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Catalytic transfer hydrogenation of furfural to furfuryl alcohol using easy-to-separate core-shell magnetic zirconium hydroxide

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A hollow core-shell magnetic zirconium hydroxide catalyst was synthesized and employed for the catalytic transfer hydrogenation (CTH) ofnumerous biomass-derived platform molecules (furfural and other carbonyl compounds). 93.9% conversion of furfural and 97.3% selectivity of furfuryl alcohol was achieved under mild reaction conditions (160 °C, 4 h, 0.1 g catalyst) with 2-propanol as the H-donor. After 7 times of reaction cycles, the catalyst retained excellent conversion (91.1%) and selectivity (97.8%) and no structural damage was found. Furthermore, a scale-up experiment was carried out, and the results proved that the catalyst has a prospect for industrial applications in the CTH reaction.

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1. Introduction

Nowadays, due to the outbreak of worldwide population and extremely increasing demand of non-renewable fossil fuels, humans are confronted with energy crisis.^{1,2} Researchers are eager to exploit eco-friendly and renewable energy for sustainable development. Biomass (cellulose and lignocellulose), an inexhaustible, renewable natural resource, is an appropriate substitute.³ Also, it can be transformed into monosaccharide (glucose and xylose),⁴ which can be further converted into platform compounds. Furfural (FAL), the product of hydrolysis and dehydration of xylan, has been identified by US Department of Energy as one of the most encouraging chemicals, which can be converted into value-added fuels and chemicals.⁵ Among all the strategies of upgrading furfural, hydrogenation is one of the most universal reactions to manufacture biofuels,⁶ including 2-methylfuran (2-MF),^{7,8} furfural alcohol (FOL),^{9,10} γ-valerolactone (GVL),^{11,12} and further-hydrogenation product tetrahydrofurfuryl alcohol (THFOL),^{13,14} and 1,5-pentanediol (1,5-PDO).¹⁵⁻¹⁷ Also, these furan-based compounds are outstanding fuels in comparison to the alcohols due to their higher energy density and octane values.18

FOL is produced industrially by the liquid- or vapour-phase hydrogenation of furfural at around 180 $^{\circ}$ C and 70–100 bar hydrogen over copper chromite catalysts (CuCr₂O₄·CuO; Cu–Cr).^{16,19}

The use of high-pressure hydrogen and environmentally harmful catalysts are the main disadvantages. Current studies are usually performed with hydrogen as the H-donor using zero-valent noble metals (Pd,^{20,21} Ru,^{22,23} Rh,²⁴ Pt^{25,26}) or some newly developed non-noble metals (Ni,^{8,27,28} Co,^{29,30} Cu^{31,32}) as the catalysts. However, catalytic transfer hydrogenation (CTH) by the Meerwein-Ponndorf-Verley (MPV) reaction offers an attractive approach for the hydrogenation of aldehydes and ketones³³⁻³⁵ using alcohols as the H-donor. Clearly, the CTH reaction seems to be a safer and more economical method avoiding the use of hydrogen gas. In the reaction, the catalysts for common use vary from oxides,^{9,36} hydroxides of transition metals to zeolites, metal-organic frameworks (MOFs) and other catalysts containing Lewis acid or basic sites. Compared with other non-noble transition metals, zirconium offers better performance in the MPV reduction, which is attributed to its strong Lewis acidity.³⁷ The recent research on Zr-zeolite,^{38,39} Zr-mesoporous silicon,40 Zr-MOFs41 and other Zr-containing materials^{40,42} has made zirconium one of the most suitable elements for its fabulous effect in the hydrogenation reaction.

In addition to the catalytic performance, the recyclability of materials should also be taken into account. Compared with the traditional separation methods of filtration or centrifugation, the simple and fast separation of magnetic nanoparticles has made the research on magnetic carriers loaded with active centres receiving extensive attention. Wang *et al.* reported a hydroxyapatite-encapsulated magnetic γ -Fe₂O₃ acting on the hydrogenation of FAL into FOL and achieved a conversion of 96.2% at 180 °C for 10 h.⁴³ He *et al.* developed a kind of aluminium and zirconium mixed oxides coated Fe₃O₄ that exhibited a high FOL yield of 90.5% in the CTH of FAL.⁴⁴



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Moreover, He *et al.* also compared the catalytic activity of Fe_3O_4 , $CoFe_2O_4$ and $NiFe_2O_4$ in the CTH reduction, and found that $NiFe_2O_4$ has the best catalytic performance among the three materials from the perspective of conversion and selectivity.⁴⁵

In this study, in order to make the best of the catalytic properties of zirconium and the convenience of magnetic materials, a magnetic zirconium hydroxide core-shell catalyst was employed, with high thermal stability cobalt ferrite (CoFe₂O₄) as the magnetic core.⁴⁶ 95.4% of the conversion from FAL to FOL and 97.7% of FOL selectivity were achieved at 160 °C for 4 h by adjusting the ratio of cobalt to zirconium and optimizing the reaction conditions. In addition, several industrial manufacturing trials have also been conducted, including the reusability of catalysts and scale-up experiments.

2. Experiment

2.1 Materials

Furfural, furfuryl alcohol, other carbonyl compounds and the corresponding hydrogenated products were bought from TCI Chemical Reagent Company (Shanghai, China). ZrCl₄, ZrOCl₂. 8H₂O were obtained from Aladdin Reagent Co. Ltd (Shanghai, China). AlCl₃, CoCl₂·6H₂O, FeCl₃, benzoic acid, pyridine and all the alcohols were purchased from Sinopharm Chemical Reagent Company (Shanghai, China).

2.2 Catalysts preparation

2.2.1 Preparation of CoFe₂**O**₄. Magnetic CoFe₂O₄ particles were prepared through a well-established hydrothermal method.⁴⁷ First, 5 mmol CoCl₂·6H₂O and 10 mmol FeCl₃ were dissolved into 35 mL of ethylene glycol solution. Then, 0.09 mol urea was added in the solution under continuous stirring for 2 h until the solid disappeared. The mixture was transferred into an autoclave and heated up at 200 °C for 12 h. The resulting precipitate was washed with deionized water and ethanol for three times and was allowed to dry at 80 °C overnight.

2.2.2 Preparation of Zr@Co. 0.234 g of $CoFe_2O_4$ was mixed into ethanol (40 mL) in which a certain amount of $ZrOCl_2 \cdot 8H_2O$ was dissolved, and dispersed ultrasonically for 15 min. Then, the solution was mechanically stirred for 30 min and then 20 mL of the sodium hydroxide aqueous solution (0.4 mol L⁻¹) was dropped into it. After stirring for 2 h, the precipitate was separated with a permanent magnet and washed with deionized water and ethanol. Finally, the brown powder (product) obtained was dried overnight at 80 °C and named $Zr(OH)_4$ @CoFe₂O₄, abbreviated as Zr@Co. Different molar ratios of the feeding Zr to Co in the catalyst were denominated as Zr@Co-0.5, Zr@Co-1 and Zr@Co-2, respectively.

2.2.3 Preparation of other hydroxides. Other hydroxides including $Fe(OH)_3$, $Al(OH)_3$, $Co(OH)_2$, and $Zr(OH)_4$ were synthesized by traditional precipitation. A certain amount of corresponding chlorides (FeCl₃, AlCl₃, CoCl₂, and ZrOCl₂) was dissolved into deionized water and the pH value was changed by adding the sodium hydroxide solution. Also, an extra catalyst

was prepared by $ZrOCl_2$ and NaOH in the alcohol solution and named as $Zr(OH)_4$ -A. The resulting products were dried at 80 °C overnight.

2.3 Catalytic conversion of FAL and product analysis

The reaction of FAL was carried out in a steel alloy autoclave (GB1220-92) with a volume of 35 mL. A mixture of substrates (0.67 mmol), solvents (20 mL), and catalysts (10–200 mg) was added to the reactor before the reactor was sealed. The reaction was conducted at a definite temperature (120–180 °C) without stirring. After a period of time (1–4 h), the reactor was cooled down to room temperature and the liquid samples were analysed by GC-MS (Thermo Scientific Trace ISQ) with a TR-WAX-MS capillary column (30.0 cm \times 320 µm \times 0.25 µm).

2.4 Catalyst characterization

A Rigaku D/max-2550 diffractometer with Cu-Kα radiation was utilized for X-ray diffraction. The morphology of the samples was investigated via scanning electron microscopy (SEM, Jeol JSM-6700F) and transmission electron microscopy (TEM, Tecnai F20). Brunauer-Emmett-Teller (BET) surface area was assessed by N2 adsorption-desorption on an Asap 2420 surface adsorption apparatus. The magnetic property was measured using a magnetic property measurement system (SQUID-VSM) with an applied force from -30 000 to 30 000 Oe at room temperature. Fourier transform infrared (FT-IR) spectra between 400 to 4000 cm⁻¹ was evaluated on a Bruker VERTEXV 80 V spectrometer. The thermogravimetric (TG) analysis was performed under air atmosphere at the heating rate of 10 °C min⁻¹ using a thermogravimetric analysis system (PerkinElmer Instruments). The elemental composition of the catalysts was determined by inductively coupled plasma (ICP) with Optima 3300 DV (Perkin-Elmer Instruments) and CHNS elemental analysis on Elementer Vario Micro.

3. Result and discussion

3.1 Catalyst screening for CTH reaction from FAL to FOL

The catalytic performance of different metal hydroxides for the CTH reaction from FAL to FOL is listed in Table 1. The results show that zirconium hydroxide gives the best catalytic performance among the four catalysts at 120 °C for 3 h (27.7% conversion and 86.3% FOL selectivity, entries 1–4), which is consistent with the literature.³⁷ Moreover, the synthesis

Table 1	Screening of unterent metal hydroxide catalysis				
Entry	Catalysts	Conversion (%)	Yield (%)	Selectivity (%)	
1	Fe(OH) ₃	5.5	1.5	27.3	
2	$Co(OH)_2$	17.5	11.6	66.2	
3	$Al(OH)_3$	12.4	7.2	58.1	
4	$Zr(OH)_4$	27.7	23.9	86.3	
5	Zr(OH) ₄ -A	53.5	47.8	89.3	
6^{b}	$Zr(OH)_4$	48.3	42.3	87.6	

Table 1 Corporations of different mostal budrowide established

 a Reaction condition: 0.67 mmol furfural, 20 ml 2-PrOH, 0.1 g catalyst, 120 $^\circ C$, 3 h. b The zirconium hydroxide here is refluxed in ethanol for 6 h before the reaction.

Table 2 Catalytic performance of different zirconium loading capacities of $\text{CoFe}_2\text{O}_4^{\ \partial}$

Entry	Catalysts	Conversion (%)	Yield (%)	Selectivity (%)
1	CoFe ₂ O ₄	8.4	6.1	72.6
2	Zr@Co-0.5	43.2	41.2	95.4
3	Zr@Co-1	60.0	56.2	93.6
4	Zr@Co-2	87.1	84.6	97.1
5^{b}	Zr@Co-2	44.3	40.7	91.8
6 ^{<i>c</i>}	Zr@Co-2	21.1	18.9	89.6

 a Reaction condition: 0.67 mmol furfural, 20 ml 2-propanol, 160 °C, 3 h. b 1 mmol pyridine was added into the reaction. c 1 mmol benzoic acid was added into the reaction.

method has a crucial influence on the catalytic effect. $Zr(OH)_4$ -A shows better catalytic performance (Table 1, entry 5) than the one prepared from the traditional precipitation with respect to conversion and selectivity (53.5% and 89.3%, respectively). It is inferred that ethanol helped changing the surface properties of the catalyst and enhanced the acid-base density by exposing coordinatively unsaturated sites.⁴⁸ To further confirm this inference, a supplementary experiment was carried out (Table 1, entry 6). Compared with the original one (entry 4), the $Zr(OH)_4$ refluxed in ethanol (entry 6) increased the conversion from 27.7% to 48.3%. Therefore, zirconium hydroxide synthesized in thre ethanol solution is the preferred catalyst for the reaction.

Revealing in Table 2, $CoFe_2O_4$ alone has little catalytic effect on the hydrogenation of FAL with a low conversion of 8.4%, which is consistent with the previous work.⁴⁵ Also, as expected, with the increase in $Zr(OH)_4$ loading, the catalytic activity of the catalysts enhanced gradually, and the conversion reached to 87.1% with 97.1% selectivity. Therefore, Zr@Co-2 is the optimal catalyst in the following researches. To further investigate the influence of acid and base sites, the poisoning experiment was conducted. A certain amount of pyridine or benzoic acid (1 mmol) was added to the reaction to block the contact of substrate and the acid or base sites in the catalyst, respectively. Also, conversion sharply declined from 87.1% to 44.3%/21.2%, indicating that the reaction is a catalytic process with concerted effects of the acid and base sites.

3.2 Characterization of the catalysts

The X-ray diffraction (XRD) patterns of the catalysts with different $Zr(OH)_4$ loading are displayed in Fig. 1. $CoFe_2O_4$ with good crystallinity is synthesized (PDF JCPDS#22-1086). As the loading of $Zr(OH)_4$ increases, the intensity of the $CoFe_2O_4$ diffraction peaks gradually decreases dramatically due to the amorphous phase of the coated zirconium hydroxide, which was verified by the broad peak of $Zr(O-2 \text{ from } 20^\circ \text{ to } 40^\circ.$

The microstructure of the catalysts was characterized by SEM and TEM (Fig. 2 and 3). Overall, $CoFe_2O_4$ reveals spherical nanoparticles with an average diameter of 260–310 nm (Fig. 2a). Also, from the charts of particle size distribution, the introduction of $Zr(OH)_4$ slightly increases the particle size to 300–350 nm and rough surfaces (Fig. 2b–d). In particular, some of the particles in Zr@Co-2 are stuck together (Fig. 2d) and the



Fig. 1 XRD patterns of catalysts with different Zr loading



Fig. 2 SEM images and particle size distribution charts of $CoFe_2O_4$ (a), Zr@Co-0.5 (b), Zr@Co-1 (c) and Zr@Co-2 (d).

TEM image (Fig. 3d) can further confirm it. Fig. 3a and d illustrate the TEM images of cobalt ferrate and cobalt ferrate coated zirconium hydroxide, respectively. The diameter of $CoFe_2O_4$ varies from 240 nm to 340 nm and mainly 280 nm (Fig. 3a), which was in agreement with the SEM image (Fig. 2a). The TEM image of $CoFe_2O_4$ (Fig. 3b) shows a hollow architecture with a bright centre. The dominant crystalline phase with a lattice distance of 0.297 nm corresponding to the lattice plane [220] of $CoFe_2O_4$ (Fig. 3c) was also identified by the XRD characterization. The formation of the hollow structure can be attributed to the Ostwald ripening process.⁴⁷ Also, $Zr(OH)_4$ and $CoFe_2O_4$ have a manifest border marked in Fig. 3e and f.



Fig. 3 TEM images of CoFe₂O₄ nanoparticle (a and b) and Zr@Co-2 (d and e). The HRTEM image of CoFe₂O₄ (c) and Zr@Co-2 (f). The dotted line is the boundary between Zr(OH)₄ and CoFe₂O₄.

The N₂ adsorption–desorption isotherms of the catalysts are exhibited in Fig. 4a. Type-IV isotherms with a typical hysteresis loop were found for all the catalysts, which are typical of mesoporous catalysts. The specific surface area (S_{bet}) value of CoFe₂O₄ is very low (15.9 m² g⁻¹, Table 3), but the stacking of Zr(OH)₄ around CoFe₂O₄ brings about a substantial increase in the specific surface area due to the mesoporous structure of Zr(OH)₄ and the S_{bet} value of Zr@Co-2 reaches 192.2 m² g⁻¹.



Fig. 4 The N_2 adsorption–desorption isotherm (a) and the magnetization curves (b) of the catalysts.

Table 3 Physicochemical property of different catalysts					
Catalysts	$S_{\mathrm{bet}}^{a} \left(\mathrm{m}^{2} \mathrm{g}^{-1}\right)$	$V_{\text{pore}}^{b} (\text{cm}^3 \text{g}^{-1})$	D_{mean}^{c} (nm)		
CoFe ₂ O ₄ Zr@Co-0 Zr@Co-1 Zr@Co-2	15.9 5 107.7 138.6 192.2	0.06 0.17 0.28 0.22	9.16 5.12 5.32 3.58		

 a BET surface area was assessed by $\rm N_2$ physisorption. b Volume of pores was estimated by the BJH adsorption cumulative volume of pores. c Average pore size was obtained from the adsorption average pore width.

The magnetic property of the catalysts was detected by a vibrating sample magnetometer and the magnetization curves of the catalysts are given in Fig. 4b. The saturation magnetization (SM) values of Zr@Co-0.5, Zr@Co-1, Zr@Co-2 are 93.14 emu g⁻¹, 41.93 emu g⁻¹, 15.11 emu g⁻¹, respectively. As expected, increase in the thickness of Zr(OH)₄ shell resulted in a decrease in the ratio of magnetic cores, causing the SM value to drop sharply as the loading of Zr(OH)₄ increases. Although the SM value of Zr@Co-2 is not very high, it is easily attracted by magnets.

3.3 Catalytic Performance of Zr@Co-2

3.3.1 Effect of reaction parameters on the CTH reaction from FAL to FOL. The influence of the reaction temperature, reaction time and catalyst dosage on the CTH reaction from FAL to FOL over Zr@Co-2 is illustrated in Fig. 5. From Fig. 5a, as the reaction temperature rose from 120 °C to 160 °C for 4 h, the yield increased unilaterally (from 55.7% at 120 °C to 93.9% at 160 °C), while the selectivity of FOL remained constant (>95%). Also, the elevation of reaction temperature from



Fig. 5 Effect of (a) temperature, (b) time and (c) catalyst dosage on the production of FOL from FAL. Reaction conditions: FAL (0.67 mmol), 2-propanol (20 ml), catalyst (0.1 g).

160 °C to 180 °C had a weak effect on the reaction. The turnover frequency (TOF) is defined as mmol (converted FAL)/[mmol (total metal) \times h (time)] and the TOF value of Zr@Co-2 is 0.842 h^{-1} at 160 °C for 4 h. It is worth noting that with the catalyst Zr@Co-2, the conversion of FAL at 120 °C (55.7%) is even better than that of FAL with pure Zr(OH)₄ as the catalyst (Table 1, entry 5). It reveals that the combination of zirconium hydroxide and CoFe₂O₄ enhances the specific surface area of Zr(OH)₄ and exposes more active sites. The influence of the reaction time at 160 $^\circ \rm C$ is also discussed in Fig. 5b. The extension of the reaction time (from 1 h to 4 h) resulted in the increase in both the conversion of FAL and the selectivity of FOL from 31.7% and 85.8% in 1 h to 87.1% and 96.8% in 4 h, respectively. With continuous extension of the reaction time to 5 h, the conversion and the selectivity remained unchanged. In the examination of the catalyst dosage (Fig. 5c), the blank experiment had little effect on the reaction (18.2% conversion of FAL and 16.4% selectivity of FOL), suggesting that the CTH reaction could barely take place without catalyst. In contrast, the FAL conversion and FOL selectivity increased rapidly with the amount of catalyst, from 30.2% and 97.1% at 0.01 g to 93.9% and 97.3% at 0.1 g. A further increase from 0.1 g to 0.2 g did not achieve a better catalytic effect. In conclusion, the optimal reaction conditions for the reaction are 4 h at 160 °C with 0.1 g catalyst.

3.3.2 Effect of different alcohols as H-donors on the reaction and CTH reaction of various substrates. The catalytic performances of Zr@Co-2 with different alcohols (from primary alcohols to tertiary alcohols) as hydrogen donors are displayed in Fig. 6a. Using



Fig. 6 CTH reaction of FAL to FOL using different alcohols as the Hdonor (a) and CTH reaction of various substrates (b) over the Zr@Co-2 catalyst. Reaction condition: 20 ml alcohol, 0.67 mmol substrate, 0.1 g catalyst, 160 °C, 4 h

primary alcohols (ethanol, n-propanol and n-butanol) as the alcohol source, the selectivity of FOL is similar, but the conversion of FAL raises up with the growth of the carbon chain (from 33.5% of ethanol, 48.9% of n-propanol to 55.7% of n-butanol). Owing to the steric effect, the transition state formed between the catalyst and the H-donor is more stable as the carbon chain grows.⁴¹ As for secondary alcohols, 2-propanol and 2-butanol exhibited a desired conversion (87.1% and 77.1%) and selectivity (96.7% and 93.2%), which are more effective H-donors in the CTH reaction. Previous studies demonstrated that β-hydride was easier to eliminate from the intermediate alkoxide species of secondary alcohol in the CTH process.⁴⁹ It is noticeable that no FOL was generated with tert-butanol as the alcohol source, which is attributed to the absence of hydrogen on the α -C of the *tert*-butanol, and a six-membered ring intermediate cannot be formed between FAL and the active sites on the surface of the catalyst.³⁶ Therefore, 2-propanol is the preferred source of alcohol.

As Zr@Co-2 revealed excellent activity towards the catalytic transfer hydrogenation of FAL, a variety of other carbonyl compounds (saturated or unsaturated aldehydes/ketones) were tested as substrates (Fig. 6b). Clearly, the catalyst showed great catalytic activity towards these carboxides resulting in at least 70% selectivity of the main products. Among them, two kinds of α , β -unsaturated aldehydes as substrates were tested as well. Also, allylic alcohols, the selectively reduced products, were gathered with a selectivity of 90%. These results indicated that the Zr@Co-2 catalyst exhibits good catalytic performance for the CTH reaction of different types of aldehydes/ketones.

3.4 Reusability of catalyst

The reusability of Zr@Co-2 was tested under optimal reaction conditions (160 °C, 4 h and 0.1 g) (Fig. 7). After the reaction, the catalyst was separated by a magnet, and the digital image is shown in Fig. 7a. After washing and drying at 80 $^\circ$ C, the catalyst



Fig. 7 Reusability tests (a) of the Zr@Co-2 catalyst and element content (b), FT-IR (c), TG curves (d) of fresh and used Zr@Co-2.

was directly applied in the next cycle without further treatment. From Fig. 7a, after 7 cycles, no obvious drop in the conversion of FAL and the selectivity of FOL was observed (91.1% and 97.8%, respectively), indicating that the catalyst is a recyclable catalyst with excellent catalytic performance and easy separation.

To further confirm the structural stability of Zr@Co-2, some characterizations of the fresh and used catalysts were accomplished (Fig. 7b-d). Compared to the fresh Zr@Co-2, carbon content of the used catalyst increased by 1.75% due to the accumulation of few organic compounds in the catalyst. Moreover, the weight percentage of zirconium decreases slightly (from 16.83% to 14.94%) after 7 cycles, revealing the good stability of the catalyst under the reaction conditions. In Fig. 7c, the infrared spectra of fresh and used catalyst are similar. The peak located in 463 cm⁻¹ and 535 cm⁻¹ belonged to the stretching vibrations of Zr-O⁵² and Fe-O,⁵³ respectively. The bands observed at 1352 and 1528 cm⁻¹ are typical characteristics of the O-H bending vibration modes of water and Zr-OH, respectively. More than that, the wide peak at 3401 cm^{-1} is ascribed to the stretching modes of O-H. However, the two extra peaks at 1475 and 1381 cm⁻¹ result from the bending vibrations of C-H on the used catalyst and confirm the carbon accumulation of the catalyst as our previous work reported.⁵² Also, the thermogravimetric (TG) curve further confirmed that. The adsorption of insoluble organic oligomers or polymers produced from the side reaction is responsible for the difference in the weight loss percentage (2.6%) at 700 °C (Fig. 7d).

3.5 Scale-Up CTH reaction of FAL

As a preliminary attempt of industrial manufacturing, a 10-fold scale-up experiment using Zr@Co-2 as the catalyst was performed in a 300 mL Teflon-lined autoclave with magnetic stirring (500 rpm). In the experiment, 1 g of Zr@Co-2 and 6.7 mmol of FAL were mixed in 200 mL of 2-propanol. The mixture was sealed in a reactor and reacted at 160 °C for 8 h. During the reaction, the sample was taken several times through liquid extraction port and analysed by GC-MS. From Fig. 8, with



Fig. 8 Scale-up CTH experiment of FAL to FOL with the Zr@Co-2 catalyst.



Scheme 1 Plausible reaction mechanism for hydrogen transfer of furfural with the Zr@Co-2 catalyst.

the rising temperature, the conversion of FAL increased gradually and reached 88.2% in 4 h, which was consistent with our previous results. The almost complete conversion of FAL and over 95% selectivity to FOL at 8 h proved that the catalyst has great potential in industrial applications.

3.6 Catalytic mechanism for the CTH reaction of FAL

Based on the above results and previous studies,^{52,54} the plausible catalytic mechanism for the hydrogenation of FAL was proposed (Scheme 1). The reduction of FAL adopted the Lewis acid-mediated MPV reaction and passed through a six-membered ring transition state. In this case, $Zr(OH)_4$ plays a critical role of the reduction of FAL as a Lewis acid.⁵⁵ First, 2-propanol was adsorbed on the surface of $Zr(OH)_4$ and interacted with acid sites (Zr^{4+}) and base sites (O^{2-}) to form metal alkoxide.³⁹ Then, the oxygen atom on the carbonyl group of FAL is activated and stabilized by Lewis acid sites.⁵² With the formation of a six-membered ring transition state, the hydride transfer from alkoxide to the carbonyl group of FAL was accomplished.^{52,53} Finally, the newly formed FOL is desorbed from the surface of the catalyst along with acetone and the Lewis acid sites were re-exposed.

We also compared the catalytic activity of Zr@Co-2 with other magnetic materials for the CTH reaction of FAL to FOL (Table 4), and Zr@CO-2 gives competitive or even the best catalytic performance.

4. Conclusion

A series of easy-to-separate hollow magnetic nanoparticles Zr@Co were synthesized, among which Zr@Co-2 manifested remarkable catalytic activity in the CTH process for the production of FOL from FAL. Under the preferred reaction conditions (160 °C, 4 h, and 0.1 g catalyst), 93.9% of FAL was hydrogenated with 97.3% selectivity of FOL using 2-propanol as the hydrogen donor. Seven cycle experiments from FAL to FOL revealed that the catalyst still maintains high catalytic activity (91.1% FAL conversion and 97.8% FOL selectivity). Furthermore, a ten-fold scale-up experiment was carried out and obtained similar

Table 4 The comparison of Zr@Co-2 with other magnetic catalysts for the CTH reaction of FAL to FOL

Entry	Catalyst	H-Donor	Temperature (°C)	Time (h)	Conversion (%)	Selectivity (%)	Ref.
1	NiFe ₂ O ₄	2-Propanol	180	6	99	95	45
2	Fe_3O_4-12	2-Propanol	160	5	97.5	92.4	50
3	γ-Fe ₂ O ₃ @HAP	2-Propanol	180	10	96.2	95.3	43
4	Al ₇ /Zr ₃ @Fe ₃ O ₄	2-Propanol	180	4	99.1	91.3	44
5	Fe ₃ O ₄ @C	2-Propanol	200	4	93.6	98.9	51
6	Zr@Co-2	2-Propanol	160	4	93.9	97.3	This work

results as those of the batch experiments, proving that the catalyst has industrial application potential in the CTH reaction of FAL.

Conflicts of interest

There are no conflicts to declare.

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