularly, renewable biomass is generally considered as the only renewable resource with the potential to replace the fossil fuels for the production of both chemicals and liquid fuels [1-3]. Obviously, the selective transformation of biomass or bio-based platform compound *via* catalytic reaction is beneficial to the increase in efficiency and reduction in energy consumption in a sustainable industrial process [4]. Furfural (FUR) is one of the most common chemicals derived from lignocellulose with an annual production volume of more than 200 000 ton [5]. FUR is often obtained from C5 carbohydrates and its industrial application is critical in valorization of hemicellulose in biomass [6-7]. A variety of chemicals can be synthesized from FUR[8], wherein FUR is converted by hydrogenation, oxidation, reductive amination, decarbonylation, nitration, condensations, etc. [9]. For example, aldol condensation of FUR with acetone has been proposed as an intermediate step to synthesize second generation biofuels from lignocellulosic biomass [10-14]. In organic chemistry, the condensation of FUR and aldehydes is a feasible pathway to form longer chain but low volatile liquid transport fuels. Furthermore, acetone and aldehydes can be produced from the oxidation of secondary and primary alcohols in the presence of molecular oxygen [15].

On the other hand, ethanol is considered as one of important molecular building blocks, having established production volume from renewable feedstock [16, 17]. The conversion of bioethanol to commodity chemicals via chemical or biochemical methods has been studied [18-20]. Thus, the

cascade transformation of alcohol oxidation and aldol condensation for the formation of furanic derivatives prove to be effective utilization of renewable chemical intermediates. However, it is inevitable that many other reaction pathways can take place in the FUR-ethanol-O₂ (FEO) system when molecular oxygen is chosen as an oxidant. As reported in our previous publication [21], the possible reaction pathways are given in Scheme 1. It is shown that the first reaction may be semi acetal reaction of FUR with ethanol, oxidation of FUR with O₂ or oxidation of ethanol with O₂, where the condensation of FUR with ethanol hardly happens. In the following, the product ethyl furoate can be obtained *via* the oxidation of ethoxy(furan-2-yl)methanol or the esterification of 2-furoic acid, while the product furan-2-acrolein can be attained from the condensation of FUR with acetaldehyde. It is obvious that the oxidative condensation reaction and the oxidative esterification reaction are two competing pathways.

In this article, we propose a selective oxidative condensation of FUR and ethanol using supported Au and base promoter as the catalyst in the presence of molecular oxygen. It is found that the main product is furan-2-acrolein where a 94.1% conversion of FUR and a 75.0% selectivity is obtained at 140 °C under 0.3 MPa of O_2 for 4 hours.

2. Experimental

2.1 Reagents and equipment

The following analytical grade chemicals were purchased from commercial venders: furfural, ethanol, HAuCl₄, NaOH, KOH, Fe₂(SO₄)₃, FeSO₄, Mg(NO₃)₂·H₂O, Al(NO₃)₃·9H₂O, Ce(NO₃)₃·6H₂O, urea, Nb₂O₅, NaCO₃, NaHCO₃, KHCO₃, Cs₂CO₃, Ca(OH)₂, Li₂CO₃, H₃PO₄, CaCO₃, MgO and CaO. The high purity oxygen gas supplied in a high-pressure cylinder was used without further treatment. X-ray diffraction (XRD) measurement was performed by diffractmeter with Cu Ka radiation (0.02 °

resolution) and the diffraction spectra were collected from a range of 20 to 80 ° [2 θ]. Moreover, the surface morphology and particle size of catalytic materials were characterized by scanning electron microscope (SEM: JSM-6301F, JEOL) and transmission electron microscope (TEM: JEM-2100, JEOL). The solid UV characterization was carried out on a U-3310 apparatus from HITACHI corporation. BET surface areas, pore volumes, and average pore diameters of the catalyst samples were measured by N₂ (77 K) adsorption using a Micromeritics ASAP2020M system. Therein, the catalyst samples were pretreated under vacuum at 250 °C for 4 hours before the measurement. The average pore diameter data were calculated according to the Barrett-Joyner-Halenda (BJH) model in absorption and desorption period.

The quantitative analysis of the products was performed on a GC with hydrogen ion flame detector. GC-MS analysis was carried out to identify chemical structures of the products (Agilent 6890/5973) In addition, nuclear magnetic resonance (NMR) measurement was performed on a Bruker 400 MHZ spectrometer.

2.2 Synthesis of Different Metal Oxides as the Supports

2.2.1 The Preparation of Alumina

A certain amount of $Al(NO_3)_3 \cdot 9H_2O$ and $(NH_4)_2CO_3$ was dissolved in deionized water, then transferred into a 250 ml three-neck flask. The pH value of the solution was controlled at about 8.5. After the precipitation is completed, the solution was stirred for another 2h. The precipitates were filtered and washed repeatedly with the deionized water. After drying at 373 K for 24 hours, the catalyst sample was calcined at 873 K for 2 hours.

2.2.2 The Preparation of Iron Oxide

Fe₂(SO₄)₃ (0.01mol) and FeSO₄ (0.01mol) were dissolved in water in a three-neck flask. The

flask was placed in water bath at 45°C, in which ammonia was added dropwise until pH=10-11. The reaction was continued for 1 hour, after which the substrate was separated using magnetic separation technique. The substrate was washed with distilled water until pH=7, then vacuum dried at 80°C overnight.

2.2.3 The Preparation of Hydrotalcite Calcined (HTc)

To prepare HTc, 30.76 g of $Mg(NO_3)_2 \cdot 6H_2O$ and 15 g $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in 400ml of water, followed by the addition of 72 g urea under agitation. The solution was maintained at boiling point for 8 hours, then cooled to room temperature under which precipitation took 12 hours to finish. The precipitates were washed with distilled water at 60°C overnight and calcined at 500°C for 3 hours. The catalyst sample was designated as HTc with molar ratio of Mg/Al being 3.

2.2.4 The Preparation of Cerium Oxide

To synthesis nanorods, 0.868 g of Ce(NO₃)₃·6H₂O and 9.6 g of NaOH were dissolved in 5 and 35 ml of deionized water, respectively. These two solutions were mixed in a Teflon bottle under agitation for 30 min. The formation of a milky slurry was observed. Subsequently, the mixed solution was transferred to a stainless steel autoclave, heated to 373 °C and held for 24 hours to form nanorods. After the hydrothermal treatment, white precipitates were separated by centrifugation, washed with deionized water and ethanol several times, followed by drying at 60 °C in air overnight.

2.3 The Preparation of Supported Au Catalysts

Au was deposited onto the above metal oxide supports *via* a precipitative deposition method. Typically, 40 ml HAuCl₄ aqueous solution (1.25 mg Au/ml) was charged into a beaker. The pH of the solution was adjusted to 9 by dropwise addition of 0.1 M NaOH solution under vigorous agitation and monitored with a pH meter. One gram of each support prepared above (Al_2O_3 , HTc,

CeO₂, Fe₃O₄ and Nb₂O₅) was separately added to the solution under agitation, and the pH values of the suspension were readjusted to 9 using 0.1 M NaOH solution. The suspension was heated to 65 °C under agitation and held at the temperature for 1 hour. The precipitates were filtered, washed with deionized water repeatedly and dried at 60 °C overnight. The catalyst samples were dried at 60 °C then calcined at 400 °C for 3 hours. These catalysts were designated as Au/Al₂O₃, Au/HTc, Au/CeO₂, Au/Fe₃O₄ and Au/Nb₂O₅ catalyst, respectively.

2.4 General Procedure for the Reaction of FUR and Ethanol in the Presence of Molecular Oxygen

Catalytic experiments were carried out in a 120 ml autoclave equipped with a magnetic agitator and automatic temperature control. A typical procedure for the reaction of FUR with ethanol is described as follow: 15 ml ethanol, 0.2 g FUR, 0.05 g Au/Al₂O₃ and 0.05 g K₂CO₃ are charged into the autoclave. The autoclaved is sealed and purged. Oxygen is introduced at room temperature till P=0.3 MPa, then heated to 140° C and kept for 4 hours. After the reaction, the autoclave was cooled, purged and the products were analyzed by GC and GC-MS.

3. Results and Discussion

3.1 The Characterization of Catalysts

3.1.1 XRD Patterns

Illustrated in Figure 1 are XRD patterns of different Au supported catalysts. The peak at 2θ =38.2°, 44.3°, 64.6° or 77.5° in the Au/Fe₃O₄, Au/HTc, Au/Al₂O₃ and Au/CeO₂ catalysts are attributed to the representative diffraction of planes of (111), (200), (220) and (311) of the Au(0) crystalline, which indicates the formation of Au crystal particles on these supports. In contrast, only the peaks

attributed to supports is exhibited in the catalyst Au/Nb₂O₅, which could be due to the low concentration of Au particles on support or irregular crystal structure of the Au nano particles.

3.1.2 BET Surface Measurement

Textural properties of the supported Au catalysts measured by nitrogen physisorption are shown in Table 1. The results indicate that the surface areas of Au/Al₂O₃ and Au/HTc catalysts are 314.1 m²·g⁻¹ and 216.6 m²·g⁻¹, respectively. The BET surface areas of Au/CeO₂ and Au/Fe₃O₄ are 93.78 m²·g⁻¹ and 37.45 m²·g⁻¹, respectively. However, the surface area of Au/Nb₂O₅ is only 0.9031 m² g⁻¹. Moreover, the pore volume of Au/Al₂O₃ catalyst is much larger than that of other catalysts which reaches about 0.5541 cm³ g⁻¹, whereas the pore volume of Au/Nb₂O₅ is only 0.0004 cm³ g⁻¹. Besides, the average pore diameters of these supported Au catalysts are between 39.58 nm to116.6 nm.

3.1.3 SEM Images

The morphology of different catalysts was characterized by SEM. Figures 2a-2d show SEM images of 4 catalysts. Loosely connected surface is observed on Au/Al₂O₃ catalyst. In contrast, on Au/HTc, irregular edges are observed, on top of which Au particles are uniformly distributed. Interestingly, tubular structure is formed on Au/CeO₂ catalyst whereas the surface of Au/Nb₂O₅ catalyst exhibits a smooth and oval-shaped structure which is consistent with low BET surface area.

3.1.5 TEM Images

These supported Au catalysts are also characterized by TEM technique. As shown in Figure 3, Au nano particles with average size of 6-7 nm are found in the image of the Au/Al_2O_3 catalyst. Moreover, the Au particle size between 7 nm to 8 nm is measured on Au/CeO_2 catalyst where the

support exhibits the obvious tubular structure from the TEM image. In contrast, the aggregation of Au particles is observed in the images of the Au/HTc catalyst and Au/Nb₂O₅ catalyst. So we can conclude that the small particle and regular distribution of gold nanoparticles were helpful to catalytic reaction in the FEO system.

3.1.6 UV-vis Characterization

Figure 4 presents the UV-vis spectra of different supported Au catalysts. In the spectra, Au particles can be detected by the appearance of well resolved plasmon peak at the wavelength of ca. 530 nm, which is a typical characteristic of metallic Au particles [22-24]. It can be observed that freshly prepared Au/Al₂O₃, Au/HTc and Au/Nb₂O₅ catalysts contain metallic Au particles, in which the peak values of Au/Al₂O₃ and Au/HTc catalysts appear at 530-535 nm, whereas the peak associated with Au/Nb₂O₅ catalyst appears at 550-560 nm. The shift of peak in the Au/Nb₂O₅ is attributed to the larger nano particles on the surface of the catalyst [25]. The peaks associated with Au/Fe₃O₄ and Au/CeO₂ catalysts are not very obvious in the spectra which is attributed to the Au particles entering into the pore channel of catalysts.

3.1.7 TPD Characterization

In order to determine acidic properties of the catalysts, the NH₃-TPD was performed from 100 to 950 ^oC, and the results were shown in Figure 5. In the TPD patterns of Au/Al₂O₃, Au/HTc and Au/CeO₂ catalysts, two signals observed at 260 ^oC and 590 ^oC were due to the presence of two different acidic sites, that of the Au/Fe₃O₄ catalyst was found at 210 ^oC and 650 ^oC, and the Au/Nb₂O₅ catalyst appeared at 590 ^oC and 850 ^oC; Obviously, Au/Al₂O₃, Au/HTc, Au/Fe₃O₄ and Au/CeO₂ mainly have

weak and middle acid sites, and Au/Nb₂O₅ mainly has middle and strong acid sites. Thus, it can be concluded that the numerous weak acid sites are helpful to catalytic reaction in FEO system.

3.2 The Reaction of FUR with Ethanol in the Presence of Molecular Oxygen

Initially, the catalytic reaction of FUR with ethanol in the presence of O_2 was carried out using different catalyst under the same reaction conditions. The reaction equation is shown in Scheme 2, where the products include furan-2-acrolein (Compound 1), ethyl furoate (Compound 2), 2-(diethoxymethyl)furan (Compound 3), and others. The experimental results with different catalytic systems are summarized in Table 2.

In the absence of catalyst, only 9.4% conversion of FUR is obtained. Using Au/Fe₃O₄ as the catalyst operated at 130°C, reaction time of 4 hours, about 29.5% conversion of FUR with 99% selectivity to Compound **3** are obtained. When a base catalyst promoter K_2CO_3 was added, the activity of Au catalyst in oxidative condensation of FUR with ethanol is obviously improved, showing 68.4% conversion of FUR and 91.3% selectivity towards Compound **1** (Entry 3). Moreover, three control experiments (Table 2, Entries 4-6) were performed in the presence of catalysts Fe_3O_4 - K_2CO_3 , K_2CO_3 and Fe_3O_4 . In these experiments, the conversions of FUR are 25.6%, 21.2% or 23.2%, respectively. When Fe_3O_4 - K_2CO_3 catalyst is used, only Compound 3 and others are formed, Compounds 1 and 2 are not observed, whereas K_2CO_3 and Fe_3O_4 are not active in the formation of Compounds 1-3. Compared with the results shown in Entries 2&3, synergistic effect between Au and K_2CO_3 is responsible for the entire reaction shown in Scheme 2, especially for the formation of Compounds 1 & 2. Furthermore, the catalytic performances of the Au/HTc- K_2CO_3 , Au/Co_3O_4 - K_2CO_3 and Au/Al_2O_3 - K_2CO_3 catalysts were also investigated (Entries 7-9). As shown in Table 2, the conversions of FUR are 78%, 80.1% and 84.9% whereas selectivities towards Compound 1 are 81%, 83.2% and

80.1%, respectively. When the Au/CeO₂ is used as a catalyst, the conversion is increased to 97.3% but the selectivity to Compound 1 is decreased to 54.9%. In the presence of Au/Nb₂O₅ - K₂CO₃, only 39.6% conversion of FUR and 84.6% selectivity of Compound 1 is attained under the same reaction conditions. The activity test is correlated to BET, XRD, SEM and TEM characterization data shown above, it is concluded that the high activity of supported Au catalyst is attributed to its large surface nanoparticles. area. large pore volume, and small Au Further investigation by temperature-programmed-desorption (TPD) measurement indicates weak acid sites play key role in the condensation reaction.

3.3 The Effect of Temperature

The effect of temperature on the reaction of FUR with C_2H_5OH was investigated with Au/Al_2O_3 - K_2CO_3 system and the results are shown in Figure 6. The conversion of FUR is gradually increased and starts to level off at 140 °C, meanwhile, the selectivity to Compound **1** is decreased on raising temperature from 110-140 °C, after which it starts to level off. The changes of selectivity to Compounds 2 and 3 show a similar trend, both leveling off at 140 °C.

3.4 The Effect of Reaction Time

The effect of reaction time on oxidative condensation of FUR with ethanol is presented in Figure 7. The conversion of FUR increases as reaction proceeds from 15 min to 4 hours, and then starts to level off. Meanwhile, the selectivity to Compound **1** increases gradually in the first 2 hours then declines afterwards. The highest yield to Compound **1** is reached at 70.6% in 4 hours reaction time in the presence of the Au/Al₂O₃-K₂CO₃ catalyst. Thus, under reaction system chosen, the optimal reaction time is 4 hours for the oxidative condensation of FUR with C₂H₅OH.

3.5 The Influence of Bases or Acids as Promotors

In order to further reveal the influence of base promoters on supported Au catalyst performance, several base promoters including Na₂CO₃, Cs₂CO₃, Li₂CO₃, KHCO₃, NaHCO₃, KOH and NaOH were chosen in the reaction of FUR with C₂H₅OH using Au/Al₂O₃ catalyst. As shown in Table 3, when Na₂CO₃ is used as a promoter, 61.7% conversion and 92.2% selectivity to Compound 1 are achieved (Entry 1). Moreover, 84.8% conversion and 79.8% selectivity to Compound 1 are attained when Cs_2CO_3 is used as a promotor (Entry 2). However, when promoter is switched to Li_2CO_3 , the conversion of FUR drops to 14.3%, selectivity to Compound 1 is 10.1% but selectivity to Compound 2 is increased to 81.9% (Entry 3). The result seems to indicate when the promoter's basicity is decreased, the reaction pathways favor the esterification reaction to form Compound 2, instead of condensation reaction which favors Compound 1. Furthermore, when KHCO₃ or NaHCO₃ are added, a 75.3% or 74% conversion of FUR are obtained in which the selectivities to Compound 1 are 86% and 80.5%, respectively (Entries 4-5). In the case of KOH, 86.3% conversion and 69.4% selectivity to Compound 1 are obtained (Entry 6). Similarly, 79.0% conversion and 81.8% selectivity to Compound 1 are attained using NaOH as a promotor (Entry 7). In addition, Ca(OH)₂, CaCO₃, CaO and MgO are also employed as the promotors for the oxidative condensation of FUR with ethanol. When Ca(OH)₂ or CaCO₃ is added as a promoter, only 27.5% or 14.8% conversion is obtained (Entry 8-9). With the promotion of CaO, the conversion and the selectivity to Compound 1 are increased to 61.3% and 68.3%, respectively (Entry 10). In contrast, when H₃PO₄ is used as an acidic additive, the selectivity to Compoud 1 decreases to almost zero Compound 3 becomes dominant (Entry 11). Considering catalytic effectiveness and the cost, K₂CO₃ is chosen as a most effictive base promoter for Au/Al₂O₃ catalyst.

3.6 The Influence of Promoter Loading on Au Catalyst Performance

It is well known that the function of carbonates as a weak base in organic synthesis is to extract proton from the substrate. Therefore, a stoichiometric excess of carbonate is generally necessary to promote a high substrate conversion except for Au-catalyzed reaction [26-28]. Herein, the effect of the amount of K_2CO_3 in the FUR oxidation is further investigated and the results are presented in Figure 8. It can be seen that both the conversion of FUR and the selectivity to Compound 1 are gradually increased with the increase in K_2CO_3 loading from 0.01 to 0.06 g. The conversion remains almost unchanged when more K_2CO_3 is added. In contrast, the selectivity to Compound 1 is slowly decreases with the increase of K_2CO_3 loading from 0.01g to 0.07g, which is attributed to the occurence of self-condensation of aldehyde. This is verified by GC-MS analysis.

3.7 The recyclability of catalysts

Furthermore, the recycling of Au/Al₂O₃ catalyst has been examined in the FEO 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 9. it was seen that the conversion of FUR still kept above 90% and the selectivity of **1** was as high as *ca*. 74% even after the Au/Al₂O₃ catalyst being recycled five times. These results showed that the Au/Al₂O₃ catalyst was efficient and kept stable in FEO system. In addition, the ICP-AES has been tested and the metal content in the filtrate is 0.05494%, which may be negligible. This result indicates that this reaction is the heterogeneous catalytic process.

3.8 Possible Reaction Mechanism

The reaction mechanism is elucidated based on experimental study and organic synthesis theories. Referring to the condensation of FUR with acetone [13, 14], the oxidation of alcohols [15] and a similar literature report to the on the oxidation-condensation of FUR with n-propanol [21], we postulate that the first step is the oxidation of ethanol to form an acetaldehyde intermediate followed by a rapid condensation between FUR and the acetaldehyde intermediate in the solution. This reaction pathway is illustrated in Scheme 3, route 1. Hydrogen transfer occurs between FUR and ethanol, in which the acetaldehyde intermediate and furfuryl alcohol are produced. The next step is the condensation reaction that takes place between FUR and the acetaldehyde intermediates. Meanwhile, the furfuryl alcohol can be oxidized to FUR by oxygen as shown in route 2 in Scheme 3. Correspondingly, throughout this study, it can be elucidated that the Au/Al₂O₃ catalyst is responsible for the selective oxidation of ethanol or furfuryl alcohol, whereas the role of base K₂CO₃ promoter is to catalyze condensation reaction to form desired product, Compound **1**.

4. Conclusion

A highly efficient and selective oxidation-condensation of FUR with ethanol process that involves using supported Au catalyst has been developed. In the presence of the Au/Al₂O₃ catalyst and potassium carbonate, the main product of oxidative condensation is found to be Compound **1**. Synergistic effect between supported Au catalyst and base promoter is observed in the formation of Compound **1**. The importance of this study is to provide an effective approach for valorization of biomass-derived hemi cellulose via catalytic process.

Acknowledgements

This work is financially supported from the Natural Science Foundation of China (No. 21003093) and the State Key Program of National Natural Science of China (No.21336008).

References

- [1] Y. Roman-Leshkov, J. N. Chheda, J. A. Dumesic, Science 312 (2006) 1933-1937.
- [2] C. Zhou, X. Xia, C. Lin, D. Tong, J. Beltramini, Chem. Soc. Rev. 40 (2011) 5588-5617.
- [3] J. C. Serrano-Ruiz, J. A. Dumesic, Energy Environ. Sci. 4 (2011) 83-99.
- [4] J. Q. Bond, A. A. Upadhye, H. Olcay, G. A. Tompsett, J. Jae, R. Xing, D. M. Alonso, D. Wang,
- T. Zhang, R. Kumar, A. Foster, S. M. Sen, C. T. Maravelias, R. Malina, S. R. H. Barrett, R. Lobo, C.
- E. Wyman, J. A. Dumesic, G. W. Huber, Energy Environ. Sci. 7 (2014) 1500-1523.
- [5] B. Kamm, P. R. Gruber and M. Kamm, Biorefineries Industrial Processes and Products. Status
- Quo and Future Directions, Wiley-VCH, 2006
- [6] K. J. Zeitsch, The Chemistry and Technology of Furfural and Its Many By-products, Elsevier Science, 2000.
- [7] S. Lima, M. Pillinger, A. A. Valente, Catal. Commun. 9 (2008) 2144-2148.
- [8] H. Guo, G. Yin, J. Phys. Chem. C 115 (2011) 17516-17522.
- [9] M. J. Climent, A. Corma, S. Iborra, Green Chem. 16 (2014) 516-547.
- [10] G. W. Huber, J. N. Chheda, C. J. Barrett, J. A. Dumesic, Science 308 (2005) 1446-1450.
- [11] J. N. Chheda, G. W. Huber, J. A. Dumesic, Angew. Chem. Int. Ed. 46 (2007) 7164-7183.
- [12] R. West, Z. Y. Liu, M. Peter, J. A. Dumesic, ChemSusChem 1 (2008) 417-424.
- [13] W. Shen, G. A. Tompsett, K. D. Hammond, R. Xing, F. Dogan, C. P. Grey, W. C. Conner, S. M.
- Auerbach, G. W. Huber, Appl. Catal. A: General 392 (2011) 57-68.
- [14] S. Dutta, S. De, B. Saha, Md. I. Alam, Catal. Sci. Technol. 2 (2012) 2025-2036.
- [15] T. Mallat, A. Baiker, Chem. Rev. 104 (2004) 3037-3058.
- [16] C. Hamelinck, G. Hooijdonk, A. Faaij, Biomass Bioenergy 28 (2005) 384-410.

- [17] P. C. Badger, Ethanol from cellulose: a general review. in: J. Jandick, A. Whipkey (Eds), Trends in New Crops and New Uses, ASHS Press, Alexandria, VA, 2002, pp 17-21.
- [18] G. O. Ezinkwo, V. P. Tretyakov, A. Aliyu, A. M. Ilolov, ChemBioEng Reviews 1 (2014) 194-203.
- [19] J. Sun, Y. Wang, ACS Catal., 4 (2014) 1078-1090.
- [20] V. L. Sushkevich, I. I. Ivanova, V. V. Ordomsky, E. Taarning, ChemSusChem 7 (2014) 2527-2536.
- [21] X. Tong, Z. Liu, L. Yu, Y. Li, Chem. Commun. 51 (2015) 3674-3677.
- [22] W. Chen, J. Zhang, W. Cai, Scr. Mater. 48 (2003) 1061-1066.
- [23] C. Lopez-Bastida, E. Smolentseva, V. Petranovskii, R. Machorro, Plasmonics 8 (2013)1551-1558.
- [24] E. Smolentseva, A. Simakov, S. Beloshapkin, M. Estrada, E. Vargas, V. Sobolev, R.Kenzhin, S.
- Fuentes, Appl. Catal. B: Environmental 115-116 (2012) 117-128.
- [25] I. Tuzovskaya, N. Bogdanchikova, A. Simakov, V. Gurin, A. Pestryakov, M. Avalos, M. Farías, Chem. Phys. 338 (2007) 23-32.
- [26] N. Zheng, G. D. Stucky, Chem. Commun. 37 (2007) 3862-3864.
- [27] L. Wang, J. Li, W. Dai, Y. Lv, Y. Zhang, S. Gao, Green Chem. 16 (2014) 2164-2173.
- [28] X. Bai, F. Ye, L. Zheng, G. Lai, C. Xia, L. Xu, Chem. Commun. 48 (2012) 8592-8594.

Figure Captions



Scheme 1. Possible reaction pathways in FUR-ethanol-O2 reaction system



Scheme 2. Possible product formation from condensation of FUR with ethanol



Scheme 3. Reaction mechanism involved in oxidative condensation of FUR with ethanol using Au/Al₂O₃-K₂CO₃ catalyst



Figure 1. The XRD patterns of different supported Au catalysts



Figure 2. The SEM images of the different nano Au catalysts (a) Au/Al₂O₃ catalyst; (b) Au/HTc

catalyst; (c) Au/CeO $_2$ catalyst; (d) Au/Nb $_2O_5$ catalyst



Figure 3. TEM images of different catalysts (a) Au/Al₂O₃ catalyst; (b) Au/HTc catalyst; (c)

Au/CeO₂ catalyst; (d) Au/Nb₂O₅ catalyst]



Figure 4. The UV-vis spectra of different nano Au catalysts



Figure 5. The TPD results for different gold supported catalysts



Figure 6. The effect of temperature in the oxidation of FUR with Au/Al_2O_3 catalyst



Figure 7. The effect of time on the oxidation of furfural with Au/Al₂O₃-K₂CO₃ catalyst



Figure 8. The effect of K₂CO₃ promoters in the oxidative condensation of FUR (0.2 g FUR, 0.05g 5%Au/Al₂O₃ catalyst, 15 ml C₂H₅OH, 0.3 MPa of O₂, 140 °C, 4 hours reaction time)



Figure 9. The recycling of the Au/Al₂O₃ catalyst in the FEO system. [Reaction conditions: 0.2 g of FUR, 0.05 g of the Au/Al₂O₃ (5 wt% Au loading) catalyst, 0.05 g K₂CO₃, in 15 mL of C₂H₅OH under 0.3 MPa of O₂ for 4 h at 140°C.]

Tables

Catalysts	DET aurfood	Pore volume — (cm ³ g ⁻¹)	Average pore diameter (nm)			
	(2 -1)		BJH	BJH		
	area (m ⁻ g ⁻)		adsorption	desorption		
Au/Al ₂ O ₃	314.1	0.5541	59.89	63.23		
Au/HTc	216.6	0.2046	37.45	39.58		
Au/CeO ₂	93.78	0.1224	54.02	67.50		
Au/Fe ₃ O ₄	37.45	0.0511	53.07	82.27		
Au/Nb ₂ O ₅	0.9031	0.0004	62.45	116.6		

Table 1. The physical property of different supported Au catalysts

 Table 2. Performance comparison of different supported Au catalysts in oxidative condensation of furfural with ethanol^[a]

Entry	Catalytic System	Conversion (%) ^[b]	Selectivity (%) ^[b]			
			1	2	3	Others
1	None (baseline)	9.4	0	0	>99%	0
2	Au/Fe ₃ O ₄	29.5	0	0	>99	0
3	Au/Fe ₃ O ₄ +K ₂ CO ₃	68.4	91.3	2.9	0	5.8
4	Fe ₃ O ₄ +K ₂ CO ₃	25.6	0	0	79.6	20.5
5	K ₂ CO ₃	21.2	0	0	0	100
6	Fe ₃ O ₄	23.2	0	0	0	100
7	Au/HTc + K_2CO_3	78.0	81.0	5.4	0	13.6
8	Au/Co ₃ O ₄ +K ₂ CO ₃	80.1	83.2	2.7	0	14.0
9	Au/Al ₂ O ₃ +K ₂ CO ₃	84.9	80.1	4.9	0	15.0
10	Au/CeO ₂ +K ₂ CO ₃	97.3	54.9	17.7	0	27.4
11	Au/Nb ₂ O ₅ +K ₂ CO ₃	39.6	84.6	3.9	0	11.5

[a] Reaction conditions: 0.2 g FUR, 0.05g nano Au (5.0 wt.% loading) catalyst, 0.05 g K₂CO₃, in 15 ml of C₂H₅OH, under 0.3 MPa of O₂, reaction time 4 hour, temperature 130 °C. [b] Internal standard was used in GC analysis. The compound **1** is furan-2-acrolein; the Compound **2** is ethyl furoate; the Compound **3** is 2-(diethoxymethyl)furan.

Entry Promotor	Dromotor	Conversion (%) ^b	Product distribution (%) ^b			
	PTOIIIOIOI		1	2	3	others
1	Na ₂ CO ₃	61.7	92.2	2.8	0	5.0
2	Cs_2CO_3	84.8	79.8	3.7	0	16.4
3	Li ₂ CO ₃	14.3	10.3	81.9	7.9	0
4	KHCO ₃	75.3	86.0	2.6	0	14.4
5	NaHCO ₃	74.0	80.5	9.7	0	9.8
6	КОН	86.3	69.4	2.8	0	27.7
7	NaOH	79.0	81.8	9.3	0	8.9
8	Ca(OH) ₂	27.5	87.4	12.7	0	0
9	CaCO ₃	14.8	0	2.6	73.8	23.6
10	CaO	61.3	68.3	0	0	30.3
11	H ₃ PO ₄	49.6	0	6.7	93.3	0

Table 3. The effects of different additive in the oxidative condensation of furfural with ethanol ^[a]

[a] Reaction conditions: 0.2 g FUR, 0.05g Au/Al $_2O_3$ (5 wt.% Au loading) catalyst, 0.05 g promotor,

15 ml of ethanol, P=0.3 MPa of O₂, reaction time 4 hours, T=140 °C.

[b] Internal standard is used in GC analysis