

Catalytic Transfer Hydrogenation of Furfural to Furfuryl Alcohol under Mild Conditions over Zr-MOFs: Exploring the Role of Metal Node Coordination and Modification

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ABSTRACT: The catalytic transfer hydrogenation (CTH) reaction is considered as a potential route for upgrading bio-based carbonyls to their corresponding alcohols. Herein, a series of Zr-based metal organic frameworks (Zr-MOFs) containing various types of metal node to ligand coordinations were synthesized and tested for CTH of furfural (FUR) to furfuryl alcohol (FOL). It was found that metal node coordination plays a more important role than porosity in Zr-MOFs. MOF-808 (synthesized using a scaled-up approach to achieve a higher batch yield), with the lowest metal node to ligand coordination (coordination number 6), was found to be the most active catalyst among the various tested Zr-MOFs. Furthermore, M-MOF-808, modified by simple methanol activation (M), outperformed the pristine MOF-808 in CTH of FUR to FOL even at 30 $^{\circ}$ C in the



presence of 2-propanol (IPA) as the hydrogen source. The simple modification of the metal node in the Zr-MOF changed the acidbase properties of the MOF-808 surface through the development of coordinatively unsaturated sites (CUS), hydroxyl and methoxy groups in the framework of the Zr-MOF, which probably help to facilitate the adsorption of FUR and IPA onto the metal node surfaces of the catalyst. To evaluate the versatility of methanol activation in CTH, further substrates, including other types of biomass and representative carbonyl compounds over M-MOF-808, were tested. To demonstrate heterogeneous catalysis, the catalyst was recycled for five consecutive cycles, with little loss after the first cycle, and was fully characterized to observe any changes in its structure. Mechanistic insights were provided by isotopically labeled 2-propanol- d_8 experiments, indicating FUR reduction through transfer hydrogenation. Finally, the reaction mechanism for CTH of FUR to FOL was proposed in detail using density functional theory (DFT) calculations over metal node modified model systems of a 6-connected Zr-MOF.

KEYWORDS: catalytic transfer hydrogenation, zirconium-based metal—organic frameworks, metal node coordination and modification, methanol activation, density functional theory

1. INTRODUCTION

Catalytic transfer hydrogenation (CTH) is a potential alternative approach for the hydrogenation of renewable lignocellulosic biomass to value-added chemicals,^{1–3} employing organic molecules as the hydrogen source. Several precious-metal-based catalysts have been reported for the CTH of furfural (FUR) to furfuryl alcohol (FOL), i.e., the most value added chemical derived from FUR.^{4–7} These catalyst systems nonetheless exhibit some drawbacks: for instance, precious metals are expensive and have limited availability. Furthermore, the reaction parameters need to be optimized carefully in order to obtain the desired products because both C=O and C=C groups in FUR can be hydrogenated and thus produce numerous hydrogenated products.^{5,6} The CTH of FUR over non-precious-metal catalysts has garnered significant attention in recent

years.^{8–12} In view of this, several Lewis acidic zeolites (Ti, Sn, Zr, and SnAl) have been reported for the process.^{8,9} For example, Bui et al. successfully demonstrated that the combination of Lewis and Brønsted acid sites in zeolites can directly convert FUR into GVL with near-quantitative yield through a cascade reaction involving sequential transfer hydrogenation and ring opening steps.¹⁰ Some Fe-based catalysts were also found to be capable of transfer hydrogenation of FUR to FOL.^{11,12} However, those catalysts could

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not produce a quantitative yield of FOL because they suffer from deactivation due to the change in pore structure and formation of oxide species that occur with successive cycles.¹¹

Numerous Zr-based catalysts have been explored for CTH reactions using various biomass-derived carbonyl compounds. including FUR.^{13–23} Li et al. prepared a series of $\hat{Z}r$ -based amorphous acid-base bifunctional nanohybrids which were demonstrated to be active in CTH reactions of biomassderived and other carbonyl compounds.^{16–18} Mesoporous Zr-SBA-15 has also been tested for the Meerwein-Ponndorf-Verley (MPV) reduction of FUR using 2-propanol (IPA) as a sacrificial alcohol, but a poor yield of FOL was obtained, primarily due to the etherification reaction of FOL with IPA. Zr-based metal-organic frameworks (Zr-MOFs) have also been examined as MPV catalysts for the selective hydrogenation of various saturated and unsaturated carbonyl compounds.²¹⁻²³ We reported CTH of ethyl levulinate to GVL over a series of functionalized and nonfunctionalized Zr-MOFs using IPA as the hydrogen source.²⁴ It was observed that metal nodes in Zr-MOFs were the active sites for CTH and that greater accessibility to the nodes by substrate molecules led to enhanced catalytic activity; however, the role of metal node to ligand coordination for greater accessibility to the nodes was not fully considered. Moreover, a strategy to enhance catalytic activity through metal node modification of Zr-MOFs has not yet been implemented for the transfer hydrogenation of biomass carbonyls. Most importantly, a variety of heterogeneous catalysts, such as metal oxides,^{13,25,26} metal hydroxides,^{14,27,28} metal com-plexes,^{15,17,29} metal–organic nanohybrids,^{16,18,30} mesoporous silica,^{19,31} supported metals and metal oxides,^{11,12,32–34} zeolites,^{8,35,36} and MOFs,^{24,37,38} have been reported for the transfer hydrogenation of biomass-derived carbonyl compounds using alcohol as a hydrogen donor, but none of these heterogeneous catalysts have been shown to be active at or near room temperature. In addition, a number of noblemetal-based catalysts, which are active at room temperature for the hydrogenation of biomass-derived carbonyls using H₂ gas as a hydrogen source, need pressurized reaction systems, and these demand the use of sophisticated instruments that may incur heavy infrastructural costs on a large scale. Therefore, the CTH reaction of biomass-derived carbonyls at room or near temperature remains a largely uninvestigated topic in biomass conversion.

Here, we explored the role of metal node coordination and modification in Zr-MOFs for CTH of FUR to FOL. The findings demonstrated that the catalytic activity is mainly dependent on the metal node to ligand coordination of Zr-MOFs and further elaborated how metal node modification in MOF-808 could lead to significant improvements in catalytic activity at nearly room temperature (30-40 °C). Owing to the high catalytic activity, the effects of alternative substrates were extended to other biomass-derived products, as well as representative carbonyl compounds. FUR reduction through transfer hydrogenation was confirmed using the deuterium isotope of IPA in combination with GC-MS analysis. Catalyst heterogeneity, leaching, and recycling experiments were also performed. Computational density functional theory (DFT) calculations were used extensively to study the CTH mechanism of FUR to FOL in detail. We anticipate that the excellent catalytic activity of MOF-808 after methanol activation under mild reaction conditions will enable the

development of Zr-based advanced porous materials as catalysts for room-temperature biomass conversion reactions.

2. EXPERIMENTAL SECTION

2.1. Synthesis of MOF-808. Considering the catalytic application of MOF-808 in the production of biomass-derived bulk chemicals, the synthesis procedure of MOF-808 was scaled up. Consequently, the concentration of precursors (metal and ligand) in the reaction mixture was increased in order to obtain a higher batch yield. The scaled-up synthesis of MOF-808 was performed in a 700 mL Teflon-lined pressure reactor. Equivalent amounts of ZrOCl₂·8H₂O (13.5 g, 0.04 mol) and 1,3,5-benzenetricarboxylic acid (9.3 g, 0.04 mol) were dissolved in a DMF/formic acid mixture (164 mL/160 mL). The reaction mixture was stirred at room temperature before heating at 135 °C for 48 h and then cooled to room temperature when the reaction was complete. The solid was collected by filtration and washed twice with DMF (1 L) to remove unreacted ligand molecules from the pores of MOF-808. The resultant powder was washed twice with acetone (1 L) to remove DMF solvent from the pores. This purification procedure took 2 days to complete. Finally, the solid powder was dried overnight at 100 °C in an oven. Synthesis procedures of other Zr-MOFs are provided in the experimental section of the Supporting Information.

2.2. Methanol Activation of MOF-808. A dried powder of MOF-808 (1 g) was immersed into 100 mL of anhydrous methanol in a 250 mL round-bottom flask (RBF). The reaction solution was refluxed to the boiling point of methanol for 8 h. The powder was filtered and washed with 150 mL of fresh methanol twice over a 24 h period at room temperature. The obtained sample was dried in a vacuum oven at 80 °C for 12 h. Methanol-treated MOF-808 powder was labeled as M-MOF-808.

2.3. Catalytic Test and Product Analysis. The catalytic activity of Zr-MOFs in the transfer hydrogenation of furfural was evaluated using various hydrogen donor alcohols. Prior to use, Zr-MOFs were dried in an oven at 100 °C for 12 h. In a typical procedure, a known amount of dried catalyst, furfural, naphthalene as an internal standard, and proton donor/solvent were placed into a two-necked RBF. The reaction mixture in the RBF equipped with a rubber septum and reflux condenser was heated at the desired temperature and for the required time. The catalyst was separated by centrifugation, washed thoroughly with hot methanol, and dried at 100 °C prior to the next cycle. The freshly distilled furfural neutralized in Na₂CO₃ was used only for recycling tests to minimize the colored and acidic impurities present in it. The filtrate collected after the reaction was subjected to quantitative analysis using gas chromatography (GC, FID detector and HP-5 column), and identification of the products was made by GC-MS (Agilent 6890 N GC and 5973 N MSD). Furfural conversion and the yield of furfuryl alcohol were determined using a multiplepoint internal standard calibration method. Other carbonyl substrates and their hydrogenated products were quantitatively analyzed using a single-point internal standard calibration method (GC, FID detector and DB-624 column).

3. RESULTS AND DISCUSSION

3.1. Role of Metal Node Coordination in Zr-MOFs for CTH. The presence of 12-, 10-, 8-, and 6-connected metal nodes $[Zr_6(\mu_3-O_4)(\mu_3-OH)_4]$ in Zr-MOFs has been previously

Table 1. Textura	al Properties and	Catalytic Activity o	f the Zr-MOFs	for the	CTH of	f FUR to FOL
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entry	Zr-MOF (CN)	$S_{\rm BET}^{a}$ (m ² /g)	$PD^{b}(Å)$	AS^{c} (mmol/g)	BS^d (mmol/g)	conversn (%)	$Y_{\rm FOL}$ (%)	$S_{\rm FOL}$ (%)	TOF (h^{-1})
1	none					<2.0	0	0	
2	UiO-66 (12)	1210	5, 6.1	0.35	0.05	2.3	1.3	56.5	0.26
3	DUT-52 (12)	1208	7.1	0.65	0.06	2.1	0.0	0.0	0.0
4	UiO-67 (12)	2518	12.7	0.60	0.04	5.2	0.1	1.9	0.02
5	DUT-67 (8)	1362	10, 4.9	0.74	0.10	16.4	13.5	82.3	2.0
6	MOF-808 (6)	1313	12.7, 15.9	0.85	0.15	81.3	66.4	81.7	11.6

 ${}^{a}S_{BET}$ is the BET surface area. ${}^{b}PD$ is the pore diameter. ${}^{c}Acid$ sites (AS) determined by NH₃-TPD. ${}^{d}Base$ sites (BS) determined by CO₂-TPD; where Y_{FOL} is the yield of furfuryl alcohol, S_{FOL} is the selectivity of the furfuryl alcohol, CN is the coordination number of the metal node to the linker, and turnover frequency (TOF) = (moles of FOL)/(moles of "Zr" from ICP analysis × time) at 2 h of reaction time. Reaction conditions: FUR, 1 g (10.4 mmol); IPA, 25 g (416 mmol); cat., 0.1 g; temperature, 82 °C (reflux); time, 2 h.

reported in the literature.⁴⁴ However, very few efforts have been undertaken to examine the role played by the metal node connectivity in Zr-MOFs in catalytic activity.44-46 Therefore, to clearly understand the role of porosity in comparison with that of metal node coordination in CTH of FUR, we synthesized a series of Zr-MOFs possessing different porosities and metal node connectivities and tested them for transfer hydrogenation of FUR. The structures of the synthesized Zr-MOFs were confirmed using powder X-ray diffraction (PXRD) and thermal gravimetric analysis (TGA), and their textural properties were determined using N2-physisorption, as shown in Figure S1. PXRD (Figure S1A) confirmed the formation of crystalline phases in all Zr-MOFs, which is in accordance with the reported structure.⁴⁶⁻⁴⁹ The crystallinity of MOF-808 is lower than that of the previously reported original structure due to the scaled-up synthesis approach, which aimed to achieve a higher batch yield.⁵⁰ TGA curves (Figure S1B) of all synthesized Zr-MOFs represent their thermal stabilities and demonstrate that Zr-MOF catalysts are sufficiently stable to carry out the CTH reaction at moderate reaction temperatures. Furthermore, all Zr-MOFs are highly porous and have welldefined pore diameters, as confirmed by N2-physisorption, shown in Figure S1C,D.

The textural properties and catalytic activities of various Zr-MOFs used for transfer hydrogenation of FUR are summarized in Table 1. When CTH of FUR was carried out without a catalyst at 82 °C (Table 1, entry 1), no FOL was formed, even after a 2 h reaction time; moreover, less than 2% FUR conversion was observed. Three different Zr-MOFs (UiO-66, UiO-67, and DUT-52) with the same ligand to metal node coordination (12) but different porous properties (such as surface area and pore diameter) were subjected to the CTH reaction (Table 1, entries 2-4). Despite UiO-67 having a higher surface area and larger pore diameter in comparison with UiO-66 and DUT-52, the conversion was increased by only 3%, indicating that improved pore size and surface area played no significant role in enhancing the catalytic activity of Zr-MOFs. This further implies that 12-connected (12 carboxylate ligands connected to metal site) Zr-MOFs are less active in the CTH reaction at 82 °C. When 8-connected DUT-67 was used, FUR conversion increased marginally in comparison with UiO-67 (Table 1, entry 5), despite the fact that the latter possesses a higher surface area and pore diameter than the former. This demonstrates that the catalytic activity associated with reducing metal node connectivity in Zr-MOFs (from 12 to 8) involved in the CTH reaction can be enhanced. Consequently, when 6-connected MOF-808 was applied to the CTH reaction of FUR, a substantial enhancement in the catalytic activity was reported: 81.3% FUR

conversion with 81.7% selectivity for FOL was achieved, a result 43 times higher than that with 12-connected UiO-67. Furthermore, the turnover frequencies (TOFs) of all the Zr-MOFs were presented for fair comparison among the catalysts, on the basis of their Zr content, which was determined using ICP analysis (Table 1 and Table S1). Once again, MOF-808 outperformed all other catalysts reported in Table 1, with the highest TOF of 11.6 h⁻¹. These results strongly support the fact that metal node connectivity plays a more important role than high porosity in Zr-MOFs for CTH of FUR. In 12connected Zr-MOFs, Zr sites are fully saturated by carboxylate ligands and therefore are the least accessible to substrate molecule adsorption. Decreasing the metal node connectivity reduces crowding around the metal node and thus enhances the accessibility of substrate molecules to Zr sites and results in a higher catalytic activity, consistent with previous reports.^{23,37}

Acid and base sites in several Zr-based catalysts were reported as active sites, considerably affecting the catalyst performance in transfer hydrogenation reactions.¹³⁻¹⁸ Consequently, NH₃-TPD and CO₂-TPD analyses were performed in order to determine the acid-base properties of the catalyst, respectively, and the results are shown in Table 1 and Figure S2. The reason for the selection of a lower desorption temperature was the stability of the Zr-MOFs. Although all of the Zr-MOFs analyzed here were quite stable up to 350 °C, triply bridged μ_3 -OH and formate groups from the modulator, which were linked to the Zr node for charge balance, disconnected on heating beyond 200 °C, as evidenced from the TGA patterns (Figure S1b). The origin of the acid-base sites in Zr-MOFs could be surface hydroxyl groups (Zr-OH, base sites), μ_3 -OH (acid sites), Zr-OH₂ (acid sites), framework oxygen Zr-O-C or Zr-O-Zr (base sites), and coordinatively unsaturated zirconium sites (Zr-CUS; acid sites) of the metal nodes. The amount and desorption temperature of NH₃ illustrate the enhancement in concentration and strength of the acid sites in the Zr-MOFs with decreasing cluster coordination, and this is presumably due to the difference in electron densities around the cluster, which can alter the charge on the zirconium nodes. The NH₃-TPD profile of DUT-67 showed two desorption peaks, likely due to the interaction of ammonia molecules with the metal node and the sulfur-containing thiophene ligand. All other Zr-MOFs did not possess any heteroatoms in their ligand ring structure and showed only one broad desorption peak, a result of the interaction of NH3 with the metal node. Both acid and base sites in the Zr-MOFs increased with decreasing cluster coordination. The MOF-808 with the highest acid and base sites, 0.85 and 0.15 mmol/g, respectively, emerged as the most active catalyst among the tested Zr-MOFs, as shown in Table





1. Therefore, it can be concluded that an enhancement in substrate accessibility and in the acid-base properties of Zr-MOFs by decreasing cluster coordination are the two main important factors that significantly enhance catalytic performance. In all cases (entries 1–6 in Table 1), the major side product acetal, followed by two aldol condensation products, has been observed in GC-MS analyses. Furthermore, undetectable and undissolved polymeric products (humin) could be generated due to the highly reactive aldehyde group of FUR, which is susceptible to condensation reactions.

3.2. Metal Node Modification of MOF-808. The uniqueness of the MOF structure lies in that it can be tuned more precisely than metal oxides and zeolites to create highly uniform and controllable reactive sites for specific catalytic applications. Consequently, owing to the high catalytic activity of MOF-808 using metal nodes as active sites, we analyzed the catalytic activity of metal nodes in modified MOF-808 during the transfer hydrogenation of FUR to FOL, as shown in Scheme 1. As-synthesized MOF-808 was activated simply using methanol at its boiling point. Hereafter, these activated MOF-808 samples will be designated as M-MOF-808. M-MOF-808 was characterized using PXRD, TGA, and N2physisorption (Figure S3) to understand the changes that occur in its structural, thermal, and porous properties, respectively. No loss of crystallinity was observed in PXRD data of MOF-808 after methanol activation (Figure S3A). TGA of pristine MOF-808 (Figure S3B) shows three weight loss regions: the first around 100 °C corresponding to physisorbed water, the second at 225 °C-350 °C belonging to remnant formate, μ_3 -OH, and trace quantities of physisorbed dimethylformamide (DMF), and the last at 400-550 °C resulting from the degradation of the framework benzenetricarboxylate (BTC) ligand. After activation, the second weight loss region vanished completely, and the sample was degraded at almost the same temperature as for pristine MOF-808. The absence of a second weight loss region (225 °C-350 °C) indicated the removal of coordinated formate, μ_3 -OH, and physisorbed DMF; this point was corroborated by ¹H NMR spectra of MOF-808 and M-MOF-808 digested in HF/ DMSO- d_6 (Figure S4). The obtained ¹H NMR data showed that formate groups and trace amounts of DMF in MOF-808 were almost completely exchanged by methanol. The slight

decline in surface area and pore size of MOF-808 following methanol activation was noted from N₂ adsorption– desorption isotherms recorded at -196 °C (Figure S3C,D). These observations suggested that the local structure of MOF-808 had been altered, but without significant effects on its crystalline and porous properties. The elemental composition and porous properties of pristine MOF-808 and M-MOF-808 are specified in Table S2.

To further explore changes in the local structure of MOF-808 after methanol activation, in situ FTIR analysis was performed (Figure 1 and Figures S5-S7 and Table S3). Two characteristic bands at 2931 and 2866 cm⁻¹ assigned to the C-H stretching of formate groups linked to Zr $(Zr-OOCH)^{51,52}$ present in the pristine MOF-808 (Figure 1A) were replaced by two C-H stretching vibration modes at 2929 and 2827 cm⁻¹ assigned to methoxy groups linked to Zr (Zr-OCH₃).⁵¹⁻⁵³ To confirm the grafting of methoxy groups on Zr sites, isotopic exchange experiments were carried out. MOF-808 was activated using deuterated methanol (CD₃OD); the activated sample was designated as d-M-MOF-808. In the FTIR spectra of d-M-MOF-808 (Figure 1A), C-H stretching bands from Zr-OOCH were completely absent, and two new bands at 2203 and 2060 cm⁻¹ were detected, resulting from the C-D stretching vibration of deuterated methoxy groups linked to Zr (Zr-OCD₃).^{51,53,54} The peak at 3086 cm⁻¹ assigned to the C-H stretching of the aromatic group (BTC) was unchanged upon methanol activation. Additionally, a new C–O vibration peak was detected in methanol-activated samples at 1155 cm⁻¹, further confirming the formation of Zr-O-C bonds in activated MOF-808 from the grafting of alcohol moieties to the metal node (Figure S5A). Note that the methanol activation process was not carried out under an inert atmosphere and MOF-808 was exposed to atmospheric water before and after the activation (reflux) step. Therefore, the replacement of some of the methoxy groups by OH groups may explain the presence of methoxy as well as terminal OH groups observed in the FTIR analysis. This kind of phenomenon has previously been reported by Yang et al. for UiO-66 and NU-1000, where methoxy groups generated by methanol activation were replaced by terminal OH groups after water vapor exposure at 393 K.53 The peak at 3674 cm⁻ in MOF-808 was assigned to bridging μ_3 -OH groups; ^{53,55,56}



Figure 1. In situ FTIR recorded at room temperature after evacuation for 2 h at 100 °C (A) in the 2000–3250 cm⁻¹ region and (B) in the 3300–3900 cm⁻¹ region characterizing (a) MOF-808, (b) M-MOF-808, and (c) d-M-MOF-808.

this disappeared after methanol activation, and four new peaks were generated in the same region (Figure 1B). The peaks at 3671 and 3765 cm⁻¹ were assigned to the μ_3 -OH stretch and non-hydrogen-bonded terminal OH groups at newly formed surfaces, respectively.^{54,57} The remaining two peaks, those at 3725 and 3639 cm⁻¹, together with a peak at 5266 cm⁻¹, were not present after heating the sample at >150 °C (Figures S5–S7). Therefore, we assigned these peaks to water molecules coordinated to Zr sites.⁵⁸

We also performed CO-FTIR analysis of pristine and activated MOF-808, as shown in Figure 2, to determine the coordinatively unsaturated Zr sites (Zr-CUS). FTIR experiments were conducted by introducing calibrated doses of CO after activating the samples at 150 °C for 6 h. In the case of M-MOF-808 (Figure 2B), a ν (CO) band centered at 2188 cm⁻¹ appeared and progressively broadened with increasing CO dosage, shifting to a lower wavenumber of 2180 cm^{-1} , which is assigned to CO coordinated to the Lewis acid site (Zr-CUS).^{59,60} The red shift in peak position reflects the possibilities of formation of multicarbonyl species on Zr-CUS. At higher CO coverage and only after the saturation of Zr-CUS, two additional ν (CO) bands were developed at 2151 and 2135 cm⁻¹. We assigned these to H-bonded CO molecules with μ_3 -OH and physisorbed CO molecules, respectively. In pristine MOF-808, virtually no peaks were detected. An extremely low intensity peak could be visible upon magnifying the initial spectrum more than 20 times (inset of Figure 2A), situated at 2183 cm⁻¹. This peak was detected at initial CO coverage and indicated a negligible amount of vacant Zr



Figure 2. FTIR spectra of (A) MOF-808 and (B) M-MOF-808 recorded at $-173\ ^{\circ}C$ during CO adsorption.

species in pristine MOF-808. At higher CO coverage, three ν (CO) bands located at 2177, 2153, and 2136 cm⁻¹ appeared simultaneously (Figure 2A). The presence of H-bonded and physisorbed CO can be confirmed using the peaks at 2153 and 2136 cm⁻¹, respectively.

We further quantified the amount of Zr-CUS present in M-MOF-808 using a plot of the peak area of 2188 cm⁻¹ versus the amount of CO adsorbed (Figure S8). The chemisorption of CO reached up to 0.48 mmol/g, confirmed using the linear correlation between peak area and amount of CO adsorption. The linearity is tented after 0.48 mmol/g of CO adsorption due to physisorbed CO molecules. This means that around 0.5 mmol/g of Zr-CUS was generated in MOF-808 after methanol activation. The quantified value of Zr-CUS may differ when MOF-808 is synthesized using different reaction conditions.

3.3. CTH of FUR to FOL over Metal Node Modified MOF-808. Methanol activation of MOF-808 changes its local structure through modification of the metal node. Consequently, its chemical properties change, and it becomes highly desirable to correlate the local structure modification with its catalytic activity. Accordingly, the M-MOF-808 catalyst was tested for CTH of FUR to FOL, and the results obtained are summarized in Table 2. When the reaction was carried out under reflux conditions at 82 °C, M-MOF-808 showed higher FUR conversion and FOL selectivity in comparison with as-synthesized MOF-808 (entries 1 and 2, Table 2). Nevertheless, the difference was not significant, probably due to reaching the equilibrium point. As previously reported, CTH reaction following the principle of the Meerwein-Ponndorf-Verley (MPV) reduction is an equilibrium reaction in which the reverse reaction is termed Oppenauer oxidation.⁵⁴ To clearly differentiate the catalytic activity of these two catalysts, we performed the reaction at 40

Tab	le 2.	Comj	parison	of	СТН	of l	FUR	over	MO	F-808,	M-MOF-808	3, and	Oth	er	Zirconium-Base	ł C	atalys	sts"
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entry	Cat.	T (°C)	time (h)	mass ratio (Cat./FUR/IPA)	conversn (%)	$Y_{\rm FOL}$ (%)	$S_{\rm FOL}$ (%)	TOF (h^{-1})
1	MOF-808	82	2	0.1/1/25	81.3	66.4	81.7	11.6
2	M-MOF-808	82	2	0.1/1/25	89.3	79.1	88.6	15.0
3	$Zr_{6}O_{4}(OH)_{4}(Mc)_{12}$	82	2	0.1/1/25	3	0.9	30	0.2
4	ZrO_2	82	2	0.1/1/25	2.7	0.2	7.4	0.01
5	$ZrO(OH)_2$	82	2	0.1/1/25	8.9	7.1	79.8	0.6
6	DUT-67	82	2	0.1/1/25	16.4	13.5	82.3	2.0
7	M-DUT-67	82	2	0.1/1/25	37.9	34.1	89.9	5.4
8 ^b	M-MOF-808	100	2	0.1/1/25	99.2	93.0	93.8	17.6
9 ^c	ZrPn	100	15	0.1/0.24/7.9	93	90	96.8	3.1
10 ^d	Zr-LS	100	1	0.1/0.1/7.9	97.5	96	98.5	4.4
11 ^e	Zr-FDCA	140	4	0.1/0.19/7.9	83	78	94.0	2.7
12	MOF-808	40	24	0.1/0.5/12.5	27.5	25.4	92.3	0.2
13	M-MOF-808	40	24	0.1/0.5/12.5	96.5	85.5	88.6	2.9

^{*a*}Turnover frequency (TOF) = (mole of FOL)/(mole of "Zr" from ICP analysis × time) at 2 h reaction time. ^{*b*}A batch type pressure reactor was used. ^{*c*}From ref 16. ^{*d*}From ref 63. ^{*c*}From ref 17.



Figure 3. (A) Hot filtration test: FUR, 1.0 g (10.4 mmol); IPA, 25 g (416 mmol); cat., 0.1 g; temperature, 82 °C (reflux). (B) Catalyst recyclability test: FUR, 0.25 g; IPA, 25 g (416 mmol); cat., 0.1 g; temperature, 82 °C (reflux); time, 1 h.

and 30 °C. Another objective was to confirm the efficiency of the catalysts at low temperature, since this is the favored route for green and sustainable development of biomass-derived chemicals. Moreover, a large amount of low-grade waste heat (specifically below 40 °C) is discharged into the environment during many industrial processes and cannot generally be utilized due to its low-quality energy.^{61,62} Utilizing this lowgrade waste heat for another application (e.g., in the production of biomass-derived chemicals) would assist industries in improving their thermal energy efficiency,^{61,62} in which the catalyst must be active at low temperatures. One could clearly observe the difference in catalytic activities of MOF-808 and M-MOF-808 at 40 and 30 °C (entries 12 and 13 in Table 2 and Figure S9). After 24 h of reaction time, MOF-808 converted only 27.5% of FUR, whereas M-MOF-808 attained 96.5% FUR conversion at 40 °C. At 30 °C, FUR conversion was 6.7% and 76.1% with 6.2% and 68.5% FOL yield for MOF-808 and M-MOF-808, respectively. The remarkable enhancement in catalytic activity of M-MOF-808 can be attributed to its modified local structure. The proton topology is changed in MOF-808 by replacing formate groups with terminal OH and methoxy groups, and the formation of Zr-CUS enhances the density of the acid and base sites (Figure S10), likely facilitating the adsorption of FUR and IPA on its

metal node and resulting in higher FUR conversion and FOL yield.

Considering the high catalytic activity of M-MOF-808 in CTH of FUR, we compared its activity with that of other Zrbased catalysts (entries 3-7 and 9-11, Table 2). Using the fully coordinated methyl acrylate (Mc) Zr cluster $Zr_6O_4(OH)_4(Mc)_{12}$ as a homogeneous catalyst enabled only 3% conversion, similar to the low activity of 12-connected Zr-MOFs. ZrO_2 also showed minor conversion (2.7%), with only 0.2% FOL yield. $ZrO(OH)_2$ showed better performance than ZrO₂ with 8.9% conversion and, importantly, good FOL selectivity. It has already been demonstrated that hydrous zirconia can strongly activate an alcohol as a proton donor through the hydroxyl groups present at the surface of the catalyst and subsequently facilitate hydride ion transfer.¹⁴ Conversely, fewer hydroxyl groups on calcined ZrO₂ are responsible for lower catalytic activity.⁶⁴ M-MOF-808 outperformed all other catalysts given in Table 2 in terms of TOF. It reaches almost quantitative conversion (99.3%) with 93.3% FOL yield by increasing the temperature from 82 to 100 °C (entry 8). Other catalysts, such as zirconium phosphonate, lignosulfonate, and carboxylate complexes, were also active for this reaction and also showed a quantitative yield of FOL (entries 9-11); however, these catalysts required higher temperatures and larger amounts of catalyst in order to reach

Entry	Substrate	Product	Time (h)	Conv. (%)	Yield (%)	Sel. (%)	TOF (h ⁻¹)
1	O H	ОМ	2	95	94.1	99.1	4.4
2	н от он	носорон	2	98.2	96.2	98.0	4.6
3	↓ O H	ОСН	6	95.0	88.0	92.6	1.4
4			24	90.7	82.8	91.3	0.3
5	0	ОН	1	93.1	93.1	100	8.8
6	CI	СІ	1	97.0	97.0	100	9.2
7	o	OH	8	92.5	92.5	100	1.1

Table 3. Substrates Tested for CTH of Various Carbonyl Compounds over M-MOF-808^a

"Reaction conditions: substrate, 2.6 mmol; IPA, 416 mmol; cat., 0.1 g (10.6 mol %); temperature, 82 °C (reflux).

the optimum yield of FOL. Furthermore, to generalize the concept of enhancement in the catalytic activity of Zr-MOFs in the CTH reaction by modification of its metal node, we selected another undercoordinated Zr-MOF: DUT-67 (8connected). Upon methanol activation, DUT-67 undergoes a metal node modification similar to that for MOF-808 (Figure S11), and the catalytic activity of M-DUT-67 is also enhanced considerably (Table 2 entries 6 and 7). Reaction parameters, such as the proton donor/solvent, reaction time, and concentration of IPA and FUR, were optimized in order to reach the higher yield and selectivity of FOL over M-MOF-808 (Figure S12). Using IPA as the hydrogen donor allowed us to reach the maximum yield of FOL (94.1% with 99.1% selectivity in 2 h of reaction time under reflux conditions). Additionally, considering the good performance of this catalyst near room temperature (Table 2 and Figure S9), the reaction conditions were further optimized by changing the IPA and initial FUR concentrations at 30 °C in order to achieve a quantitative yield and high selectivity of the FOL. The maximum FOL yield reached 90% with 94.2% selectivity after 24 h of reaction time (Figure S13). A detailed explanation regarding reaction optimization is provided in the results and discussion (Figures S12 and S13) of the Supporting Information. Major byproducts of the reaction were analyzed using GC-MS (Figure S14), from which a plausible reaction network was proposed and described (Scheme S1).

3.4. Reusability of the Catalyst. To demonstrate the heterogeneity of the catalyst, two parallel experiments were performed using M-MOF-808 catalyst with or without separating the catalyst from the hot reaction mixture after 1 h (Figure 3A). After stirring for 4 h under identical conditions, M-MOF-808 had continued to smoothly catalyze the

conversion of FUR to FOL, whereas almost no reaction was observed to occur for the reaction system in which the catalyst was filtered out after 1 h. Inductively coupled plasma (ICP) analysis showed that both filtrates contained no "Zr" species, demonstrating the heterogeneous character of M-MOF-808 catalyst in the CTH of FUR. The recyclability of the M-MOF-808 catalyst was also studied under optimized reaction conditions, however, at lower conversion in order to clearly observe the changes in catalytic activity (Figure 3B). A small decrease in catalytic activity was observed in the second cycle, and the conversion dropped from around 75% in first cycle to 64% in the second cycle. In subsequent catalytic cycles, the conversion remained stable at around 64%. FOL selectivity was maintained at over 97% in all cycles. This indicates that some of the active sites of the catalyst might have been blocked after the first cycle due to minor amounts of substrate or produced molecules having strong interactions with the catalyst surface. To investigate the structural changes in M-MOF-808, PXRD, TGA, in situ FTIR, SEM, and TEM were used and are discussed in detail in the results and discussion part of the Supporting Information (Figures S15 and S16).

3.5. Substrate Scope. Having demonstrated the excellent catalytic performance of M-MOF-808 in CTH of FUR, the scope of multiple substrates was tested using other biomass-derived carbonyl compounds, as well as representative aldehydes and ketones (Table 3). All examined carbonyl compounds can be efficiently catalyzed by M-MOF-808 to produce their corresponding alcohols in high yields. Notably, a longer reaction time is required for CTH of ketones (entries 4 and 7). The M-MOF-808 catalyst can promote the transfer hydrogenation of the important biomass-derived platform chemical 5-hydroxymethylfurfural (HMF) into 2,5-bis-



Doubly modified Zr-node

Figure 4. (A) Optimized geometries for model systems describing singly (top) and doubly (bottom) modified Zr nodes in MOF-808. A hydroxyl group and water molecule are used for the modification of the Zr node while other Zr centers are still blocked with formate groups to reduce the complexity of DFT computations. The reaction site is illustrated using a ball-and-stick model (Zr, blue; O, red; C, dark gray; H, white), and the other parts are simply presented with a stick model for clarity. (B) Proposed CTH reaction path.

(hydroxymethyl)furan (BHMF) with a high selectivity of 98.0% (Table 3, entry 2). When a methyl group is introduced in FUR at position 5 (5-MF), a longer reaction time (6 h) is essential to achieve a similar conversion to FUR (95%). This is due to the electron-donating nature of methyl groups increasing the electron density on the C atom of the carbonyl group. Consequently, the situation did not favor hydride ion attack on carbonyl carbon. Moreover, steric hindrance can also contribute to the slowing of the reaction rate. In contrast, an electron-withdrawing group attached to the aromatic ring at the para position improved the rate of the CTH reaction (entries 5 and 6, Table 3). To illustrate the competency of M-MOF-808 in transfer hydrogenation reactions near room temperature, a substrate scope study was undertaken using the same carbonyls utilized in Table 3 at 30 °C (Table S4). All of the carbonyl compounds were successfully converted into their respective alcohols with high selectivity, though lower substrate to catalyst ratios and longer reaction times were required (Table S4). These results illustrate the great potential applications of M-MOF-808 for CTH reactions in both organic synthesis and biomass transformation at low reaction temperatures.

3.6. Mechanistic Insights Using Isotopically Labeled 2-Propanol. Isotopically labeled 2-propanol- d_8 GC-MS methods have been used in previous studies with different heterogeneous catalyst systems to determine whether the reaction proceeds through direct hydrogen transfer from 2-propanol to the carbonyl groups of the substrate or whether sequential metal hydride formation and subsequent carbonyl group reduction occurred.^{16,37} We applied the same method with M-MOF-808 to understand the mode of the reaction mentioned above. Here, 2-propanol- d_8 was used with 2methyl-2-propanol in a molar ratio of 1:3. The absence of β -H in 2-methyl-2-propanol prevents it from playing the role of a hydrogen donor. However, it is capable of exchanging H atoms from its OH groups to the OD groups of 2-propanol- d_8 , as well as with the active H/D from the catalyst surface.⁷ Further, due to the excess of 2-methyl-2-propanol used, it can replace almost all of the OD of 2-propanol-d₈ into OH, leaving 2propanol- d_7 as the major D donor to FUR (Scheme S2). FOL products formed by the hydrogenation of FUR with 2propanol- d_0 and 2-propanol- d_8 were analyzed by GC-MS, and the difference of 1 amu (from 98 to 99) in their molecular ion peaks (Figure S17) suggests that hydrogen from IPA was directly transferred to the carbonyl group of FUR without being adsorbed on the catalyst surface. Mechanistic insights therefore suggest that basic sites of the catalyst (Zr-OH/Zr- OCH_3) absorb the hydrogen atoms from IPA, which assist the formation of 2-propoxide on Zr sites and that subsequently facilitates the transformation of β -H from alcohol via an eightmembered transition state.

3.7. Reaction Mechanism Based on Computational Study. The metal node modification of Zr-based MOF accomplished by the removal of formate groups is an essential procedure in achieving the high catalytic activity for CTH of FUR to FOL. The poor reactivity of 12-connected Zr-MOFs



Figure 5. Reaction energy diagrams for CTH paths of FUR to FOL (see Figure 4B) with singly (blue) and doubly (black) modified Zr node model systems. The Gibbs free energy (ΔG) throughout the reaction processes is presented in kcal/mol.

can thus be easily understood through modification available only at the defective sites of the Zr node due to their lack of formate groups. Nevertheless, the dependence of CTH on the coordination and modification of Zr nodes and its detailed reaction mechanism has not yet been described for Zr-based MOFs. To assess this, we carried out a computational study based on DFT (see the Supporting Information for computation details). On the basis of the three-dimensional network of MOF-808, the feasible geometries of Zr nodes due to modification, i.e., singly (top) and doubly (bottom) modified Zr nodes (s and d Zr nodes) of MOF-808, are depicted in Figure 4, where modified Zr centers are occupied with one -OH group and one water molecule. In the proposed model systems, the -OMe group introduced by methanol activation (see Scheme 1) was substituted with an -OH group in the modified Zr center, whereas the other Zr centers remained blocked with formate groups, in order to reduce the complexity of DFT computations. Note that replacing the -OMe groups with -OH groups might occur due to experimental conditions as reported earlier in this paper (section 2.2) and in a previous study.⁵³ The computationally suggested CTH mechanism, where two IPA molecules are sequentially required as a hydrogen donor, is presented in Figure 4B, and the corresponding reaction energy profiles (ΔG) obtained with DFT calculations are provided in Figure 5 (see Figure S18 for optimized geometries). The initiation step of CTH, i.e., the binding process of the first IPA molecule onto a surface-modified Zr node, proceeds through the substitution of an -OH group with a deprotonated IPA (S \rightarrow A). Whereas the reaction energy for $S \rightarrow A$ is estimated to be endothermic by +8.49 kcal/mol for the s Zr node of MOF-808 (blue), the corresponding reaction energy for the d Zr node (black) is reduced to -11.26 kcal/mol, as shown in Figure 5. Therefore, the d Zr node can easily initiate the CTH reaction with a highly exothermic binding process involving the first IPA molecule in comparison with the s Zr node, for which the initiation step is thermodynamically unfavorable with endothermic energy. In addition, the corresponding reaction energies for the s and d Zr nodes are +8.46 and -9.63 kcal/ mol, respectively, when the -OMe group is not substituted with an -OH group for simplicity (Figure S19). These values are comparable with those obtained using the simplified Zr

node model systems and indicate that our approach does not significantly influence the reaction energy profile. The catalytic cycle after binding the first IPA molecule to a Zr node, i.e., the formation of A, is schematically presented in Figure 4B, where colored hydrogens indicate transferred hydrogen species during the reaction. The first and second IPA molecules provide hydrogens as a hydride (H1, $B \rightarrow C$) and as a proton $(H2, D \rightarrow E)$ to FUR. The first hydrogen transfers from IPA to FUR (B \rightarrow C) occurs with an activation energy (E_a) of 11.83 and 11.47 kcal/mol for the s and d Zr nodes, respectively, following the replacement of the remaining water molecules with FUR (A \rightarrow B). The hydride transfer from alkoxy carbon to carbonyl carbon is the rate-determining step, and the corresponding E_2 values are almost identical for both the s and d Zr nodes (Figure 5), where the transition state structure can be defined with an atomic configuration of an eight-membered ring involving two Zr centers (Figure S18). The CTH reaction of aldehyde to alcohol has usually been thought to follow the Meerwein-Ponndorf-Verley (MPV) mechanism, which requires a six-membered-ring transition state for hydride transfer.²¹⁻²³ The binding of FUR and IPA molecules to the same Zr metal center is required for the MPV reaction process. Neither the local minimum nor the transition state structures corresponding to the traditional MPV mechanism on the s Zr node system were found because of the significant steric hindrance of the neighboring formate groups. Conversely, the d Zr node systems may lead to the binding of FUR and IPA to the same Zr metal center, which has no bond with formate groups (see Figures S20 and S21 for the reaction energy diagram and optimized geometries, respectively, for the MPV process in the d Zr node). However, the MPV process in d Zr nodes requires a much higher energy for hydrogen transfer (B \rightarrow C) in comparison with the proposed mechanism in the presented computational results, which has the eightmembered-ring transition state involving the closest two Zr centers (Figure 5). A similar reaction mechanism deviated from the MPV process and was also reported in a previous study regarding the CTH reaction of cyclohexanone with IPA on a zirconia surface.65

Thereafter, the acetone molecule should be substituted with a second IPA as a hydrogen donor $(C \rightarrow D)$. This process is expected to be facilitated due to hydrogen bonding between a

newly inserted IPA and the neighboring oxygen of deprotonated FOL formed by hydride transfer to FUR. The exothermic reaction energy of -11.50 kcal/mol for the s Zr node is twice as large as that for the d Zr node (-5.08 kcal)mol), which is related to the strength of the hydrogen bond: the hydrogen bond lengths for s and d Zr nodes are 1.44 and 1.54 Å, respectively (Figure S18). The neighboring functional groups formed with activation processes, i.e. the -OH group and water molecule, occupy larger spaces in comparison with a formate group and thus weaken the hydrogen bonding of IPA. The formation of FOL $(D \rightarrow E)$ can easily be achieved through proton transfer from IPA to deprotonated FOL along the hydrogen bonding between them with small (3.23 kcal/ mol) and negligible ($\sim 0 \text{ kcal/mol}$) E_2 values for both s and d Zr nodes, respectively, in which the transition state has a sixmembered-ring configuration also involving two Zr centers (Figure S18). The computationally obtained negative E_a of a negligible extent (-0.6 kcal/mol) for a d Zr node indicates a barrierless reaction process. In contrast to the substitution of acetone with IPA, the desorption of FOL (+10.60 kcal/mol) for the s Zr node is twice as unfavorable as that for the d Zr node (+4.97 kcal/mol), which is also related to hydrogen bonding between FOL and deprotonated IPA: the hydrogen bond lengths for s and d Zr nodes are 1.37 and 1.43 Å, respectively (Figure S18). Our DFT computations suggest that a highly modified Zr node in a Zr-MOF with lower connectivity can provide higher catalytic activity due to the following features: (i) the d Zr node can easily initiate a catalytic cycle with exothermic insertion of the first IPA molecule and (ii) the produced FOL can be more easily released from the d Zr node in comparison with the s Zr node due to slightly weakened hydrogen bonding, although both s and d Zr nodes have an almost identical activation energy at the rate-determining step.

4. CONCLUSIONS

To summarize, a series of Zr-MOFs exhibiting different metal node connectivities (12, 8, and 6) were synthesized and tested for CTH of FUR to FOL in order to understand the role of metal node coordination. It was found that metal node to linker connectivity plays a dominant role over high porosity of the Zr-MOFs. MOF-808, with the lowest metal node connectivity (6), enhances the accessibility of reactant molecules to active sites (metal node), resulting in the highest catalytic activity among the other tested Zr-MOFs with a higher connectivity (8 and 12). Further, the metal node of MOF-808 was modified by methanol activation and extensively studied with various characterization techniques to evaluate any changes to its local structure. Significant enhancement in the catalytic activity of MOF-808 for CTH of FUR to FOL was reported at low reaction temperatures (30-40 °C) after metal node modification. The modification enhanced the acid-base sites of MOF-808 by developing Zr-CUS and surface hydroxyl groups, which presumably facilitate the adsorption of FUR and 2-propanol onto the Zr node surface.

The catalyst was recycled five times with little observed drop in activity and without a change in FOL selectivity after the first cycle. The structural stability of the catalyst was maintained after five cycles, as confirmed by PXRD, SEM, and TEM analyses; however, strong adsorption of organic moieties from reactant or product molecules might have blocked some active sites of the catalyst surface after the first cycle. This was recognized using TGA and *in situ* FTIR study. The substrate scope was extended to a number of biomassderived and other representative carbonyl compounds over M-MOF-808. Mechanistic insights were provided by isotopically labeled 2-propanol- d_8 experiments, showing FUR reduction through the transfer hydrogenation path. Finally, the reaction mechanism for CTH of FUR to FOL was investigated in detail using DFT computations, which suggests that a highly modified Zr node feasible in a Zr-MOF with lower connectivity can provide higher catalytic activity. The work presented here should encourage the development of new Zrbased advanced porous materials as catalysts to tackle the challenges associated with room- or low-temperature biomass conversion reactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.9b05085.

Experimental section including synthesis and characterizations of Zr-MOFs, computational methods and simulations, additional catalyst characterizations (XRD, TGA, surface area analysis, digested ¹H NMR, SEM, TEM, EA, *in situ* FTIR, NH₃ and CO₂ TPD, mass spectra of major products), plausible reaction networks, and additional catalytic tests (PDF)

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Notes

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