Catalysis Letters
https://doi.org/10.1007/s10562-019-02748-0

Porous Zr–Thiophenedicarboxylate Hybrid for Catalytic Transfer Hydrogenation of Bio-Based Furfural to Furfuryl Alcohol

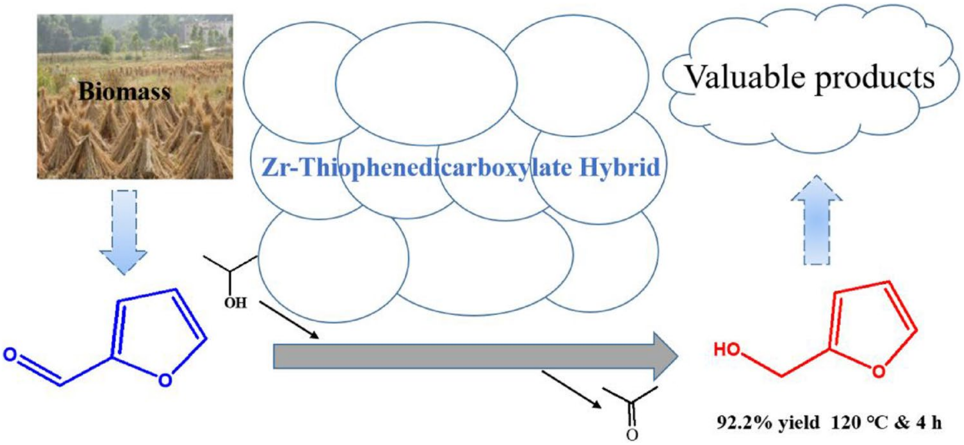
Tao Wang[1] · Aiyun Hu[1] · Guangzhi Xu[1] · Chen Liu[1] · Haijun Wang[1] · Yongmei Xia[2]

Received: 18 January 2019 / Accepted: 11 March 2019

Abstract

Furfural (FAL) is one of the most important biomass-derived platform compounds. The catalytic transformation of FAL was investigated with three porous Zr–thiophenedicarboxylate hybrids for the production of furfuryl alcohol (FOL). Three Zr-based catalysts, including DUT-67(Zr), DUT-68(Zr) and DUT-69(Zr) were synthesized through a facile assembly of 2,5-thiophenedicarboxylate acid with $ZrCl_4$ using the acetic acid as a modulator under hydrothermal conditions. These catalysts were also characterized using FT-IR, XRD, SEM, TEM, N_2 adsorption–desorption, XPS and TG. The specific surface area of the DUT-69(Zr) is smaller than that of the DUT-68(Zr) and slightly larger than that of the DUT-67(Zr), but it has a relatively large pore volume and pore diameter. Although all three catalysts showed excellent catalytic activity towards the catalytic transfer hydrogenation of FAL into FOL, the DUT-69(Zr) material has slightly higher catalytic activity than the other two catalysts. Besides, considering the cost of catalyst preparation, the DUT-69(Zr) material was used as the optimal catalyst and studied in detail. A high FOL yield of 92.2% at 95.9% FAL conversion was achieved at 120 °C for 4 h over DUT-69(Zr). Meanwhile, the DUT-69(Zr) could be reused more than six times with a minor decrease in catalytic activity. Finally, a plausible mechanism for catalytic transfer hydrogenation of carbonyl compounds to produce corresponding alcohols was presented based on the results of the experiments and previous reports.

Graphical Abstract



Keywords Furfural · Carbonyl compounds · Furfuryl alcohol · Catalytic transfer hydrogenation · Zr–thiophenedicarboxylate hybrid · DUT-69(Zr)

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10562-019-02748-0) contains supplementary material, which is available to authorized users.

Extended author information available on the last page of the article

1 Introduction

The massive depletion of non-renewable fossil fuels, such as oil, coal and natural gas, has caused serious environmental pollution problems, which is irreconcilable with people's growing health and environmental awareness [1–3]. In addition to the unstable factors of oil price and supply worldwide, it is of great practical significance to explore sustainable resources in the long term. Biomass, as one of the potential substitutes of fossil fuels, has been identified as an ideal feedstock for the production of liquid fuels and high-valued chemicals [4–6]. In industry, Furfural (FAL) can be produced by direct catalytic degradation of lignocellulose biomass (e.g. corncob and straw) with dilute acid. It has been considered as one of the most significant biomass-based platform compounds [7–9]. FAL is a cheap, readily available renewable resource, and its downstream products are not only rich but also have high economic value [10, 11]. It has aldehyde functional groups, which can be oxidized, hydrogenated and condensated to produce various derivatives because of its active chemical properties.

Hydrogenation reaction of FAL is a very important technology for production of high-added value products like furfuryl alcohol, tetrahydrofurfural, tetrahydrofurfuryl alcohol, furan, 2-methylfuran [12–16]. Among these compounds, furfuryl alcohol (FOL) is recognized as a momentous intermediate that can be prepared various products such as resins, adhesives, lubricants and fibers [17, 18]. Therefore, the conversion of FAL–FOL is considered to be one of the key steps in the transformation of biomass. Not only can this solve the technical bottleneck problem that restricts the development of furfural industrial chain, but also has far-reaching significance to the national economic green and sustainable development strategy [19, 20].

Concerning the synthesis of FOL, two main methods have been reported. Cu–Cr oxide was widely used as a commercial catalyst for the production of FOL [21]. This method may achieve high selectivity of FOL, but high toxicity of Cr^{6+} can lead to serious environmental pollution after the ultima treatment of the catalyst [22]. Therefore, researchers focus on exploring the use of chromium-free catalysts in the reaction of FAL to produce FOL. These reactions, which were catalyzed by precious metal catalysts such as Re, Pt, Ru and Pd [23–27], generally were carried out in the atmosphere of external molecular hydrogen. Although these catalysts showed excellent catalytic activities in the process from FAL to FOL via catalytic transfer hydrogenation (CTH). The shortcomings of high cost, flammable and explosive nature of hydrogen limited their wide applications [28, 29]. Consequently, we are looking forward to finding an appropriate hydrogen source for the synthesis of FOL.

For the last few years, it has been a more reasonable approach for the CTH of FAL to produce FOL by using alcohols as the hydrogen source and solvent. These alcohols are safe and abundant. More importantly, these reactions could be carried out in a relatively simple device without dangerous hydrogen. The CTH procedure with alcohols depend on Meerwein–Ponndorf–Verley (MPV) reduction reaction, where carbonyl compounds were converted to corresponding alcohols [30]. Recently, various catalytic systems have been developed for the conversion of FAL–FOL. For example, earth-abundant metal nanoparticles, such as Al–Zr@Fe_3O_4, B–Al_2O_3, Cu/MgO–Al_2O_3, γ-Fe_2O_3@HAP, $NiFe_2O_4$, Fe–L1/C-800, Co/SBA-15 and NiFe/SiO_2 were used as catalysts to obtain high yield of FOL [31–38]. In addition, Zr- and Hf-based phosphate hybrid materials, such as Zr-PhyA, ZrPN and PhP-Hf (1:1.5) had been prepared to catalyze the CTH of FAL–FOL efficiently [39–41]. In particular, several Zr- and Hf-based metal–organic composites showed pronounced catalytic performances in the MPV reaction [42–46]. Zirconium and hafnium have multi-coordination sites. In addition to coordination with large organic ligands (e.g. 1,4-benzenedicarboxylic acid, 1,3,5-benzenetricarboxylic acid and 2,5-furandicarboxylic acid) [42, 44, 46], Zr^{4+} and Hf^{4+}combine some small solvent molecules to meet their coordination number requirements, such as water, ethanol, DMF, etc. When these guest molecules are removed, the vacancies left can produce permanent pores. These combined factors contribute to their porosity and high specific surface area, which can facilitate the effective diffusion of reactant molecules and provide a large number of easily accessible catalytic active sites, resulting in their highly efficient catalytic performances. Fortunately, these catalysts exhibited robustness, thermal and chemical stability owing to the higher co-ordination number of Zr or Hf in their structure.

Similar to the structure of 2,5-furandicarboxylic acid that is used as an organic ligand for MOFs preparation [42, 46], 2,5-thiophenedicarboxylate acid (H_2tdc) also contains two -COOH groups at the same position, making it conducive to the manufacture of MOFs. In the present work, three porous Zr–thiophenedicarboxylate hybrids, including DUT-67(Zr), DUT-68(Zr) and DUT-69(Zr) were obtained through a facile assembly of H_2tdc with $ZrCl_4$ using the acetic acid as a modulator under hydrothermal conditions [47, 48]. Different materials were prepared by varying the thermal reaction time, reaction solvent and the proportion between materials, resulting in the difference in their physical properties. Among the three Zr-based catalysts, the specific surface area of the DUT-69(Zr) is smaller than that of the DUT-68(Zr) and slightly larger than that of the DUT-67(Zr), but it has a relatively large pore volume and pore diameter. It is well known that the specific surface area and pore size of the catalyst affect the catalytic activity of the catalyst. Although all three catalysts showed excellent catalytic activity on the CTH of FAL into FOL, DUT-69(Zr) has a slightly higher activity than the other two catalysts and is cheaper to prepare. Based on the above-mentioned factors, the DUT-69(Zr) material was used as the most ideal catalyst and studied in detail. To the best of our knowledge, the application of DUT-69(Zr) in CTH reaction had never been reported. The optimal reaction conditions were investigated systematically and a plausible reaction mechanism was put forward based on the findings acquired from the experiments and previous reports.

2 Experimental

2.1 Chemicals

Furfuryl alcohol and $ZrCl_4$ (98%) were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). 2,5-thiophenedicarboxylic acid (H_2tdc, 98%) was supplied by Adamas-beta. *N,N*-dimethylformamide (DMF), acetic acid (99.7%), 1-methyl-2-pyrrolidone (NMP), zirconium dioxide, furfural, ethanol, 2-propanol, naphthalene and other chemicals were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Commercial chemicals were of analytical grade and used directly without further purification. Deionized water was produced by using a laboratory water-purification system (RO DI Digital plus).

2.2 Catalyst Preparation

Three porous Zr–thiophenedicarboxylate hybrids were synthesized by solvothermal method with appropriate modifications according to previously reported procedures [47].

2.2.1 Preparation of DUT-67(Zr)

In a typical procedure, 0.92 g (4 mmol) of $ZrCl_4$ was first dissolved in the mixture of DMF (50 mL) and NMP (50 mL) by sonication for 20 min. Then, 0.44 g (2.68 mmol) of H_2tdc was added to the mixture and sonicated for another 10 min. Thereafter, 28 mL (468 mmol) of acetic acid was added to the above mixture and sonicated additional 20 min. After that, the resulting mixture was transferred to a 200 mL Teflon-lined pressure vessel and heated in an oven for 48 h at 120 °C. Finally, the generated precipitates were filtered, washed initially with DMF and then with ethanol twice, and dried at 120 °C under vacuum conditions for 12 h.

2.2.2 Preparation of DUT-68(Zr)

In a typical procedure, 1.15 g (5 mmol) of $ZrCl_4$ was first dissolved in DMF (125.0 mL) by sonication for 20 min. Then, 1.29 g (7.50 mmol) of H_2tdc was added to the mixture and sonicated for another 10 min. Thereafter, 55 mL (915 mmol) of acetic acid was added to the above mixture and sonicated additional 20 min. After that, the resulting mixture was transferred to a 200 mL Teflon-lined pressure reactor and heated in an oven for 72 h at 120 °C. Finally, the generated precipitates were filtered, washed initially with DMF and then with ethanol twice, and dried at 120 °C under vacuum conditions for 12 h.

2.2.3 Preparation of DUT-69(Zr)

In a typical procedure, 0.69 g (3 mmol) of $ZrCl_4$ was first dissolved in DMF (150 mL) by sonication for 20 min. Then, 0.52 g (3 mmol) of H_2tdc was added to the mixture and sonicated for another 10 min. Thereafter, 9 mL (150 mmol) of acetic acid was added to the above mixture and sonicated additional 20 min. After that, the reaction mixture was transferred to a 200 mL Teflon-lined pressure reactor and heated in an oven for 12 h at 120 °C. Finally, the generated precipitates were filtered, washed initially with DMF and then with ethanol twice, and dried at 120 °C under vacuum conditions for 12 h.

2.3 Catalyst Characterization

FT-IR measurements of all the catalysts were recorded using a Nicolet iS50 FT-IR spectrometer with the KBr pellet technique in the range of 4000–400 cm^{-1} at room temperature. Powder X-ray diffraction (XRD) patterns were carried out on a Bruker D2 Phaser instrument employing Cu Kα radiation ($\lambda = 0.15406$ nm) in the 2θ range of 4°–80° with a step size of 0.01° at 30 kV and 10 mA. SEM images of the as-prepared samples were performed on a HITACHI S-4800 field-emission scanning electron microscope at 3 KV. All the catalysts were coated with a thin layer of gold to prevent the accumulation of negative charges. TEM images of all the samples were recorded by using a JEM-2100plus with an accelerating voltage of 200 kV. Thermal gravimetric analysis (TGA) of the samples was performed on a TGA/DSC1/1100SF thermal analyzer. The analysis started at 50 °C with a heating rate of 10 °C/min until 700 °C in nitrogen atmosphere (50 mL/min). Texture properties including specific surface areas, pore volumes and pore diameters were tested at – 196 °C using the Micromeritics ASAP 2020 msystem, the samples were degassed at 120 °C for 12 h in a vacuum before N_2 adsorption. The chemical composition and the chemical state of the elements in the samples were determined using a Thermo Scientific Escalab 250Xi X-ray photoelectron spectrometer.

2.4 Catalytic Tests

In a typical experiment, the cylindrical stainless steel high-pressure vessel was loaded with FAL (1 mmol), 2-propanol (5 mL) and the catalyst (0.1 g), and then heated at a certain designated temperature for the desired reaction time with magnetic stirring. Upon completion, the resulting liquid products were analyzed quantitatively by gas chromatography (GC 9790 II) using naphthalene as the internal standard, and identification of the products was done by GC-MS (GCMS-QP2010 Ultra). The yield of FOL, the conversion of FAL and the selectivity to FOL were calculated on the basis of the following formula.

$$\text{Yield} = \frac{\text{Final moles of FOL}}{\text{Initial moles of FAL}} \times 100\% \tag{1}$$

$$\text{Conversion} = \frac{\text{Initial moles of FAL} - \text{Final moles of FAL}}{\text{Initial moles of FAL}} \times 100\% \tag{2}$$

$$\text{Selectivity} = \frac{\text{Final moles of FOL}}{\text{Initial moles of FAL} - \text{Final moles of FAL}} \times 100\% \tag{3}$$

3 Results and Discussion

3.1 Catalyst Characterization

The prepared DUT-69(Zr) was characterized by FT-IR, XRD, SEM, TEM, N_2 adsorption–desorption isotherm, XPS and TGA techniques. The FT-IR spectrum of the DUT-69(Zr) was shown in Fig. 1a. It can be seen that DUT-69(Zr) displayed the characteristic symmetric (1393 cm^{-1}) and asymmetric vibrations (1500–1700 cm^{-1}) of carboxylate anions [49]. The spacing between these two peaks is about 190 cm^{-1}, indicating that the coordination mode of H_2tdc to Zr is bridging [43, 50]. By comparison, FT-IR spectrum of H_2tdc showed a splitting of approximately 250 cm^{-1} between these two peaks, which further confirmed the tight combination between Zr and carboxyl groups of H_2tdc. The powder XRD pattern of the DUT-69(Zr) was shown in Fig. 1b. It has been clearly observed that the DUT-69(Zr) material is amorphous owing to a few wide diffraction peaks, despite one sharp diffraction peak at 2θ = 8.6°, which is analogous

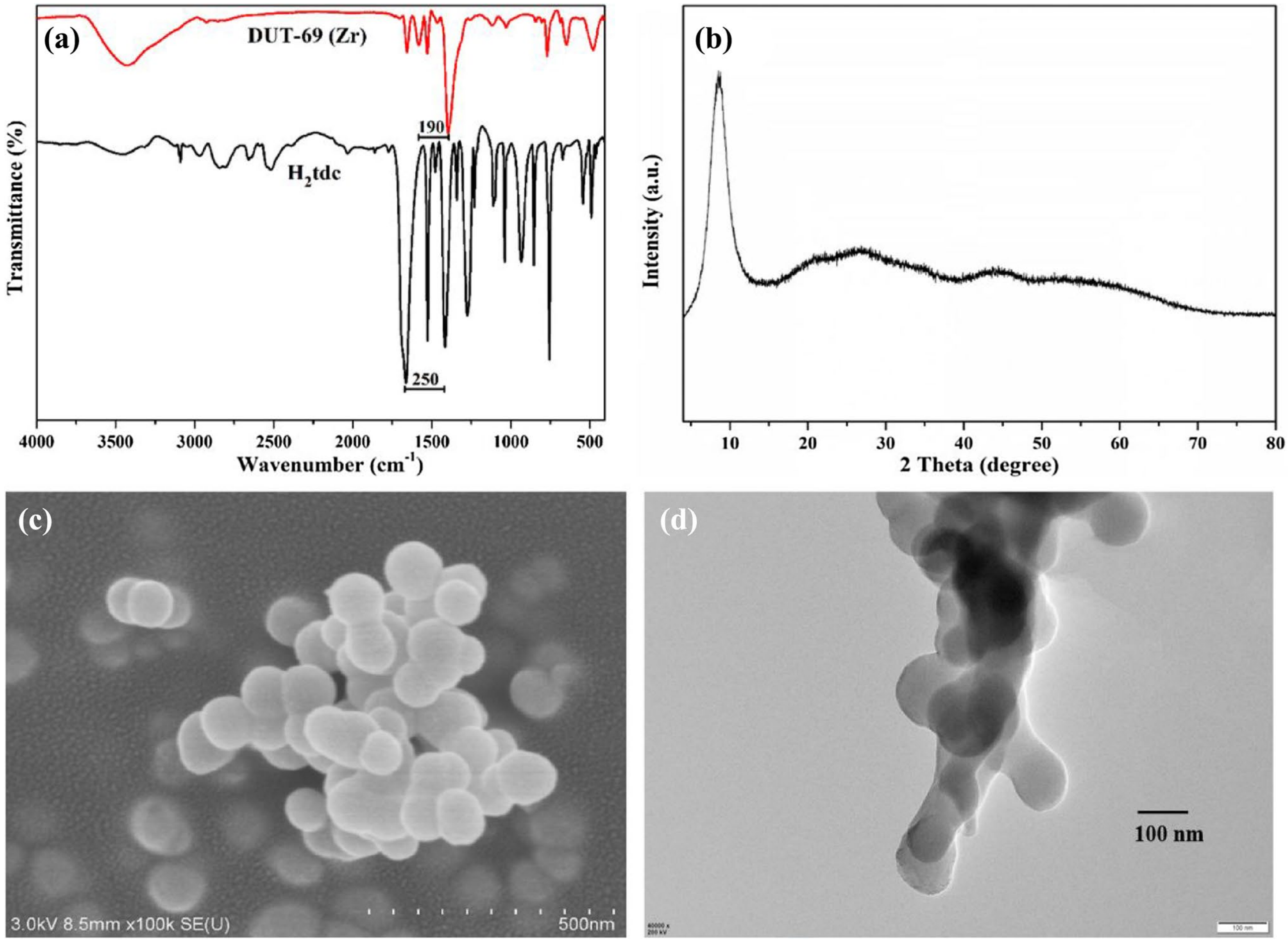


Fig. 1 Characterization of the as-prepared DUT-69(Zr) by **a** FT-IR spectra, **b** Powder XRD pattern, **c** SEM image and **d** TEM image

to diffraction of Zr-FDCA-T [42]. Especially, the SEM and TEM images indicated that nanoparticles (100–120 nm) of the DUT-69(Zr) are slightly aggregated (Fig. 1c, d). As shown in Fig. 2a, the N_2 adsorption–desorption isotherm of the DUT-69(Zr) belonged to type III mode with a large amount of adsorption between the relative pressure of 0.75–1.0. In addition, the DUT-69(Zr) was porous with mesoporous centered about 12.0 nm, and the specific surface area and pore volume were 158.1 m^2/g and 0.60 cm^3/g, respectively. This may increase the accessibility of catalytic sites for the reactant compared with ZrO_2 [51, 52]. We inspected the local environment of Zr species in DUT-69(Zr) and ZrO_2 by the Zr 3d XPS. As shown in Fig. 2b, the binding energies of Zr 3d in DUT-69(Zr) were higher in comparison with ZrO_2, which illustrated a higher positive charge on the Zr atoms in DUT-69(Zr) and led to a stronger Lewis acidity of Zr. The higher Lewis acidity of Zr species was helpful to improve the performance of DUT-69(Zr) catalyst. TG analysis of the catalyst was performed to gain an insight into the thermal stability of the DUT-69(Zr). As shown in Fig. S1, the weight loss in the temperature range from 350 to 500 °C could be ascribed to the elimination of TDC ligand from the structure, thus resulting in the destruction of catalyst structure and the formation of zirconium oxide [47, 48]. It proved that the DUT-69(Zr) catalyst had pronounced stability at the reaction temperatures (below 140 °C). DUT-67(Zr) and DUT-68(Zr) catalysts were also synthesized and characterized to explore their differences. No obvious differences among DUT-67(Zr), DUT-68(Zr) and DUT-69(Zr) were found from FT-IR spectra and XRD patterns (Figs. S2, S3). The SEM images demonstrate that they have different sizes of nanoparticles (Fig. S4). The particle size of DUT-67(Zr) is below 100 nm, while those of DUT-68(Zr) and DUT-69(Zr) are relatively larger. The specific surface area of the DUT-69(Zr) is smaller than that of the DUT-68(Zr) and slightly larger than that of the DUT-67(Zr), but it has a relatively large pore volume and pore diameter (Table S1).

3.2 Catalytic Activity of Various Catalysts for the CTH Reaction of FAL

In the initial experiment, we chose FAL as the model substrate to examine the catalytic performance of various catalysts for the formation of FOL through CTH reactions. As summarized in Table 1, it can be seen that the reaction could not be conducted in the absence of any catalysts (Table 1, entry 1). All the synthesized porous Zr–thiophenedicarboxylate hybrids catalysts showed pronounced catalytic activity on the CTH of FAL into FOL (Table 1, entries 2–4). Especially, the prepared DUT-69(Zr) catalyst showed the highest activity with the FOL yield of 92.2% at 120 °C with

Table 1 CTH reaction of FAL to produce FOL catalyzed by various catalysts.

Entry	Catalyst	Conversion (%)	Yield (%)	Selectivity (%)
1	None	0	0	0
2	DUT-69(Zr)	95.9	92.2	96.1
3	DUT-68(Zr)	91.6	87.7	95.7
4	DUT-67(Zr)	92.7	89.5	96.5
5	H_2tdc	8.8	0	0
6	$ZrCl_4$	20.2	1.1	5.4
7	ZrO_2	16.6	7.1	42.8

Reaction conditions: 0.1 g catalyst, 1 mmol FAL, 5 mL 2-propanol, reaction temperature = 120 °C, reaction time = 4 h

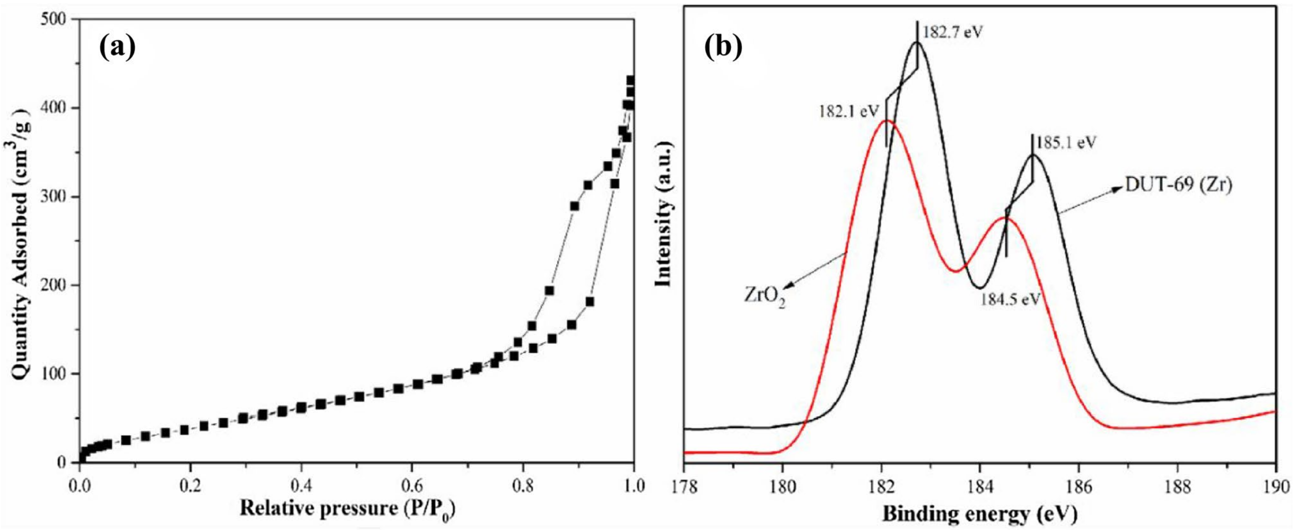


Fig. 2 Characterization of the as-prepared DUT-69(Zr) by **a** N_2 adsorption–desorption isotherms and **b** Zr 3d XPS spectra

a reaction time of 4 h (Table 1, entry 2). However, H_2tdc alone, which possessed two carboxyl functional groups, was not active for the production of FOL (Table 1, entry 5). This showed that the Brønsted acidity of the carboxylic acid had no catalytic performance for the CTH reaction of FAL–FOL. The precursor $ZrCl_4$ used for Zr–thiophenedicarboxylate hybrids synthesis yielded less than 2% of FOL (Table 1, entry 6). In addition, the commercial ZrO_2 showed inferior performance with a FOL yield of 7.1% (Table 1, entry 7). These results revealed that three porous Zr–thiophenedicarboxylate hybrids could be used to catalyze the CTH of FAL and the DUT-69(Zr) prepared in this study was an excellent catalyst for CTH of FAL.

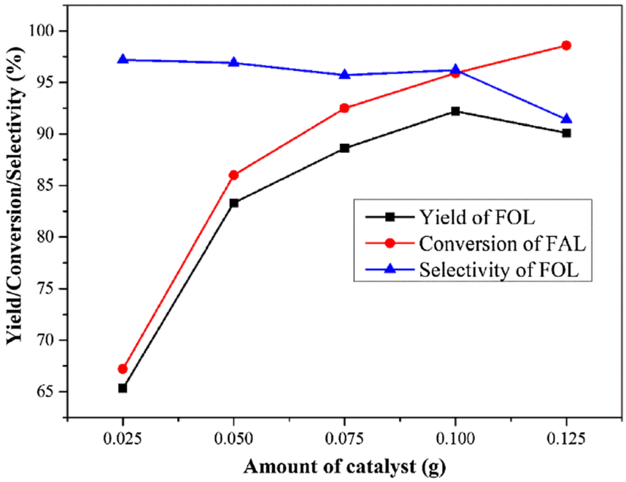


Fig. 3 Effect of catalyst amount on the CTH reaction of FAL to produce FOL. Reaction conditions: 1 mmol FAL, 5 mL 2-propanol, reaction temperature = 120 °C, reaction time = 4 h

3.3 Effect of Catalyst Amount

The effect of the amount of DUT-69(Zr) on the transformation of FAL into FOL was investigated in 2-propanol at 120 °C with a reaction time of 4 h (Fig. 3). The amount of catalyst plays a key role in the CTH of FAL, where more DUT-69(Zr) could increase the conversion of FAL and the yield of FOL at the beginning. FAL conversion and FOL yield substantially increase from 67.2 and 65.3% to 86.0 and 83.3% respectively when the amount of DUT-69(Zr) increases from 0.025 to 0.05 g. Greater than 95% conversion of FAL and 92% yield of FOL were obtained when the DUT-69(Zr) dosage was 0.1 g. After which, FOL yield and selectivity declined slightly with a catalyst dosage of 0.125 g, largely because more catalytic sites promoted the production of more by-products including 5-methylfurfural and 2-acetylfuran as revealed from GC-MS spectra (Fig. S7), these by-products are observed in the CTH of FAL–FOL in other literature [53]. Given the above, 0.1 g of the catalyst would be an appropriate amount under our reaction conditions.

3.4 Effect of Reaction Temperature and Time

Figure 4 showed the effect of the reaction temperature and time on FOL synthesis. It was clear that the reaction temperature and time influenced the activity of the DUT-69(Zr) catalyst. Especially in the time range of 1–2 h, the FAL

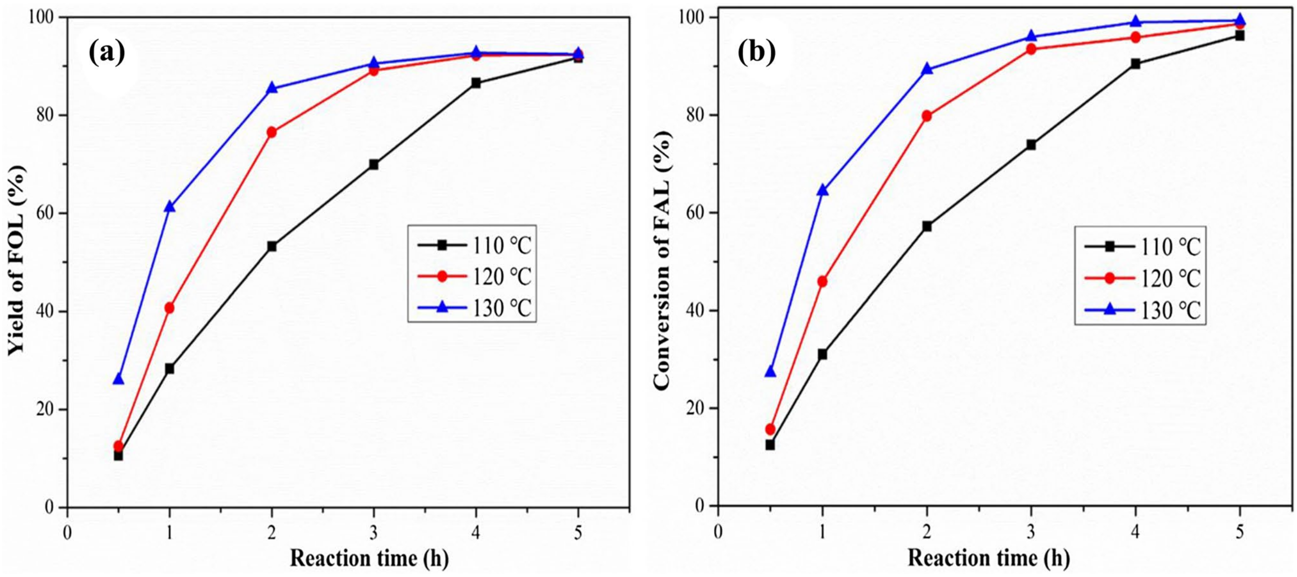


Fig. 4 Effect of reaction temperature and time on the FOL yield (**a**) and FAL conversion (**b**). Reaction conditions: 0.1 g catalyst, 1 mmol FAL, 5 mL 2-propanol

conversion and FOL yield greatly increased with increasing temperature. However, FOL yield hardly relied on the reaction temperature above 120 °C and reaction time surpassing 4 h. GC detection showed peak enhancement of side-products at higher temperatures and longer times. From the standpoint of efficiency, the optimum reaction temperature and reaction time were selected at 120 °C and 4 h, respectively, under our reaction conditions.

The CTH of FAL has been reported to be pseudo-first order with regard to FAL concentration [54]. As shown in Fig. 5a, increasing the reaction temperature from 110 to 130 °C promoted FAL conversion, leading to an elevated reaction rate constant (k) from 0.01151 to 0.01822 min^{-1}, matching well with the above analysis results (Fig. 4). From an Arrhenius plot of the data (Fig. 5b), the activation energy (Ea) of CTH of FAL–FOL over DUT-69(Zr) in 2-propanol was evaluated to be 29.5 kJ/mol, which is close to and even lower than values previously reported in literature [34, 35, 54]. The results demonstrate that the as-synthesized DUT-69(Zr) is highly active in the CTH of FAL–FOL.

3.5 Heterogeneity and Reusability of the Catalyst

To examine the heterogeneity of DUT-69(Zr), the catalyst was removed from the reaction mixture via filtering after the reaction was carried out at 120 °C for 2 h, and the reaction was continued to 5 h in the absence of catalyst under the identical reaction conditions to observe if the yield of FOL further increased. As shown in Fig. 6a, it was found that FOL yield remained unchanged around 76.5% after removing DUT-69(Zr), confirming that there was no loss of active sites in DUT-69(Zr) and the reaction was conducted under heterogeneous catalyst. The reusability of the catalyst was also studied. As shown in Fig. 6b, it was observed that DUT-69(Zr) could be reused more than six cycles with only a slight decline in its catalytic performance. Meanwhile, the recovered DUT-69(Zr) after six cycles was also characterized by SEM, XRD, FT-IR and TG (Fig. S8), and the results indicated that the structures of the catalyst had not changed significantly after reused for six cycles. These results demonstrated that the as-prepared DUT-69(Zr) was stable under the studied reaction conditions.

3.6 Catalytic Effect of DUT-69(Zr) on Different Substrates

Delighted by the remarkable activity of the catalyst for the transformation of FAL, we also tested CTH of other carbonyl compounds catalyzed by the DUT-69(Zr) using 2-propanol as the solvent (Table 2). The results demonstrated that the DUT-69(Zr) could also exhibited good performance for all selected aldehydes and ketones. Biomass-derived 5-hydroxymethyl furfural and 5-methyl furfural yielded 86.2% 2,5-dihydroxymethylfuran and 91.5% 5-methyl furfuryl alcohol respectively, although this required a longer reaction time and relatively higher reaction temperature (Table 2, entries 2 and 3). Compared with benzaldehyde, the reaction conditions of acetophenone are more demanding, which resulted from the steric hindrance and electron-donating properties of methyl (Table 2, entries 4 and 5) [51]. Especially, the C=O bond of cinnamaldehyde could be selectively reduced, while the C=C bond outside the benzene ring was retained (Table 2, entry 6). Hence, the DUT-69(Zr) catalyst exhibited good universality for CTH of carbonyl compounds.

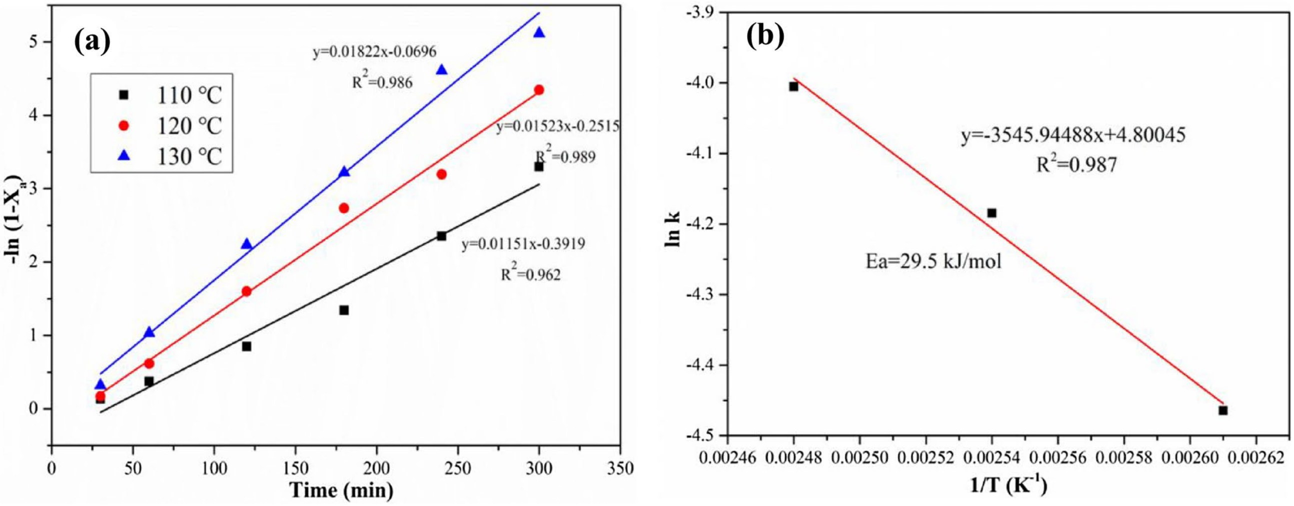


Fig. 5 –ln(1−Xa) versus time (min) (**a**) and ln(k) versus reciprocal of reaction temperature (**b**) in CTH of FAL over DUT-69(Zr) (where Xa = FAL conversion). Reaction conditions: 0.1 g catalyst, 1 mmol FAL, 5 mL 2-propanol, reaction time = 0.5–5 h

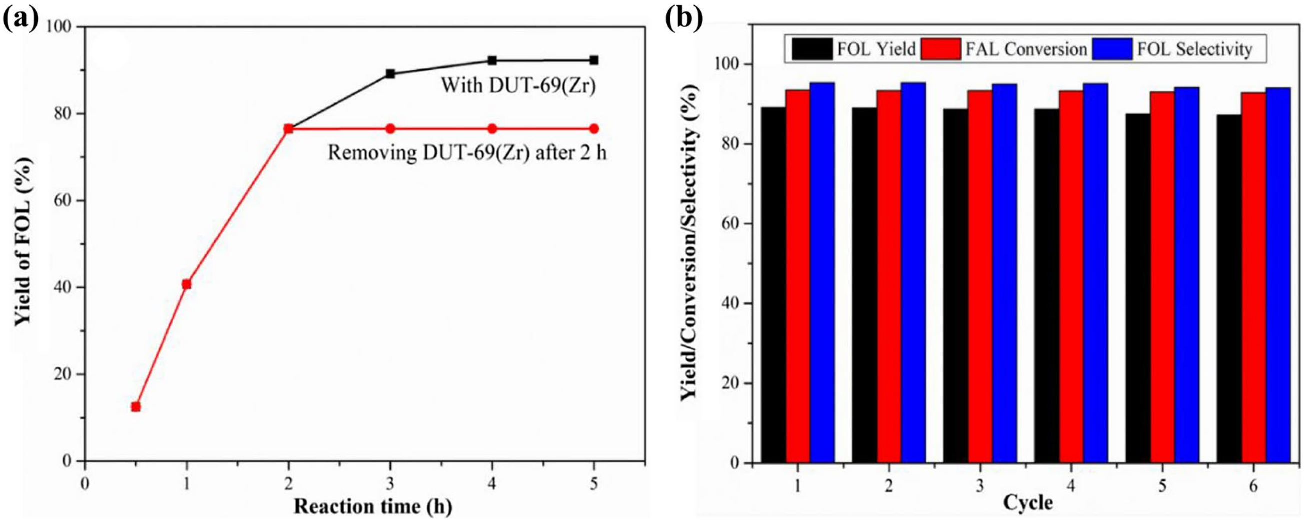
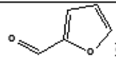
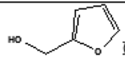
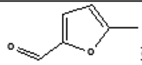
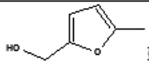
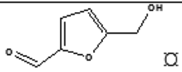
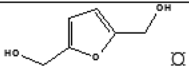
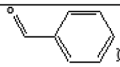
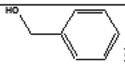
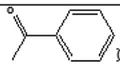
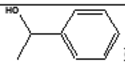
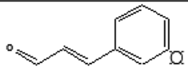
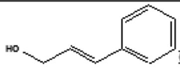


Fig. 6 **a** Time-yield plots for CTH reaction of FAL to FOL with DUT-69(Zr) (black line) or removing DUT-69(Zr) after 2 h (red line) and **b** reusability of the DUT-69(Zr). Reaction conditions: 1 mmol FAL, 5 mL 2-propanol, 0.1 g catalyst, reaction temperature = 120 °C, reaction time = 3 h

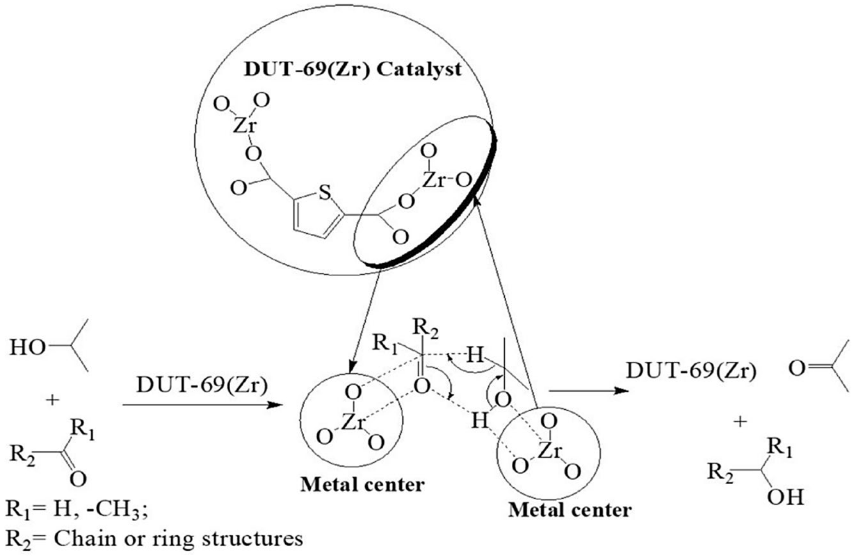
Table 2 CTH of different carbonyl compounds to produce corresponding alcohols catalyzed by DUT-69(Zr)

Entry¤	Substrate¤	Product¤	Temp.· (°C)¤	Time· (h)¤	Conv.· (%)¤	Yield· (%)¤	Select.· (%)¤
1¤	 ¤	 ¤	120¤	4¤	95.9¤	92.2¤	96.1¤
2¤	 ¤	 ¤	120¤	6¤	96.2¤	91.5¤	95.1¤
3¤	 ¤	 ¤	130¤	6¤	97.2¤	86.2¤	88.7¤
4¤	 ¤	 ¤	120¤	6¤	96.8¤	90.5¤	93.5¤
5¤	 ¤	 ¤	130¤	6¤	71.6¤	64.7¤	90.4¤
6¤	 ¤	 ¤	130¤	6¤	97.5¤	92.3¤	94.7¤

Reaction conditions: 1 mmol substrate, 0.1 g DUT-69(Zr), and 5 mL 2-propanol

3.7 Mechanism Analysis

In combination with the experimental results and some previous reports [40, 41, 55–58], we put forward a possible reaction mechanism of the DUT-69(Zr)-catalyzed hydrogen transfer reaction of carbonyl compounds to produce corresponding alcohols based on MPV reduction (Scheme 1). It was reported that acidic and basic sites in the catalysts were critical for their high performance in MPV reduction [39, 51]. In Zr-based MOFs catalysts, the acid and basic sites derived from the Zr^{4+} and O^{2-} (carboxylate groups), respectively [42–44]. Typically, a pair of acid-base sites (Zr^{4+}–O^{2-}) helps to adsorb 2-propanol onto DUT-69(Zr) and could result in the generation of corresponding alkoxide



Scheme 1 Possible mechanism for CTH of carbonyl compounds to produce corresponding alcohols catalyzed by DUT-69(Zr)

and hydrogen by dissociation. Simultaneously, the carbonyl groups in reactant molecules were activated by acidic Zr^{4+} species, thus leading to six-link intermediates to generate the corresponding products and acetone.

4 Conclusions

In summary, three porous Zr–thiophenedicarboxylate hybrids, namely DUT-67(Zr), DUT-68(Zr), and DUT-69(Zr) were constructed through a facile assembly of 2,5-thiophenedicarboxylate acid with $ZrCl_4$ using the acetic acid as a modulator under hydrothermal conditions. These three different materials were prepared by varying the thermal reaction time, reaction solvent and the proportion between materials. All three catalysts were verified to be highly efficient for the conversion of FAL into FOL. Considering the cost of catalyst preparation, the DUT-69(Zr) material was used as the most ideal catalyst and systematically studied. In the presence of DUT-69(Zr), 95.9% FAL conversion and 92.2% FOL yield were attained under optimal reaction conditions. Moreover, it has been proved that the DUT-69(Zr) was a heterogeneous catalyst in the reaction process, and the high performance of DUT-69(Zr) might be attributed to the synergistic effect the Lewis acid sites (originating from Zr^{4+}) and basic sites (resulting from O^{2-} in carboxylate groups). Besides, DUT-69(Zr) could be reused more than six successive cycles with minor decrease of catalytic activity. In addition, a possible reaction mechanism of the DUT-69(Zr) catalyst for the CTH reactions of carboxyl compounds was proposed. We believe that the prepared porous Zr–thiophenedicarboxylate hybrids have great potential for application in the CTH of carbonyl compounds, whether or not they are derived from biomass.

Acknowledgements This work was financial supported by the MOE & SAFEA for the 111 Project (B13025).

Compliance with Ethical Standards

Conflict of interest All authors declare that they have no conflicts of interest.

References

1. Climent MJ, Corma A, Iborra S (2014) Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels. Green Chem 16:516–547
2. Besson M, Gallezot P, Pinel C (2014) Conversion of biomass into chemicals over metal catalysts. Chem Rev 114:1827–1870
3. Zhou CH, Xia X, Lin CX, Tong DS, Beltramini J (2011) Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels. Chem Soc Rev 40:5588–5617
4. Chatterjee C, Pong F, Sen A (2015) Chemical conversion pathways for carbohydrates. Green Chem 17:40–71
5. Binder JB, Raines RT (2009) Simple chemical transformation of lignocellulosic biomass into furans for fuels and chemicals. J Am Chem Soc 131:1979–1985
6. Dutta S, Pal S (2014) Promises in direct conversion of cellulose and lignocellulosic biomass to chemicals and fuels: combined solvent-nanocatalysis approach for biorefinary. Biomass Bioenergy 62:182–197
7. Li XD, Jia P, Wang TF (2016) Furfural: a promising platform compound for sustainable production of C_4 and C_5 chemicals. ACS Catal 6:7621–7640
8. Yan K, Wu GS, Lafleur T, Jarvis C (2014) Production, properties and catalytic hydrogenation of furfural to fuel additives and value-added chemicals. Renew Sust Energy Rev 38:663–676
9. Gallezot P (2012) Conversion of biomass to selected chemical products. Chem Soc Rev 41:1538–1558
10. Nandi S, Saha A, Patel P, Khan NH, Kureshy RI, Panda AB (2018) Hydrogenation of furfural with nickel nanoparticles stabilized on nitrogen-rich carbon core-shell and its

transformations for the synthesis of γ-valerolactone in aqueous conditions. ACS Appl Mater Interfaces 10:24480–24490

11. Lange JP, van der Heide E, van Buijtenen J, Price R (2012) Furfural-a promising platform for lignocellulosic biofuels. ChemSusChem 5:150–166
12. Yan YX, Bu CY, He Q, Zheng ZJ, Ouyang J (2018) Efficient bioconversion of furfural to furfuryl alcohol by *Bacillus coagulans* NL01. RSC Adv 8:26720–26727
13. Rodiansono R, Khairi S, Hara T, Ichikuni N, Shimazu S (2012) Highly efficient and selective hydrogenation of unsaturated carbonyl compounds using Ni-Sn alloy catalysts. Catal Sci Technol 2:2139–2145
14. Huang RJ, Cui QQ, Yuan QQ, Wu HH, Guan YJ, Wu P (2018) Total hydrogenation of furfural over Pd/Al_2O_3 and Ru/ZrO_2 mixture under mild conditions: essential role of tetrahydrofurfural as an intermediate and support effect. ACS Sustain Chem Eng 6:6957–6964
15. Wang CT, Liu ZQ, Wang L, Dong X, Zhang J, Wang GX, Han SC, Meng XJ, Zheng AM, Xiao FS (2018) Importance of zeolite wettability for selective hydrogenation of furfural over Pd@Zeolite catalysts. ACS Catal 8:474–481
16. Zheng HY, Zhu YL, Teng BT, Bai ZQ, Zhang CH, Xiang HW, Li YW (2006) Towards understanding the reaction pathway in vapour phase hydrogenation of furfural to 2-methylfuran. J Mol Catal A 246:18–23
17. Reddy BM, Reddy GK, Rao KN, Khan A, Ganesh I (2007) Silica supported transition metal-based bimetallic catalysts for vapour phase selective hydrogenation of furfuraldehyde. J Mol Catal A 265:276–282
18. Chen XF, Zhang LG, Zhang B, Guo XC, Mu XD (2016) Highly selective hydrogenation of furfural to furfuryl alcohol over Pt nanoparticles supported on g-C_3N_4 nanosheets catalysts in water. Sci Rep 6:28558
19. Bui L, Luo H, Gunther WR, Román-Leshkov Y (2013) Domino reaction catalyzed by zeolites with Brønsted and Lewis acid sites for the production of γ-valerolactone from furfural. Angew Chem Int Ed 52:8022–8025
20. Jiménez-Gómez CP, Cecilia JA, Durán-Martín D, Moreno-Tost R, Santamaría-González J, Mérida-Robles J, Mariscal R, Maireles-Torres P (2016) Gas-phase hydrogenation of furfural to furfuryl alcohol over Cu/ZnO catalysts. J Catal 336:107–115
21. Corma A, Iborra S, Velty A (2007) Chemical routes for the transformation of biomass into chemicals. Chem Rev 107:2411–2502
22. Nagaraja BM, Padmasri AH, Raju BD, Rama Rao KS (2007) Vapor phase selective hydrogenation of furfural to furfuryl alcohol over Cu-MgO coprecipitated catalysts. J Mol Catal A 265:90–97
23. Tamura M, Tokonami K, Nakagawa Y, Tomishige K (2013) Rapid synthesis of unsaturated alcohols under mild conditions by highly selective hydrogenation. Chem Commun 49:7034–7036
24. Merlo AB, Vetere V, Ruggera JF, Casella ML (2009) Bimetallic PtSn catalyst for the selective hydrogenation of furfural to furfuryl alcohol in liquid-phase. Catal Commun 10:1665–1669
25. Yuan QQ, Zhang DM, Haandel LV, Ye FY, Xue T, Hensen EJM, Guan YJ (2015) Selective liquid phase hydrogenation of furfural to furfuryl alcohol by Ru/Zr-MOFs. J Mol Catal A 406:58–64
26. Fulajtárova K, Soták T, Hronec M, Vávra I, Dobročka E, Omastová M (2015) Aqueous phase hydrogenation of furfural to furfuryl alcohol over Pd-Cu catalysts. Appl Catal A 502:78–85
27. Pang SH, Medlin JW (2011) Adsorption and reaction of furfural and furfuryl alcohol on Pd (111): unique reaction pathways for multifunctional reagents. ACS Catal 1:1272–1283
28. Gilkey MJ, Xu BJ (2016) Heterogeneous catalytic transfer hydrogenation as an effective pathway in biomass upgrading. ACS Catal 6:1420–1436
29. Vaidya PD, Mahajani VV (2013) Kinetics of liquid-phase hydrogenation of furfuraldehyde to furfuryl alcohol over a Pt/C catalyst. Ind Eng Chem Res 42:3881–3885
30. Corma A, Domine ME, Nemeth L, Valencia S (2002) Al-free Sn-beta zeolite as a catalyst for the selective reduction of carbonyl compounds (Meerwein-Ponndorf-Verley Reaction). J Am Chem Soc 124:3194–3195
31. He J, Li H, Riisager A, Yang S (2017) Catalytic transfer hydrogenation of furfural to furfuryl alcohol with recyclable Al-Zr@Fe mixed oxides. ChemCatChem 9:1–10
32. López-Asensio R, Cecilia JA, Jiménez-Gómez CP, García-Sancho C, Moreno-Tost R, Maireles-Torres P (2018) Selective production of furfuryl alcohol from furfural by catalytic transfer hydrogenation over commercial aluminas. Appl Catal A 556:1–9
33. Chen H, Ruan HH, Lu XL, Fu J, Langrish T, Lu XY (2018) Efficient catalytic transfer hydrogenation of furfural to furfuryl alcohol in near-critical isopropanol over Cu/MgO-Al_2O_3 catalyst. Mol Catal 445:94–101
34. Wang F, Zhang ZH (2017) Catalytic transfer hydrogenation of furfural into furfuryl alcohol over magnetic γ–Fe_2O_3@HAP Catalyst. ACS Sustain Chem Eng 5:942–947
35. He J, Yang S, Riisager A (2018) Magnetic nickel ferrite nanoparticles as highly durable catalyst for catalytic transfer hydrogenation of bio-based aldehydes. Catal Sci Technol 8:790–797
36. Li J, Liu JL, Zhou HJ, Fu Y (2016) Catalytic transfer hydrogenation of furfural to furfuryl alcohol over nitrogen-doped carbon-supported iron catalysts. ChemSusChem 9:1339–1347
37. Audemar M, Ciotonea C, Vigier KDO, Royer S, Ungureanu A, Dragoi B, Dumitriu E, Jérôme F (2015) Selective hydrogenation of furfural to furfuryl alcohol in the presence of a recyclable cobalt/SBA-15 catalyst. ChemSusChem 8:1885–1891
38. Jia P, Lan XC, Li XD, Wang TF (2018) Highly active and selective NiFe/SiO_2 bimetallic catalyst with optimized solvent effect for the liquid-phase hydrogenation of furfural to furfuryl alcohol. ACS Sustain Chem Eng 6:13287–13295
39. Song JL, Zhou BW, Zhou HC, Wu LQ, Meng QL, Liu ZM, Han BX (2015) Porous zirconium-phytic acid hybrid: a highly efficient catalyst for Meerwein-Ponndorf-Verley reductions. Angew Chem Int Ed 54:9399–9403
40. Li H, He J, Riisager A, Saravanamurugan S, Song BA, Yang S (2016) Acid-base bifunctional zirconium N–alkyltriphosphate nanohybrid for hydrogen transfer of biomass-derived carboxides. ACS Catal 6:7722–7727
41. Li H, Li Y, Fang Z, Smith RL (2019) Efficient catalytic transfer hydrogenation of biomass-based furfural to furfuryl alcohol with recyclable Hf-phenylphosphonate nanohybrids. Catal Today 319:84–92
42. Li H, Liu XF, Yang TT, Zhao WF, Saravanamurugan S, Yang S (2017) Porous zirconium-furandicarboxylate microspheres for efficient redox conversion of biofuranics. ChemSusChem 10:1761–1770
43. Kuwahara Y, Kango H, Yamashita H (2017) Catalytic transfer hydrogenation of biomass-derived levulinic acid and its esters to γ–valerolactone over sulfonic acid-functionalized UiO-66. ACS Sustain Chem Eng 5:1141–1152
44. Valekar AH, Cho KH, Chitale SK, Hong DY, Cha GY, Lee UH, Hwang DW, Serre C, Chang JS, Hwang YK (2016) Catalytic transfer hydrogenation of ethyl levulinate to γ-valerolactone over zirconium-based metal-organic frameworks. Green Chem 18:4542–4552
45. Song JL, Wu LQ, Zhou BW, Zhou HC, Fan HL, Yang YY, Meng QL, Han BX (2015) A new porous Zr-containing catalyst with a phenate group: an efficient catalyst for the catalytic transfer hydrogenation of ethyl levulinate to γ-valerolactone. Green Chem 17:1626–1632

46. Li H, Yang TT, Fang Z (2018) Biomass-derived mesoporous Hf-containing hybrid for efficient Meerwein-Ponndorf-Verley reduction at low temperatures. Appl Catal B 227:79–89
47. Bon V, Senkovska I, Baburin IA, Kaskel S (2013) Zr- and Hf-based metal-organic frameworks: tracking down the polymorphism. Cryst Growth Des 13:1231–1237
48. Drache F, Bon V, Senkovska I, Marschelke C, Synytska A, Kaskel S (2016) Postsynthetic inner-surface functionalization of the highly stable zirconium-based metal-organic framework DUT-67. Inorg Chem 55:7206–7213
49. Verpoort F, Haemers T, Roose P, Maes JP (1999) Characterization of a surface coating formed from carboxylic acid-based coolants. Appl Spectrosc 53:1528–1534
50. Lausund KB, Nilsen O (2016) All-gas-phase synthesis of UiO-66 through modulated atomic layer deposition. Nat Commun 7:13578
51. Xue ZM, Jiang JY, Li GF, Zhao WC, Wang JF, Mu TC (2016) Zirconium-cyanuric acid coordination polymer: highly efficient catalyst for conversion of levulinic acid to γ-valerolactone. Catal Sci Technol 6:5374–5379
52. Xie YD, Li F, Wang JJ, Wang RY, Wang HJ, Liu X, Xia YM (2017) Catalytic transfer hydrogenation of ethyl levulinate to γ-valerolactone over a novel porous zirconium trimetaphosphate. Mol Catal 442:107–114
53. Ghashghaee M, Sadjadi S, Shirvani S, Farzaneh V (2017) A novel consecutive approach for the preparation of Cu-MgO catalysts with high activity for hydrogenation of furfural to furfuryl alcohol. Catal Lett 147:318–327
54. Srivastava S, Solanki N, Mohanty P, Shah KA, Parikh JK, Dalai AK (2015) Optimization and kinetic studies on hydrogenation of furfural to furfuryl alcohol over SBA-15 supported bimetallic copper-cobalt catalyst. Catal Lett 145:816–823
55. Sha YF, Xiao ZH, Zhou HC, Yang KL, Song YM, Li N, He RX, Zhi KD, Liu QS (2017) Direct use of humic acid mixtures to construct efficient Zr-containing catalysts for Meerwein-Ponndorf-Verley reactions. Green Chem 19:4829–4837
56. Natsir TA, Hara T, Ichikuni N, Shimazu S (2018) Highly selective transfer hydrogenation of carbonyl compounds using La_2O_3. Bull Chem Soc Jpn 91:1561–1569
57. He J, Schill L, Yang S, Riisager A (2018) Catalytic transfer hydrogenation of bio-based furfural with NiO nanoparticles. ACS Sustain Chem Eng 6:17220–17229
58. Puthiaraj P, Kim K, Ahn W (2019) Catalytic transfer hydrogenation of bio-based furfural by palladium supported on nitrogen-doped porous carbon. Catal Today 324:49–58

Affiliations

Tao Wang[1] · Aiyun Hu[1] · Guangzhi Xu[1] · Chen Liu[1] · Haijun Wang[1] · Yongmei Xia[2]

✉ Haijun Wang
wanghj329@outlook.com

[1] Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China

[2] State Key Laboratory of Food Science & Technology, Jiangnan University, Wuxi 214122, China