Selective Transfer Hydrogenation of Furfural into Furfuryl Alcohol on Zr-Containing Catalysts Using Lower Alcohols as Hydrogen Donors

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ABSTRACT: A series of zirconium-based catalysts were prepared for the selective transfer hydrogenation of biomass-derived furfural (FFR) into furfuryl alcohol with lower alcohols as hydrogen sources. The sample structures were clearly characterized using various methods, such as X-ray powder diffraction, thermogravimetric analysis, scanning electron microscope, NH3-temperature-programmed desorption (TPD), CO2-TPD, and nitrogen physisorption. Excellent furfuryl alcohol yield of 98.9 mol % was achieved over Zr(OH)4 using 2-propanol as a hydrogen donor at 447 K. The poisoning experiments indicated that basic centers displayed pronounced effect for FFR transfer hydrogenation. Moderate monoclinic phase content in ZrO2-x enhanced the conversion rate and furfuryl alcohol selectivity, whereas acid–basic site density ratio had slight influence on FFR conversion. Besides, Zr(OH)4 revealed good performance and stability after being repeated four times. The possible mechanism for this transfer hydrogenation process over Zr(OH)4 catalyst with 2-propanol as the hydrogen source was proposed.

1. INTRODUCTION

The rapid depletion of fossil fuel resources and significant deterioration of environmental problems have motivated the researchers worldwide to explore alternative renewable feedstocks for the sustainable manufacture of liquid fuels and chemicals. In recent decades, the catalytic conversion of biomass and related derivatives to chemicals has received wide range of attention. Furfural (FFR), a potential platform for the production of synthetic chemicals, is mainly obtained by acid-catalyzed hydrolysis and dehydration of C5 carbohydrates. For instance, Yan et al. reported that hydrotalcite-derived Cu–Mg–Al catalyst could catalyze FFR hydrogenation using 2-propanol as hydrogen donor. Marchi et al. found that Cu–Mg–Al catalyst could catalyze FFR hydrogenation using 2-propanol as hydrogen donor. Lee et al. synthesized alumina–carbon composite catalysts for the conversion of FFR in 2-propanol, with a desired FA yield of 95.8% at 403 K for 6 h. Recently, low-cost eco-friendly metal hydroxides/oxides are found to allow efficient transformation of biomass-derived chemicals via MPV reduction in various alcohols. For example, Dumesic’s group described the CTH of levulinic acid and its esters into γ-valerolactone via MPV reaction over metal oxides using alcohols as the hydrogen sources. Lin et al. reported an effective CTH route to convert ethyl levulinate into γ-valerolactone over ZrO2·xH2O and ZrO2 in subcritical alcohols. Particularly, Zr-containing catalysts are much more efficient for the CTH of biomass derivatives in the presence of alcohols.

Inspired by the above findings, a series of low-cost and environmentally benign Zr-based materials were synthesized for the CTH of FFR. The influences of varied reaction parameters, attention, in which high-pressure gaseous hydrogen is replaced by alcohols to avoid defects, such as storage, safety, solubility, etc. For this reason, much effort has been devoted to the expansion of various catalysts for upgrading FFR via the hydrogen transfer method. Marchi et al. found that Cu–Mg–Al catalyst could catalyze FFR hydrogenation using 2-propanol as hydrogen donor. Lee et al. synthesized alumina–carbon composite catalysts for the conversion of FFR in 2-propanol, with a desired FA yield of 95.8% at 403 K for 6 h. Recently, low-cost eco-friendly metal hydroxides/oxides are found to allow efficient transformation of biomass-derived chemicals via MPV reduction in various alcohols. For example, Dumesic’s group described the CTH of levulinic acid and its esters into γ-valerolactone via MPV reaction over metal oxides using alcohols as the hydrogen sources. Lin et al. reported an effective CTH route to convert ethyl levulinate into γ-valerolactone over ZrO2·xH2O and ZrO2 in subcritical alcohols. Particularly, Zr-containing catalysts are much more efficient for the CTH of biomass derivatives in the presence of alcohols.

Inspired by the above findings, a series of low-cost and environmentally benign Zr-based materials were synthesized for the CTH of FFR. The influences of varied reaction parameters,
such as hydrogen source, catalyst type, temperature, and catalyst dosage, were systematically discussed to gain high FFR conversion and FA selectivity. Meanwhile, a comprehensive structure characterization of the fresh and spent catalysts was conducted. The results indicated that Zr(OH)\(_4\) exhibited excellent performance toward FFR transfer hydrogenation with 2-propanol as the hydrogen source and was reusable over multiple cycles without significant loss of activity. Furthermore, a plausible reaction mechanism for the CTH of FFR to FA via MPV reduction over Zr-containing materials in 2-propanol was proposed.

2. EXPERIMENTAL SECTION

2.1. Materials. Furfural (FFR, 99%) and furfuryl alcohol (FA, 98%) were provided from Aladdin Reagent Co. Ltd. (Shanghai, China). ZrOCl\(_2\)-8H\(_2\)O (98%), ammonia water (25–28%), butanol (anhydrous, 99%), 2-butanol (anhydrous, 99%), ethanol (anhydrous, 99.5%), 2-propanol (anhydrous, 99.5%), and other commercially available chemicals were purchased from Guangzhou Chemical Reagent Co. Ltd. (Guangzhou, China). Notably, FFR was distilled under vacuum before use.

2.2. Catalysts Preparation. First, ZrOCl\(_2\)-8H\(_2\)O was dissolved in deionized water to obtain a 0.4 mol L\(^{-1}\) solution, and then NH\(_3\)·H\(_2\)O was added dropwise to regulate the pH value to 9–10 under vigorous agitation, followed by aging at room temperature for 24 h. The resulting precipitate was thoroughly washed with deionized water until residual Cl\(^-\) was completely removed, based on 0.05 mol L\(^{-1}\) AgNO\(_3\) detection. The precipitate was dried at 383 K overnight and was further ground to obtain Zr(OH)\(_4\) powder. Then, Zr(OH)\(_4\) sample was calcined at a heating rate of 2 K min\(^{-1}\) in air flow for 3 h for the synthesis of ZrO\(_2\)-x (x represents the given calcination temperatures), in which x was varied from 623 to 1023 K with an interval of 100 K.

2.3. Catalyst Characterization. X-ray powder diffraction (XRD) was performed on a Panalytical X’Pert Pro diffractometer using a Cu K\(\alpha\) radiation source at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) measurements were obtained on a Kratos Ultra system using an Al K\(\alpha\) radiation source. The binding energies for each spectrum were calibrated with a C 1s spectrum of 284.6 eV. The Brunauer–Emmett–Teller (BET) surface area was determined with N\(_2\) adsorption–desorption isotherms at 77 K (SI-MP-10, Quantachrome). Before test, the samples were degassed under vacuum at 433 K for 20 h. The sample morphology was realized on field emission scanning electron microscope (FESEM, Hitachi S-4800). Chemical analysis of leached Zr\(^{4+}\) was measured by a thermo elemental inductively coupled plasma optical emission spectrometry (ICP-AES) spectrometer.

The quantitative analysis of acid site density was carried out on a Quantachrome ChemStar chemisorption analyzer through NH\(_3\) temperature-programmed desorption (TPD). For each run, the sample was heated up to 573 K at a rate of 10 K min\(^{-1}\) and kept for 0.5 h in a He flow to remove adsorbed impurities. Then, the sample was cooled down to 373 K for the adsorption of NH\(_3\). After flushing with He to remove physically adsorbed NH\(_3\), the TPD data were collected from 373 to 1273 K with a ramp of 10 K min\(^{-1}\). CO\(_2\)-TPD test was performed by using a similar procedure, where NH\(_3\) was replaced with CO\(_2\) during the adsorption process.

Using a SDT Q 600 instrument, thermogravimetric/differential thermic analyses (TGA/DTA) were measured over fresh and spent Zr(OH)\(_4\) to identify the amount of absorbed carbohydrate over the catalyst surface. Specifically, a sample of around 200 mg was typically used for the test at temperatures from room temperature to 1273 K, with a heating rate of 10 K min\(^{-1}\) in an air atmosphere.

2.4. Catalytic Test. In a typical run, catalyst, substrate FFR (1.2 mmol), and hydrogen source (15 mL) were put into a 100 mL stainless steel reactor. Subsequently, the air in the reactor was flushed out using inert atmosphere (N\(_2\)) five times. Then, the reactor was initiated at a designated temperature with a stirring rate of 600 rpm under 1 MPa N\(_2\) atmosphere. After predetermined time, the reactor was cooled to room temperature in an ice water, and the filtered samples from the mixtures were further analyzed.

2.5. Product Analysis. The quantity analysis of liquid samples was completed on Fuli GC9790 II equipped with a flame ionization detector and a KB-5 capillary column (30.0 m × 0.25 μm × 0.25 μm) using nitrogen as the carry gas. The operating conditions were as follows: injector port temperature, 533 K; column temperature, initial temperature 343 K (0.5 min), gradient rate 5 K min\(^{-1}\); end temperature 428 K (0.5 min), flow rate 75 mL min\(^{-1}\).

The formulas for calculating FFR conversion, FA yield, and selectivity are defined below

\[
\text{conversion (mol %)} = \frac{(\text{mole of FFR converted/mole of FFR fed}) \times 100}{(\text{mole of FA produced/mole of substrate fed}) \times 100}
\]

\[
\text{selectivity (%)} = \left(\frac{\text{FA yield/FFR conversion}}{100}\right) \times 100
\]

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization. Figure 1 shows X-ray diffraction patterns of prepared zirconium-based materials.

Specifically, fresh and recycled Zr(OH)\(_4\) exhibited similar patterns with two broad and weak peaks in an angle range from 25 to 60\(^\circ\), suggesting that the samples were characteristic of an amorphous structure and no new phase was observed after reuse. Through calcination treatment, typical peaks composed of monoclinic and tetragonal phases were obviously formed in ZrO\(_2\)-x (x = 623, 723, 823, 923, and 1023). Noticeably, XRD
spectrum of ZrO2-623 revealed typical peaks of tetragonal zirconia at 30.2 and 50.3° that agreed well with that of the standard pattern of JCPDS file no. 79-1769. Furthermore, characteristic peaks at 2θ of 17.4, 28.2, 31.5, 34.4, 49.3, 54.2, and 55.7° (JCPDS file no. 37-1484), indicative of the presence of monoclinic zirconia, were observed in ZrO2-x (x = 723, 823, 923, and 1023 K). The percentages of the monoclinic and tetragonal phases are also given in Table 1, as calculated from corresponding peak areas. Apparently, higher temperatures facilitated monoclinic zirconia formation, and an increasing

| sample     | \(^{a}\text{BET (cm}^2\text{ g}^{-1})\) | \(^{b}\text{PV (cm}^3\text{ g}^{-1})\) | \(^{c}\text{A (mmol g}^{-1}\) | \(^{d}\text{B (mmol g}^{-1}\) | \(^{e}\text{A/B}\) | \(^{f}\text{TP (%)}\) | \(^{g}\text{MP (%)}\) |
|------------|--------------------------------|--------------------------------|----------------|----------------|----------------|----------------|----------------|
| Zr(OH)\(_4\) | 242.3 | 0.21 | 1.29 | 1.36 | 0.95 | |
| \(^h\)Zr(OH)\(_4\) | 193.2 | 0.16 | | | |
| ZrO2-623 | 78.9 | 0.078 | 0.85 | 0.69 | 1.23 | 29.8 | 70.2 |
| ZrO2-723 | 38.6 | 0.085 | 0.65 | 0.38 | 1.71 | 25.9 | 74.1 |
| ZrO2-823 | 20.7 | 0.083 | 0.31 | 0.22 | 1.41 | 10.2 | 89.8 |
| ZrO2-923 | 11.5 | 0.075 | 0.26 | 0.16 | 1.63 | 7.7 | 92.3 |
| ZrO2-1023 | 9.0 | 0.070 | 0.13 | 0.11 | 1.18 | 7.6 | 92.4 |

\(^a\text{BET, specific surface area.}\)\(^b\text{PV, total pore volume.}\)\(^c\text{A, acid site density, determined by NH}_3\text{-TPD.}\)\(^d\text{B, basic site density, determined by CO}_2\text{-TPD.}\)\(^e\text{Ratio of acid site density to basic site density.}\)\(^f\text{Percentage of tetragonal phase (TP) ZrO}_2.\)\(^g\text{Percentage of monoclinic phase (MP) ZrO}_2.\)\(^h\text{After the third run.}\)

Figure 2. XPS characterization of prepared Zr-based samples: (A) full spectra; (B) O 1s; (C) Zr 3d.
intensity of these peaks was observed along with the increase in calcination temperatures.

XPS characterization was undertaken to investigate the surface chemical state of selected Zr-based materials. As depicted in Figure 2A, the full range XPS spectra of prepared samples were monitored to find out C 1s, O 1s, and Zr 3d species. Clearly, high-resolution scans of the XPS spectra of O 1s and Zr 3d with different intensity scales as ordinate are observed in Figure 2B and C. High-resolution O 1s spectra (Figure 2B) verified two surface species with binding energies of 529.8 and 531.3 eV for the fresh Zr(OH)₄⁺, characteristic of ZrO₂ and Zr-OH, respectively. This result further indicated that prepared Zr(OH)₄ might actually existed in the form of ZrO(OH)₂·xH₂O. However, calcination favored surface dehydroxylation at high temperatures, which produced zirconium oxides in various crystalline forms. Therefore, it is clearly seen that characteristic peak at 531.3 eV assigned to Zr-OH gradually disappeared in the ZrO₂-x (x = 623, 723, 823, 923, and 1023) samples. With respect to Zr 3d species, the binding energies of corresponding photoelectron peaks were allocated to 181.8 eV for the Zr 3d₃/₂ line and 184.2 eV for the Zr 3d₅/₂ line, indicating the presence of Zr⁴⁺ species in ZrO₂ and Zr-OH (Figure 2C).

The textural characterizations of zirconium-based materials are further analyzed via N₂ physisorption. As indicated in Figure 3A, weak interaction between synthesized Zr-based samples and N₂ in low-pressure region (P/P₀: 0–0.1) was observed, especially for ZrO₂-x obtained at higher temperatures above 723 K. Typically, Zr(OH)₄ and ZrO₂-x (x = 623 and 723) were characteristic of IV isotherm with a H₂ hysteresis loop, whereas ZrO₂-823, ZrO₂-923, and ZrO₂-1023 revealed V isotherm with a H₃ hysteresis loop. Table 1 summarizes the resulting BET surface area and total pore volume, it is clearly seen that fresh Zr(OH)₄ had larger BET surface area and total pore volume of 242.3 m² g⁻¹ and 0.21 cm³ g⁻¹ respectively, as compared with those of calcined ZrO₂-x samples. Actually, higher calcination temperatures (>623 K) cause a significant drop in the BET surface area and total pore volume, presumably attributable to particles crystallization. For the spent Zr(OH)₄ an acceptable drop in the BET surface area and total pore volume was mainly due to the presence of carbon residues. Figure 3B also gives the pore width distributions of prepared Zr-based materials. In comparison, the pore diameters of Zr(OH)₄ and ZrO₂-x (x = 623 and 723) centered at around 3–5 nm, whereas larger pore diameters in a size range of 15–45 nm appeared for ZrO₂-x (x = 823, 923, and 1023) samples. It is inferred that small particles crystallization and sintering under higher temperatures might be responsible for the occurrence of larger pore diameters.

Figure 4 presents the SEM images of zirconium-based materials. It is apparent that fresh and spent Zr(OH)₄ consisted of amorphous crystallites in a size of around 20 nm, which was well consistent with that of XRD test. No obvious variation in the primary crystallite size and the surface morphology were detected before and after use (Figure 4A,B,F). For the calcined samples, the crystallite size increased to 50–100 nm with elevating the temperature to 823 K, and then much crystallites in an irregular shape were identified at 1023 K (Figure 4E).

TGA–DTA analysis was conducted to evaluate the carbon deposits on the spent Zr(OH)₄ (after the third run). As described in Figure 5, fresh Zr(OH)₄ afforded an initial weight loss of 3.5 wt % before being heated to around 385 K, and the existence of physisorbed water and surface hydroxyl groups largely accounted for this phenomenon. A further weight loss of 8.8 wt % was recorded from 390 to 730 K owing to the removal of intercalated water, implying the structure transformation of amorphous Zr(OH)₄ into crystalline zirconia, in good accordance with the results from XRD and SEM analyses. Weight loss of 9.3 wt % in the TGA profile of spent Zr(OH)₄ was registered in the temperature range of 410–800 K, suggesting that only small quantity of organic carbon compounds accumulated on the catalyst surface during the recycling experiments. Furthermore, TGA curves showed that the practical weight losses of both of the fresh and recycled samples were much lower than the theoretical value of 22.6 wt %, indicating that the actual state of catalyst might existed as ZrO(OH)₂·xH₂O, rather than Zr(OH)₄⁻⁴.
NH₃-TPD and CO₂-TPD measurements were investigated to characterize the acid–basic properties (Scheme 1) and concentration in the synthesized materials, and the acid–basic site density and ratio of acidity to basicity were provided in Table 1. Figure 6 shows the TPD profiles of desorbed ammonia, medium to strong acid sites at desorption temperature range of 640–800 K could be identified for all samples. For fresh Zr(OH)₄, intensive desorption peaks at ~700 K indicated the presence of higher level of acid site density. However, the calcined samples ZrO₂-x (x = 623, 723, 823, 923, and 1023) revealed relatively moderate acid site density. Generally, higher temperatures led to the reconfiguration of surface structure, in which much water molecules were removed from the initial structure. In this regard, the amount of coordination unsaturated Zr⁴⁺ species increased significantly, but the Brønsted acid sites decreased due to the diminishing of surface hydroxyl groups and protons. On the other hand, higher temperature treatment resulted in a rapid decline in BET surface area, therefore the amount of surface metal ions available was reduced as well, finally leading to a significant decrease in Lewis acid sites. On the basis of above discussion, the total surface acid amount would be much lowered for calcined ZrO₂ catalysts, especially for high-temperature-treated ZrO₂-x. In the CO₂-TPD profiles (Figure 7), a broad CO₂ desorption peak assigned to the strong basic sites occurred at ~800 K. It is obvious that medium basic sites at desorption temperature of 450 K were dominant in Zr(OH)₄ sample. Intriguingly, in the ZrO₂-x (x = 623, 723, 823, 923, and 1023), the peak of medium temperature region shifted to a higher temperature. As is well known, the Zr⁴⁺–O²⁻ acid–basic pair sites existed in the prepared catalysts, so total surface basic content also was gradually lowered for ZrO₂-x samples, as
compared with Zr(OH)\textsubscript{4}. Also interesting is that A/B value of ZrO\textsubscript{2}-x first rose and then dropped, with the increase in calcination temperature. It is concluded that Zr-containing samples obtained via calcination treatment, with relatively larger amount of tetragonal phase, could contribute to higher acid–basic concentration.

3.2. Catalytic Activity. The catalytic activity of synthesized zirconium series for the transfer hydrogenation of FFR was discussed. First, the reaction was conducted at 423 K with ethanol as both the solvent and hydrogen donor, and the catalyst dosage was set to 75 mg. As shown in Table 2 (runs 1–6), different Zr-based catalysts exhibited significant variations in the catalytic transfer hydrogenation performance. Zr(OH)\textsubscript{4} catalyst gave a high FA yield of 39.0 mol % after 2.5 h, with a remarkable FA selectivity of 65.9%. In the case of calcined ZrO\textsubscript{2}-x (x = 623, 723, 823, 923, and 1023), lower selectivity to FA was observed at similar conversions, particularly for ZrO\textsubscript{2}-923 and ZrO\textsubscript{2}-1023. The higher activity of Zr(OH)\textsubscript{4} could be due to the appropriate acid–basic site concentration, larger surface area, and higher total pore volume, thus facilitating H-transfer process during FFR conversion.

To get more insight toward understanding the activity discrepancy among above materials, probable correlations between ratios of A/B and M/T (monoclinic phase to tetragonal phase) and catalytic activity are put forward in Figure 5.

Scheme 1. Types of Acid and Basic Sites on the Surface of Zr(OH)\textsubscript{4} (A, B) and ZrO\textsubscript{2} (C, D)
As indicated in Figure 8A, A/B ratio had very little impact on FFR conversion. Zr(OH)\(_4\) bearing much more medium to strong acid−basic sites effectively catalyzed FFR hydrogenation into FA with a high selectivity, whereas ZrO\(_2\)−x possessing insufficient acid−basic sites gave poor FA selectivity. Although relative strong acid−basic sites appeared in the calcined ZrO\(_2\)−x, the limited amount of Zr\(^{4+}\)−O\(^{2−}\) acid−basic pair sites and higher A/B ratios (above 1.0) reduced the transfer hydrogen capacity. As for M/T ratio effect, it is observed that moderate monoclinic phase content enhanced the conversion rate and FA selectivity. Usually high temperatures caused the phase change that produced large number of monoclinic ZrO\(_2\). In this aspect, diminishing of surface hydroxyl groups and BET surface area also occurred for those monoclinic ZrO\(_2\), thus resulting in the decrease of acid−basic site density. It is known that acid−basic sites played a crucial role in the MPV reduction of FFR\(^{41}\), therefore catalysts containing high content of monoclinic ZrO\(_2\) showed weak activity for FFR transfer hydrogenation. Compared comprehensively, amorphous Zr(OH)\(_4\) featuring with high acid−basic site density, exhibited outstanding activity for FA synthesis via the H-transfer method. Subsequently, the influences of hydrogen sources on the conversion of FFR into FA were thoroughly investigated (Table 2, runs 1 and 7−11). Generally, the hydrogen-donating capacity for FFR transfer hydrogenation greatly depends on the reduction potential of applied reducing lower alcohols, i.e., the lower reduction potential of alcohols, the stronger the reducing capacity. According to the previously reported literatures\(^{42,43}\), the reduction potential of reducing alcohols were ranked in the following sequence: methanol > ethanol > 1-butanol > 2-butanol > 2-propanol. Thus methanol, with higher reduction potential, showed the poor CTH capacity for FFR upgrading (Table 2, run 7). The secondary alcohol, especially 2-propanol, had the lowest reduction potential, revealing the great reducing capacity for H-transfer procedure. As expected, conversion of FFR reached 95.7 mol % in 2-propanol, with a FA selectivity of 96.1% (Table 2, run 8). In the case of 2-butanol, 42.6 mol % yield toward FA was obtained with a 61.6% selectivity, whereas undesirable results were found in the presence of butanol under identical conditions. On the basis of above discussion, 2-propanol was selected as the optimal hydrogen donor for subsequent experiments.

![Figure 7. CO\(_2\)-TPD profiles of zirconium-based samples.](image)

**Table 2. Transfer Hydrogenation of FFR Using Various Zr-Based Catalysts and Hydrogen Sources\(^a\)**

| run | catalyst | solvent | FFR conv. (mol %) | FA yield (mol %) | FA selec. (%) |
|-----|----------|---------|-------------------|-----------------|--------------|
| 1   | Zr(OH)\(_4\) | ethanol | 59.2 | 39.0 | 65.9 |
| 2   | ZrO\(_2\)-623 | ethanol | 58.0 | 5.8 | 10.0 |
| 3   | ZrO\(_2\)-723 | ethanol | 62.7 | 8.3 | 13.2 |
| 4   | ZrO\(_2\)-823 | ethanol | 59.2 | 8.4 | 14.2 |
| 5   | ZrO\(_2\)-923 | ethanol | 59.9 | 2.5 | 4.2 |
| 6   | ZrO\(_2\)-1023 | ethanol | 59.0 | 0.4 | 0.7 |
| 7   | Zr(OH)\(_4\) | methanol | 54.4 | 13.2 | 24.3 |
| 8   | Zr(OH)\(_4\) | 2-propanol | 95.7 | 92.0 | 96.1 |
| 9   | Zr(OH)\(_4\) | butanol | 72.5 | 26.5 | 36.6 |
| 10  | Zr(OH)\(_4\) | 2-butanol | 69.2 | 42.6 | 61.6 |
| 11  | ZrO\(_2\)-823 | 2-propanol | 52.4 | 30.7 | 58.6 |
| 12\(^b\) | Zr(OH)\(_4\) | 2-propanol | 97.9 | 54.1 | 55.3 |
| 13\(^c\) | Zr(OH)\(_4\) | 2-propanol | 97.8 | 90.8 | 92.9 |

\(^a\)Conditions: FFR 1.2 mmol, solvent 15 mL, catalyst dosage 75 mg, 423 K, 2.5 h, 600 rpm, N\(_2\) 1 MPa. \(^b\)75 mg boric acid. \(^c\)75 mg pyridine.

![Figure 8. Effects of A/B and M/T ratios on FFR transfer hydrogenation.](image)
poisoning could be ascribed to the imbalance acid–base couple sites, and 2,2’-difurfuryl ether and 4-(2-furyl)-3-buten-2-one were formed through acid sites-catalyzed etherification and aldol condensation reactions, respectively. The above results implied that Zr(OH)₄ catalyst is rather irritable to boric acid, thus the active basic site of catalyst was demonstrated to display much more pronounced effect for this reaction. On the other hand, it can be concluded that synergistic effect of acid–basic couple sites in Zr-containing materials also was very important for MPV reduction of FFR.

The influence of temperature on the catalytic transfer hydrogenation of FFR with 2-propanol was investigated using Zr(OH)₄ in a range of 403–453 K. As indicated in Figure 9, within a 2.5 h of CTH reaction at 403 K, the conversion of FFR was up to 78.3 mol %. Subsequently, elevating the reaction temperature to 423 and 433 K gave a higher FFR conversion of 95.7 and 97.5 mol %, respectively. Besides, the selectivity to FA remained high (around 90.0%) for reaction temperature below 443 K. A further rise in the temperature to 453 K also significantly increased the FFR conversion to 99.8 mol %, but decreased the FA selectivity to 87.9%, probably caused by the formations of furan-based polymers via acidic–basic sites-catalyzed condensation reactions. Therefore, the optimum temperature for this reaction was set to 443 K.

Figure 10 depicts the effect of catalyst dosage ranging from 65 to 85 mg on FA formation as a function of reaction time, with the aim of finding the optimum conditions. One can clearly observe that the FA yield was greatly promoted at higher dosage that achieved a promising level of 81.5 mol % at a dosage of 85 mg in 0.5 h. One reasonable explanation is that the increased total number of active acid and basic sites accelerated the progress of CTH process, thus facilitating the gradual accumulation of targeted product FA. Generally, properly increasing time facilitated the rapid generation of FA. It is noted that lower catalyst dosage might require longer reaction time to reach the equilibrium state due to insufficient active sites. For 75 mg catalyst dosage, the FA yield gradually increased as the reaction proceeded, which achieved the appreciable value of 98.9 mol % yield of FA at nearly complete conversion in 2.5 h. It is noteworthy that remarkable decrease in the yield and selectivity toward FA was observed with the further prolonging of reaction time, which could be ascribable to the appearance of etherification reaction. After 3.0 h of reaction, the total yield of 2,2’-difurfuryl ether and 2-(isopropoxymethyl)furan reached up to ~15 mol %. Therefore, the optimal catalyst dosage of 75 mg and reaction time of 2.5 h were adopted for the CTH reaction of FFR.

Herein, we further evaluated the reusability of the most active catalyst Zr(OH)₄ for the transfer hydrogenation of FFR at 443 K. After each recycling experiment, the spent catalyst was separated from the reaction mixture by filtration, followed by being repeatedly washed with plenty of deionized water. After drying at 323 K overnight, the catalyst was tested again under identical conditions. Specific surface area and TGA–DTA characterizations of spent catalyst indicated the adsorption of certain amounts of carbohydrates on the catalyst surface, which prevented the sufficient contact between FFR and acid–basic sites. Thus, slight decrease in the FFR conversion from 99.8 to 92.1 mol % was observed after three consecutive runs, as revealed in Figure 11. In the following two runs, the catalyst displayed relatively good performance, in which the FFR conversion remained around 90 mol %.

Elemental analysis of Zr⁴⁺ in the solution after five successive cycles by ICP-AES revealed that Zr⁴⁺ concentration was below
the limit of detection. The aforementioned results reflected the good stability and reusability of Zr(OH)$_4$.

Comparison of catalytic activity among various catalysts is presented in the Table 3. It can be seen that 2-propanol was a common choice and served as an excellent hydrogen donor for the CTH of FFR. In comparison of catalyst type, bifunctional zirconium N-alkyltriphosphate nanohybrid (ZrPN), characteristic of high basicity/acidity, exhibited better activity at 413 K.\textsuperscript{30} Homogeneous Lewis acid catalyst (DyCl$_3$) effectively converted FFR into FA using 2-propanol as the solvent and hydrogen donor,\textsuperscript{26} however, issues, including product separation and catalyst reuse, were also put forward. Other metallic catalysts, such as $\gamma$-Fe$_2$O$_3$@HAP, Fe-L1/C-800, and Cu/AC−SO$_3$H, could give good FFR conversion (above 90%) at relatively higher temperature so with longer reaction time.\textsuperscript{28,29,31} By contrast, Zr(OH)$_4$ synthesized by the simple precipitation method displayed desirable activity toward FFR transfer hydrogenation, and nearly complete conversion rate and 98.9% FA yield were achieved in a 2.5 h reaction.

On the basis of the above experimental results and previous literatures,\textsuperscript{32−35,46−48} a plausible reaction mechanism for the CTH reaction of FFR via MPV reduction over Zr(OH)$_4$ was suggested, as illustrated in Scheme 2. First, adsorption of 2-propanol into the catalyst occurred, followed by dissociation to the corresponding alkoxide A. Next, the aldehyde group in FFR matched well with alkoxide A to produce a six-membered ring transition state B. Then, hydrogen transfer took place between activated FFR and alkoxide in a concerted manner, with the formation of intermediate C. Meanwhile, the new carbonyl chemical acetone was released from intermediate species C and generated the intermediate D. Finally, another 2-propanol molecule participated in the reaction, giving off the end product FA as well as initial active site alkoxide A. As mentioned earlier,\textsuperscript{49} each step in the cycle of FFR transfer hydrogenation was supposed to be reversible.

4. CONCLUSIONS

In summary, we prepared a series of zirconium-based catalysts for the synthesis of FA via a CTH process using 2-propanol as a hydrogen donor. Among these catalysts, Zr(OH)$_4$ with much more medium to strong acid−basic sites and high acid−basic site density was identified as the most active one, in which a yield of 98.9 mol % FA was achieved at nearly 100 mol % conversion. As comparison, ZrO$_2$−x possessing insufficient acid−basic sites only gave poor FA selectivity. High calcination temperatures resulted in the formation of monoclinic ZrO$_2$ in large numbers, but resulting poorer BET surface area and pore volume were not conducive to the transfer hydrogenation of FFR into FA. Relatively, proper amount of monoclinic ZrO$_2$ in calcined samples improved the conversion rate and FA selectivity, and acid−basic site density ratio had slight influence on FFR conversion. Moreover, the poisoning experiments revealed that active basic sites on the catalyst surface displayed pronounced effect for FFR conversion. Furthermore, the Zr(OH)$_4$ catalyst exhibited good performance and stability that was reusable over multiple cycles without significant loss of catalytic activity. The possible reaction mechanism for this CTH process over Zr(OH)$_4$ with 2-propanol as the hydrogen source was proposed.

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