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# Surfactant-assisted synthesis of mesoporous hafnium- imidazoledicarboxylic acid hybrids for highly efficient hydrogen transfer of biomass-derived carboxides

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# ABSTRACT

Catalytic transfer hydrogenations of biomass-derived carbonyl compounds to produce corresponding alcohols are important pathway for biomass transformation. Herein, a facile route was developed to synthesize the surfactant-assisted heterogeneous acid-base bifunctional 4,5-imidazoledicarboxylic acid-hafnium hybrid catalyst (Hf-H<sub>3</sub>IDC-T) by hydrothermal self-assembly method. The as-prepared Hf-H<sub>3</sub>IDC-T was characterized by SEM and TEM, FT-IR spectra, N<sub>2</sub> adsorption-desorption, X-ray diffraction patterns (XRD), X-ray photoelectron spectroscopy (XPS), Thermogravimetry analysis (TG), NH<sub>3</sub>/CO<sub>2</sub>-TPD, NMR, GC–MS, ICP-OES and elemental analysis. Hf-H<sub>3</sub>IDC-T hybrid had mesoporous structure and acid-base couple sites. A quantitative yield (99.2%) of furfuryl alcohol (FFA) was obtained from furfural (FUR) over Hf-H<sub>3</sub>IDC-T using 2-propanol as the hydrogen source under mild conditions. It's found that the amino groups on the imidazole ring is beneficial to enhance the base sites of catalyst. Meanwhile, the addition of hexadecyl trimethyl ammonium bromide (CTAB) as template agents can improve the specific surface area of the catalyst. Dynamic analysis showed that the apparent activation energy of FUR reduction was as low as 50.89 kJ / mol. The as-prepared catalyst has good stability and can be recycled. Finally, the catalyst also has a good catalytic effect on the hydrogenation reaction of aldehydes and ketones of biomass-derived compounds.

#### 1. Introduction

Over the past years, the development of renewable energy as a substitute for diminishing fossil fuels has gradually attracted the attention of the chemical field [1,2]. As a sustainable and readily available resource, biomass feedstock is an unique alternative to traditional fossil resources from which energy, fuels and chemicals can be obtained [3]. In the existence of acidic catalysts, simultaneously combined with basic/metallic sites, sugars and lignin components can be selectively converted into a variety of products, such as organic acids (e.g., levulinic acid and lactic acid) [4], furanic compounds (e.g., furfural (FUR), 5-hydroxymethylfurfural (HMF), and 5-ethoxymethylfurfural (EMF)) [5], polyols (e.g., sorbitol, mannitol, xylitol, and ethylene glycol) [6], and phenolics (e.g., vanillin and veratraldehyde) [7].

FUR is one of the main products derived from the conversion of lignocellulosic biomass. The presence of aldehyde groups and aromatic rings makes FUR become a multi-purpose chemical intermediate [8,9].

Due to its high reactivity, FUR can be converted to other high valueadded products by the several chemical routes [7,10]. In the catalytic process, the focus is on the further use of FUR by hydrogenation, oxidation, alkylation and rehydration. Especially, the use of H-donor sources to increase the hydrogen content of oxygenates is one of the significant steps in the efficient and safe production of energy-intensive molecules [11].

Nevertheless, an effective alternative to conventional catalytic hydrogenation using hydrogen as a reducing agent is catalytic transfer hydrogenation, which has been proposed for the conversion of ketones or aldehydes in alcohols because it avoids the use of high hydrogen pressure [12–14]. As reported, Meerwein-Ponndorf-Verley (MPV) can reduce aldehydes and ketones by secondary alcohols in the presence of Lewis acidic or basic catalysts [15]. The Lewis acid sites is capable of activating the C=O bond of the aldehyde or ketone, while the alcohol is deprotonated. Moreover, it is speculated that the formation of the sixmembered intermediate is due to the participation of hydrogen at the

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Ca position, and the aldehyde/ketone and the deprotonated alcohol being directly activated on the Lewis acid sites [16-18]. The heteroatoms-modified zeolites and mesoporous silica can be used to prepare Lewis acid catalyst, with which FUR conversion was carried out by MPV reaction [19]. Hydrogenation of the FUR produces FFA, which can be reacted with secondary alcohol to form furfuryl ethers. Noble metals such as Au, Pt and Pd, and non-noble metals such as Cu, Co and Ni are commonly used as catalysts to obtain a target product in a sufficient yield [20,21]. In addition, Such as zirconia, hydrotalcite, hydroxyapatite, zeolite, etc., solid materials are also used as heterogeneous catalysts for biomass conversion [22,23]. Some reports indicated that the assembly of organic molecules (such as polyphenols, porphyrins, and phytic acids) with inorganic metal ions (such as Cu<sup>2+</sup>, Co<sup>2+</sup>, and Zr<sup>4+</sup>) could mimic natural structures and generate a series of active frameworks with good stability, which was a more convenient and controllable alternative for the MPV reaction [24-27]. For this purpose, the preparation of FFA produced by MPV reaction with high efficiency and easy recovery of the organic-inorganic framework structure catalyst still is a subject worthy of study.

When considering the use of MOFs as catalysts for the reaction process, the metal oxide nodal component of the MOFs framework is usually used as the active site [28,29]. In general, the introduction of more basic sites to enhance the basicity of the catalyst is an attractive method to improve catalytic efficiency for the MPV reaction of FUR to produce FFA [30]. In our work, we synthesized a new surfactant-assisted, heterogeneous and acid-base functional organic-inorganic Hfbased/nitrogen-containing hybrid catalyst (named Hf-H<sub>3</sub>IDC-T) based on HfCl<sub>4</sub> and H<sub>3</sub>IDC in N, N-dimethylformamide (DMF) by hydrothermal method (Scheme S1). It provides the possibility to design effective catalysts with high basicity by using H<sub>3</sub>IDC as a structural unit. Additionally, surfactant (hexadecyl trimethyl ammonium bromide (CTAB)) was used as template agents for synthesis of Hf-H<sub>3</sub>IDC-T. The surfactant is commonly used to augment the porous structure of metalorganic framework topology [30]. The catalytic process uses 2-propanol as the hydrogen source to catalyze the MPV reaction to provide a satisfactory FFA yield. The structure and performance of the prepared catalysts were comprehensively investigated.

#### 2. Experimental section

#### 2.1. Materials

4,5-imidazoledicarboxylic acid (H<sub>3</sub>IDC, 97%), Hafnium chloride (HfCl<sub>4</sub>, 99.5%), Hafnium oxide (HfO<sub>2</sub>,99.9%), 2-propanol-d8 (2-PrOHd8,99.5%)were purchased from Macklin Corporation, Furfural (FUR, > 99.5%), Furfuryl alcohol (FFA, 98%), 5-hydroxymethylfurfural (HMF, > 99.0%), 5-methylfurfural (> 99%), cinnamaldehyde (> 99.5%), citral (> 97%), veratraldehyde (> 99%), and 2-propanol (> 99.0%), hexadecyl trimethyl ammonium bromide (CTAB, 99%), 2,5-Furandicarboxylic acid (FDCA, 98%) were purchased from Aladdin Corporation. All other reagents were used as received unless otherwise stated and were not treated at all.

#### 2.2. Catalyst preparation

The catalyst (Hf-H<sub>3</sub>IDC-T) was prepared by self-assembly of H<sub>3</sub>IDC with metal chloride (HfCl<sub>4</sub>) in DMF under hydrothermal conditions. The preparation process is as follows, H<sub>3</sub>IDC (6 mmol, 0.94 g) and HfCl<sub>4</sub> (6 mmol, 1.92 g) were dissolved in DMF (31 ml, 0.4 mol), respectively. The two solutions, which are completely dissolved, are then mixed and transferred to a 100 ml stainless steel reactor. The sealed autoclave was placed in an oven at 120 °C for 24 h under static conditions. After completion of the reaction, the obtained white precipitate was removed by filtration, and then washed with DMF and ethanol for 6–8 times until a colorless transparent filtrate was observed, and then vacuum dried at 100 °C overnight to obtain a target sample designated as Hf-H<sub>3</sub>IDC. In

order to further expand the structure of Hf-H<sub>3</sub>IDC, CTAB was added as a co-reagent under otherwise identical conditions, and the obtained catalyst was defined as Hf-H<sub>3</sub>IDC-T. In addition, the CTAB was removed as a co-reagent by filtration and washing. For comparison, Hf-FDCA was also synthesized by hydrothermal method of FDCA with metal chloride (HfCl<sub>4</sub>) in DMF, according to previously reported procedures [23,28]. HfO<sub>2</sub> was calcined at 150 °C for 12 h. All solid samples were dried at 90 °C for 5 h prior to catalytic performance testing and catalyst characterization.

## 2.3. Catalyst characterization

The structure and morphology of the catalyst were examined using a scanning electron microscope (SEM) and a high-resolution transmission electron microscope (JEM-2100F) equipped with an EDX analyzer operated at 200 kV. FT-IR spectra were recorded on a Perkin Elmer 1710 spectrometer (KBr disk) with a wavenumber range of  $4000-400 \text{ cm}^{-1}$ . X-ray photoelectron spectroscopy (XPS) analysis was performed on a physical electron Quantum 2000 scanning ESCA microprobe (Al-Ka Mono, hv = 1486.6 eV), and the binding energy was corrected using C1 s orbital (284.8 eV). X-ray diffraction (XRD) patterns of the powder samples were obtained using a Rigaku International D/max-TTR III Xray powder diffractmeter with Cu-K $\alpha$  ( $\lambda = 1.542$  Å) radiation and 2 $\theta$ scanned from 5° to 90°. Thermogravimetry (TG) was used to determine the thermal properties of catalysts on a NETZSCHSTA 429 instrument under N2 in a flow rate of 30 ml/min at a programmed temperature range of 50–900 °C with a heating ramp of 10 °C/min. BET surface area, Barrett-Joyner-Halenda (BJH) pore size and volume were measured by N<sub>2</sub> physisorption (TriStar II 3flex) at liquid N<sub>2</sub> temperature. The determination of acidity and basicity of different samples by NH<sub>3</sub> and CO<sub>2</sub> (NH<sub>3</sub> / CO<sub>2</sub>-TPD) temperature programmed desorption by a Micromeritics AutoChem II 2920 equipment. The catalyst was firstly degassed under a flowing He (30 ml/min) at 150 °C for 2 h, and then the system was cooled to room temperature in the presence of He. After the solid samples were adsorbed with NH<sub>3</sub> or CO<sub>2</sub>, the system was purged at 50°C heat flow and the TPD results were gained from 50 °C to 300 °C under flowing He. The ratios of Brønsted and Lewis acid sites of the solid catalysts were determined by pyridine adsorption FT-IR fitted with a Bruker VERTEX V70v system, based on integral area and the characteristic peak position in the wavenumber range of 1400–1700 cm<sup>-1</sup>. The Hf elemental composition was measured by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) equipment (Spectro Arcos FHX22).

## 2.4. Catalytic reaction

The MPV reaction of the biomass-derived compounds with 2-propanol was carried out in an oil-heated condition in a 15 ml Ace pressure tube (Synthware, Beijing). Typically, aldehydes (1.0 mmol), catalysts (0.1 g), and 2-propanol (10 mL) were added into the reactor, and then placed into the oil bath at stated temperature of 80–140 °C, followed by the magnetic stirring for specific time at 600 rpm. After completion, the reaction tube was cooled to room temperature with cold water in a beaker. The reaction mixture was centrifuged and collected for analysis. Quantitative analysis of reactants and products on a standard sample using toluene as an internal standard on a GC (Shimadzu Nexis GC-2030) equipped with an HP-5 capillary column (30.0 m  $\times$  250 mm  $\times$  0.25 mm) and a flame ionization detector. Identification of products were observed using GC–MS (GCMS-QP2010 Ultra) equipped with HP-5MS capillary column (30.0m  $\times$  250 mm  $\times$  0.25 mm).

#### 2.5. Reusability of the prepared Hf-H<sub>3</sub>IDC-T

In order to research the reusability of  $Hf-H_3IDC-T$ , the catalyst was recovered by the centrifugation, and washed five times with DMF and ethanol. After drying at 100 °C for 5 h in an oven, the recovered catalyst

was reused for the next cycle of the reaction. The solid residue was removed by filtration, and then the Hf element content immersed in the reaction solution was analyzed by ICP, and the filtrate was diluted with water to an equal volume.

## 2.6. Isotopic labelling experiments

For Isotopic kinetic study of the MPV reaction of FUR to FFA,  $^1H$  NMR spectra of the reaction mixture after different time durations were performed in cosolvent tert-butanol and 2-propanol-d8 with a molar ratio of 3:1 on a JEOL-ECX 500 NMR spectrometer operating at 500 MHz at room temperature. To reveal the occurrence of direct hydrogen transfer other than metal hydride route, mass fragmentation analysis was further conduced with GC–MS using a cosolvent tert-butanol and 2-propanol-d8 with a molar ratio of 3:1. In the resulting medium, tert-butanol is not able to act as hydrogen source due to the absence of  $\beta$ -H, while it can exchange most D species of –OD group in 2-propanol-d8 to –OH group and replace active D on metal surface with H [31].

### 3. Results and discussion

#### 3.1. Characterization of catalysts

The synthetic procedure for Hf-H<sub>3</sub>IDC and Hf-H<sub>3</sub>IDC-T were described in detail in the experimental section. The synthesized Hf-H<sub>3</sub>IDC and Hf-H<sub>3</sub>IDC-T was primarily characterized by SEM, TEM, STEM-HAADF, as shown in Figs. 1 and S1. The Hf-H<sub>3</sub>IDC-T hybrid was small particles with porous surface (Fig. 1a and b). By comparison, the HfO<sub>2</sub> was in small ball structure (Fig. S2). Compared to the SEM and TEM images of Hf-H<sub>3</sub>IDC hybrid (Fig. S1), the introduction of the CTAB in preparation process not only caused the formation of the network layer structure (Fig. 1c), but also change the surface and porous structure of Hf-H<sub>3</sub>IDC-T. As observed from the corresponding elemental mappings and the STEM-HAADF image in Fig. 1d and the Hf, O, N and C compositions (i.e., Hf<sup>4+</sup> and  $-CO^{2-}$  moieties) in Hf-H<sub>3</sub>IDC-T are evenly distributed in Fig. 1e–h.

The structural and textural of the as-prepared catalysts were further investigated. Fig. 2a and b showed the  $N_2$  adsorption-desorption isotherms and pore volume of HfO<sub>2</sub>, Hf-H<sub>3</sub>IDC and Hf-H<sub>3</sub>IDC-T,

respectively. This indicated that the introduction of organic species (i.e., H<sub>3</sub>IDC) greatly increased the adsorbed quantity of N<sub>2</sub> and generated more distribution of micropores and mesopores, possibly due to the formation of assembled organic-inorganic networks (Fig. 2a), especially in the case of Hf-H<sub>3</sub>IDC-T. Hf-FDCA had inferior surface area  $(9.73 \text{ m}^2 \text{g}^{-1})$  and pore volume  $(0.0326 \text{ m}^3 \text{g}^{-1})$  (Table 1), although its average pore size is mesoporous (14.02 nm). In contrast, Hf-H<sub>3</sub>IDC and Hf-H<sub>3</sub>IDC-T showed much higher surface areas (ca.89.59 and  $153.50 \text{ m}^2 \text{g}^{-1}$ ) and average pore sizes of 14.49 and 12.94 nm, respectively (Table 1, Fig. 2b). Therefore, the CTAB used in the preparation of Hf-H<sub>3</sub>IDC-T can enlarge the surface areas of the catalysts, and improving the accessibility of active sites for the substrates [30]. The composition of the catalyst elements was determined by ICP-OES and elemental analysis in Table S1. The results showed that the molar ratio (HfCl<sub>4</sub>:H<sub>3</sub>IDC = 1:1) of the synthetic catalyst is reasonable coordination pattern (Scheme S1).

FT-IR spectra of HfO2, Hf-H3IDC, and Hf-H3IDC-T in Fig. 2c showed the characteristic signals of Hf-O bonds at 800 cm<sup>-1</sup>. For Hf-H<sub>3</sub>IDC and Hf-H<sub>3</sub>IDC-T, the enhanced absorptions at 1470 and 1500–1700 cm<sup>-1</sup> shows symmetric and asymmetric stretching vibrations of the  $-CO_2$  – group, respectively [32,33]. The bridging coordination mode of H<sub>3</sub>IDC and Hf (Scheme S2) can be demonstrated by splitting about 93 cm<sup>-1</sup> between symmetric and asymmetric peaks, which is consistent with the Hf-FDCA structure (Fig. S3) [34]. In the case of pure H<sub>3</sub>IDC, only a single stretching vibrations having a split of 205 cm<sup>-1</sup> was observed, which was very consistent with the monodentate C–OH (2500–3200 cm<sup>-1</sup>) of the carboxyl group in H<sub>3</sub>IDC [30]. In addition, the broadband at 3300 cm<sup>-1</sup> for Hf-H<sub>3</sub>IDC and Hf-H<sub>3</sub>IDC-T not only were from the protonated carboxyl group (-COOH) of the H<sub>3</sub>IDC moieties that are incompletely coordinated with Hf, but also are ascribed to adsorbed water and other hydroxyls [32]. The use of the CTAB for preparation of Hf-H<sub>3</sub>IDC-T had enhanced the binding of the carboxylate compound to Hf, and its weaker band was well supported at about 3300 cm<sup>-1</sup> compared to Hf-H<sub>3</sub>IDC [30,33]. Meanwhile, the blue shift in the stretching vibrations of the hydroxyl group of Hf-H<sub>3</sub>IDC-T means that there is an unstable -OH group, possibly corresponding to a weak Brønsted acid site, compared to pure H<sub>3</sub>IDC. Fig. 2d illustrated the XRD patterns of HfO2, Hf-H3IDC, and Hf-H3IDC-T. Compared to the HfO<sub>2</sub> having high crystallinity (Fig. 2d) and the clear crystal lattice, these Hf-containing materials hybrids was all amorphous. The intense



Fig. 1. SEM images (a), TEM images (b) and HR-TEM (c) images of Hf-H<sub>3</sub>IDC-T; STEM-HAADF image (d) and corresponding elemental mappings of Hf(e), C(f), N(g) and O(h) of Hf-H<sub>3</sub>IDC-T.



Fig. 2.  $N_2$  adsorption-desorption isotherm (a), pore size distribution by  $N_2$  adsorption-desorption isotherm (b), FTIR spectra (c), XRD patterns (d) of the various catalysts.

Table 1Texture and acid-base properties of Hf-containing catalysts.

Catalyst	$\substack{S_{BET}\\m^2g^{-1}}_a$	$\begin{array}{c} V_{pore} \\ m^3 g^{-1} \\ {}_{b} \end{array}$	D <sub>pore</sub> nm <sup>c</sup>	Basicity mmolg <sup>-1</sup> d	Acidity mmolg <sup>-1</sup> d	Base/ acid ratio
HfO <sub>2</sub>	8.59	0.0226	11.18	0.37	0.81	0.46
Hf-H <sub>3</sub> IDC	89.59	0.3135	14.49	0.66	1.51	0.44
Hf-H <sub>3</sub> IDC-T	153.50	0.4791	12.94	0.78	1.41	0.55
Hf-H <sub>3</sub> IDC-T <sup>e</sup>	133.77	0.2274	7.31	0.72	1.38	0.52
Hf-FDCA	9.73	0.0326	14.02	0.48	0.68	0.71

 $^{\rm a}\,$  BET surface area determined by  $N_2$  adsorption isotherm.

<sup>b</sup> Pore volume estimated by BJH adsorption cumulative volume of pores.

 $^{\rm c}$  Average pore size was estimated from the adsorption average pore diameter.

 $^{\rm d}\,$  Basicity and acidity of the catalysts were determined by  $\rm CO_2$  and  $\rm NH_3\text{-}TPD$ , respectively.

<sup>e</sup> Recovered Hf-H<sub>3</sub>IDC-T in the sixth cycle.

peaks of  $Hf-H_3IDC$  and  $Hf-H_3IDC-T$  were typical reflection, which is similar to that of Hf-FDCA (Fig. S4) [34].

The thermal stability of selected  $HfO_2$ ,  $Hf-H_3IDC$  and  $Hf-H_3IDC$ -T samples was investigated by thermogravimetric (TG) analysis at 50–900 °C (Fig. S5). As indicated by these results,  $Hf-H_3IDC$  and  $Hf-H_3IDC$ -T were relatively stable at 50–300 °C. Particularly, in the temperature range of 50–300 °C, the weight of  $Hf-H_3IDC$  and  $Hf-H_3IDC$ -T are reduced by about 10%, which is slightly higher than  $HfO_2$ . This is probably own to the removal of extra Brønsted acidic species (–OH) and organic solvent residues (e.g., DMF) inside pores of  $Hf-H_3IDC$  and  $Hf-H_3IDC$ -T besides physically adsorbed water, and it is consistent with results gained by N<sub>2</sub> adsorption-desorption and FT-IR (Fig. 2a–c). The results indicated that the as-prepared catalysts  $Hf-H_3IDC$  and  $Hf-H_3IDC$ -T were stable under the reaction conditions which will be discussed in the later parts [35].  $CO_2$  and  $NH_3$ -TPD were carried out to obtain more

information about the acid/base sites for these solid hybrids (Fig. 3a and b, Table 1). Hf-H<sub>3</sub>IDC and Hf-H<sub>3</sub>IDC-T have relatively higher contents of both basic and acidic species, as compared with those of HfO<sub>2</sub>. The formation of acid-base sites in these catalysts could be attributed to the formation of robust Hf-O-C frameworks with the better heat resistance both acidic (Hf<sup>4+</sup>) and basic (O<sup>2-</sup>) species during thermal treatment of H<sub>3</sub>IDC and HfCl<sub>4</sub> [35]. Furthermore, Hf-H<sub>3</sub>IDC and Hf-H<sub>3</sub>IDC-T possesses relatively higher contents of basic than Hf-FDCA (Scheme S3). This may be due to the presence of amino groups on the imidazole ring in Hf-H<sub>3</sub>IDC and Hf-H<sub>3</sub>IDC-T. (Scheme S1).

In addition, it was demonstrated that the presence of Brønsted acidic sites was also beneficial for the Lewis acid-mediated hydrogentransfer process [36-38]. As shown in Fig. 4a, pyridine-adsorbed FT-IR spectra of both HfO2, Hf-H3IDC and Hf-H3IDC-T were recorded. The bands at wavenumber of 1450 and 1545 cm<sup>-1</sup> were attributed to the pyridine interacting with Lewis acid sites (LA) and Brønsted acid sites (BA), respectively (Fig. 4a). Compared to HfO<sub>2</sub>, the acid density of Hf-H<sub>3</sub>IDC and Hf-H<sub>3</sub>IDC-T was increased obviously. Hf-H<sub>3</sub>IDC and Hf-H<sub>3</sub>IDC-T exhibited relatively larger bands than those of HfO<sub>2</sub> at around 1580 and 1620 cm<sup>-1</sup>, which were assigned to hydrogen-bonded pyridine and pyridine-adsorbed on Lewis acidic centers, respectively. It further demonstrated that Hf-H<sub>3</sub>IDC-T had higher Lewis and Brønsted acid strength. The results of pyridine-adsorbed FT-IR proved the simultaneous presence of Hf-O-C frameworks and protonated carboxyl groups (-CO<sub>2</sub>H) of H<sub>3</sub>IDC moieties, which contributed to the formation of Lewis acid/base sites and Brønsted acidic species, respectively [37,39]. Apart from the nature and density/content of acid and base sites, the acid-base strength of Hf-H3IDC, Hf-H3IDC-T, Hf-FDCA, and HfO2 was proved by analysis the local environment of the Hf and O element in different materials by XPS technique. The survey spectra further confirmed the presence of the Hf, O, C and N elements in Hf-H<sub>3</sub>IDC-T (Fig. 4b). A higher Hf 4f binding energy corresponds to the larger positive charge of Hf species, demonstrating that the Lewis



Fig. 3. CO<sub>2</sub>-TPD (a) and NH<sub>3</sub>-TPD (b) of the various catalysts.

acidity of these Hf centers was increased (Fig. 4c) [40,41]. Additionally, the binding energy of O 1s belonging to Hf-O-C coordination interactions in hafnium-based hybrid was higher than for Hf-O-Hf interactions in HfO<sub>2</sub> (Fig. 4d) [40,42]. The medium binding energy of O 1s assigned to negative charge on the oxygen atoms indicated the medium basic strength of Hf-H<sub>3</sub>IDC-T. Evidently, these nitrogen-containing groups in Hf-H<sub>3</sub>IDC-T could facilitate the formation of the basic sites. These results showed the functional groups in H<sub>3</sub>IDC could increase the basic contents and stabilize Lewis acidic Hf<sup>4+</sup> species achieved by the formation of porous Hf-O-C framework structure [43]. As consistent to FT-IR (Fig. 2c), the results of pyridine-adsorbed FT-IR (Fig. 4a) certified the simultaneous presence of Hf-O-C frameworks and protonated carboxyl groups ( $-CO_2H$ ) of H<sub>3</sub>IDC moieties, which contributed to the formation of Lewis acid/base sites and Brønsted acidic species, respectively.

3.2. Catalytic performance evaluation of the various catalysts

FUR derived from lignocellulose-derived carbohydrates is one of key components in bio-oil, while its reactive aldehyde group is susceptible to formation of humins by condensation reactions [44]. Herein, the conversion of FUR to FFA was selected as a model reaction to study the catalytic performance of Hf-H<sub>3</sub>IDC-T in MPV reduction. (Table 2). No significant conversion of FUR was detected without catalysts (Table 2, Entry 1). Then, different hafnium-containing compounds (HfCl<sub>4</sub> and HfO<sub>2</sub>) were tested (Table 2, Entry 2–3). Neither Lewis acidic (HfCl<sub>4</sub>) nor HfO<sub>2</sub> with enhanced basic strength could efficiently catalyze this reaction. Furfural diisopropyl acetal (FDIA) obtained by acetalization of FUR with 2-propanol was detected as major by-product. And the H<sub>3</sub>IDC precursor showed little conversion to FUR, indicating that the building block for catalyst synthesis were not active in this reaction under the



Fig. 4. FT-IR spectra after pyridine adsorption and evacuation at 110 and 250 °C (a) of various catalysts; Survey spectrum of different samples (b) and XPS spectra of Hf 4f peaks (c) and O 1s peaks (d) of various catalysts.

Table 2					
MPV reduction	of FUR	to FFA	with	various	catalysts.

Entry	Catalyst	Conv (%) <sup>b</sup>	FFAYield (%)	Select (%) <sup>b</sup>	IPMA yield (%) <sup>c</sup>	FDIA yield (%) <sup>d</sup>	FFA formation rate ( $\mu molg^{-1}h^{-1})$ $^{\rm e}$
1	none	0	0	0	0	0	_
2	HfCl <sub>4</sub>	79.0	0.43	0.55	14.3	36.0	43
3	HfO <sub>2</sub>	26.6	0.47	1.77	0	26.2	47
4	H <sub>3</sub> IDC	1.1	0	0	0	1	-
5	Zr-H <sub>3</sub> IDC	65.7	50.2	76.3	6.51	9.06	5015
6	Hf-H <sub>3</sub> IDC	84.5	70.8	83.8	7.86	3.09	7084
7	Hf-FDCA	63.6	46.8	73.5	2.6	14.2	4679
8 <sup>f</sup>	Hf-H <sub>3</sub> IDC-T (0.5:1)	53.5	27.2	50.8	0	26.3	2717
9	Hf-H <sub>3</sub> IDC-T	100	99.2	99.2	0	0.8	9920
10 <sup>g</sup>	Hf-H <sub>3</sub> IDC-T (2:1)	97.8	97.2	99.3	0.64	0	9719
11 <sup>h</sup>	Hf-H <sub>3</sub> IDC-T	63.9	44.3	69.3	0	10.3	4438
12 <sup>i</sup>	Hf-H <sub>3</sub> IDC-T	75.6	64.8	85.7	0	2.7	6487
13 <sup>j</sup>	Hf-H <sub>3</sub> IDC-T	96.4	91.6	95.1	2.97	1.81	9160

<sup>a</sup> Reaction conditions unless specified otherwise: 1 mmol FUR in 10 ml 2-propanol,100 mg catalyst, 120 °C, 1 h.

<sup>b</sup> Conv is FUR conversion, and Select is FFA selectivity.

<sup>c</sup> IPMA is 2-(isopropoxy)methyl furan.

<sup>d</sup> FDIA is furfural diisopropyl acetal (the acetalization product of FUR with 2-propanol).

 $^{\rm e}\,$  FFA formation rate is defined as (mol of formed FFA)/ (catalyst amount  $\times$  time).

<sup>f</sup> the molar ratio of the synthetic catalyst (HfCl<sub>4</sub>:H<sub>3</sub>IDC = 0.5:1).

 $^{g}$  the molar ratio of the synthetic catalyst (HfCl<sub>4</sub>:H<sub>3</sub>IDC = 2:1).

 $^{\rm h}\,$  Base sites of Hf-H\_3IDC-T were poisoned by adding 100 mg benzoic acid.

 $^{\rm i}\,$  Acid sites of Hf-H\_3IDC-T were poisoned by adding 100 mg pyridine.

<sup>j</sup> Scaled-up reaction: 5 mmol FUR in 50 ml 2-propanol, 500 mg catalyst, 120 °C, 1 h.

studied conditions (Table 2, Entry 4). Zr-H<sub>3</sub>IDC exhibited a slightly lower FUR conversion (65.7%) and FFA selectivity (76.3%), as compared with Hf-H<sub>3</sub>IDC (Table 2, Entry 5-6). This indicated that hafniumbased hybrid has better catalytic performance compared to zirconiumbased hybrid. In addition, Hf-H<sub>3</sub>IDC also showed a relatively higher catalytic performance than Hf-FDCA (Table 2, Entry 7). The interaction between the intrinsic amino groups and the hydroxyl groups could also activate the dissociation of 2-propanol to corresponding alkoxide and proton, which was beneficial for the MPV reaction [45]. It should be noted that, the prepared Hf-H<sub>3</sub>IDC-T (Table 2, Entry 9), which had both the higher strength and the higher content of acidic and basic sites, manifested the highest conversion (100%), FFA formation rate  $(9920 \,\mu molg^{-1} h^{-1})$  with high selectivity (99.2%) among these examined catalysts. Due to the surfactant (CTAB) as template agents for preparation of Hf-H<sub>3</sub>IDC-T can enlarge surface areas, and facilitate the diffusion and mass transfer of the substrate. Moreover, the conversion of FUR was obviously increased from 53.5% to 100% as the initial HfCl<sub>4</sub>/H<sub>3</sub>IDC mole ratios being increased from 0.5:1 to 1:1 (Table 2, Entry 8-10). However, further increasing HfCl<sub>4</sub>-initial loading amounts had slightly reduced the FFA selectivity. This is because the amount of carboxylic acid groups in H<sub>3</sub>IDC is constant. H<sub>3</sub>IDC could only coordinate with the certain content of Hf<sup>4+</sup> (Table S1). Based on the results mentioned above, the existence of both the acidic and basic sites with suitable content in catalysts was the main reason for the high selective MPV of FUR into FFA. In order to understand the effect of the acid-base active sites on the MPV reaction in Hf-H<sub>3</sub>IDC-T, pyridine and benzoic acid were separately introduced into the reaction system as poisoning additives. The catalysts were poisoned with benzoic acid and pyridine respectively before the experiment. In the case of the addition of benzoic acid, a sharp drop in FUR conversion and FFA selectivity was observed, indicating that Hf-H<sub>3</sub>IDC-T catalyzed MPV reduction was closely related to the basic sites on the catalyst surface (Table 2, Entry 11). It was possible that benzoic acid possessed a higher acidity and poisoned a large number of basic sites, destroying the synergistic effect of the acid-base coupling sites and reducing the activity of the catalyst. However, the presence of pyridine also reduced the conversion of FUR but had few negative effects on the selectivity of FFA (Table 2, Entry 12). It was reported that the poisoning eff ;ect of pyridine (for acidic sites) is weak when compared with benzoic acid (for basic sites), the addition of pyridine only slightly reduced the conversion of FUR due to

partial poisoning of acidic sites [46,49]. We found the similar results in our work, that is, the effect of poison on basic sites was higher than that on acidic sites for the catalytic performance of Hf-H<sub>3</sub>IDC-T and evidently displaying the concerted eff ;ect of acid-base couple sites for this reaction. Even the reaction (Table 2, Entry 9) was carried out at a magnification of five times, interestingly, there still exhibited a high conversion of 96.4% and selectivity of 95.1% (Table 2, Entry 13, Fig. S6). This indicated that the reaction has great potential to be scaled-up.

#### 3.3. Effects of hydrogen donor and the dosage of surfactant (CTAB)

Different alcohols were investigated as hydrogen sources in the MPV of FUR to FFA with Hf-H3IDC-T at 120 °C for 1 h, as are showed in Fig. 5a. An extremely low conversion of FUR was found when tert-butanol was regarded as H-donor. This is because there is no hydrogen atom next to the hydroxyl group in the tert-butanol, which provides a cyclic six-membered transition state with FUR at the acid-base site of the catalyst as a prerequisite for the hydrogen transfer process [47,48]. In contrast, both primary and secondary alcohols could treat as H-donors for the MPV of FUR. However, the secondary alcohols shown the higher FFA selectivity than primary alcohols (Fig. 5a) [48]. Moreover, the conversion of FUR decreased slightly with the increasing of carbon number in secondary alcohol. The lower FUR conversions in 2-butanol and 3-pentanol compared to 2-propanol were attributed to steric eff ;ect from the relative long carbon chain of 2-butanol and 3-pentanol, which prevents the substrate molecules from diffusing into the channel of Hf- $H_3$ IDC-T. We also found similar results from other references [10,44]. Hence, 2-propanol was the best H-donor and solvent for MPV reduction of aldehydes with Hf-H<sub>3</sub>IDC-T as the catalyst.

As it was well-known, the performance of the catalyst is highly depended on the structure. This work, the structure of catalysts (Hf- $H_3IDC$ ) are modified by adding different molar amount of CTAB. As shown in Fig. 5b, the conversion of FUR and the selectivity of FFA were both increased when the catalyst was treated with CTAB. The use of surfactant (CTAB) as structure-directing agents enhance surface areas, and facilitate the diffusion and mass transfer of the substrate, therefore improve the catalytic performance of Hf-H\_3IDC-T. It should be noted that the performance of catalysts was increased with the molar amount of CTAB used. However, when the molar amount of CTAB used being above 1.8 mmol, the catalytic performance did not change obviously.



**Fig. 5.** Influence of hydrogen donor on MPV reduction of FUR catalyzed by Hf-H<sub>3</sub>IDC-T. Reaction conditions:1 mmol FUR in 10 ml solvent, 100 mg Hf-H<sub>3</sub>IDC-T (21 mol% Hf), 120 °C, 1 h (a); Effect of the CTAB dosage used for Hf-H<sub>3</sub>IDC-T preparation on the conversion of FUR to FFA; Reaction conditions:1 mmol FUR in 10 ml 2-propanol, 100 mg catalyst, 120 °C, 1 h (b).

#### 3.4. Effects of the reaction time and temperature and reaction kinetics study

The effect of reaction time and temperature on FUR conversion to FFA with Hf-H<sub>3</sub>IDC-T was also investigated. As shown in Fig. 6a and b, the reaction temperature indicated obvious effect on the catalytic performance of Hf-H<sub>3</sub>IDC-T for the MPV reaction of FFA from 353 K to 393 K. When the reaction was maintained at a relatively low reaction temperature (353 K) for 30 min, both the FUR conversion (15.4%) and FFA selectivity (87.2%) were relatively low. As the reaction temperature increased to 413 K, the higher 85.1% conversion of FUR with 92.5% of FFA selectivity could be achieved. Meanwhile, the acetalization product of FUR and 2-propanol (furfural diisopropyl acetal) gradually decreased when the reaction temperature rose from 353 K to

393 K (Fig. S9a). This indicated that the equilibrium transition from the acetalization reaction to the MPV reduction could be improved by increasing the reaction temperature [49]. However, the FFA selectivity gradually declined due to the etherification of FFA with 2-propanol to 2-(isopropoxy) methyl furan when the reaction temperature was further increased to 413 K (Fig. S9b). Additionally, the reaction time also had a great influence on the MPV reduction. It could reach nearly full conversion of FUR (100%) and 99.2% of FFA selectivity when the reaction time was prolonged to 1 h at 393 K.

To further confirm the apparent activation energy ( $E_a$ ) of the FUR transfer hydrogenation, the kinetics were studied at temperatures ranging from 353 to 413 K. Since the amount of the catalyst was constant, and 2-propanol had an extremely high concentration compared to FUR,



Fig. 6. Effects of the reaction time and temperature for the conversion of FUR (a) and selectivity of FFA (b) over the Hf-H<sub>3</sub>IDC-T. First-order kinetic fit (c) for the MPV of FUR to FFA and the corresponding Arrhenius plots (d) for Hf-H<sub>3</sub>IDC-T. Reaction conditions: 1 mmol FUR in 10 ml 2-propanol, 100 mg Hf-H<sub>3</sub>IDC-T (21 mol% Hf).

the formula for the rate of FUR transfer hydrogenation could be expressed by the Eq. (1) Assuming that the reaction was the first-order reaction ( $\gamma = 1$ ),  $c_0$  was the initial concentration of FUR conversion, and  $c_t$  was the FUR concentration after the reaction time t, Eq. (1) could be expressed as Eqs. (2) or (3). Based on the results in Fig. 6c,  $\ln(c_0/c_t)$  had a linear relationship with t. The reaction rate constant (k) were determined from the corresponding slope of the linear relationship at each temperature. The value of  $E_a$  was calculated to be 50.89 kJ mol<sup>-1</sup> according to the Arrhenius equation and its variable equation (Eq. (4)), and the corresponding curve presented in Fig. 6d. This value was lower than that of Zr-LS for the same reaction in our previous work (52.25 kJ/mol) [49]. It is also comparable to the latest reported catalysts for FFA production from FUR which were summarized in Table S2.

There were mainly three reasons accounting for the excellent catalytic performance of Hf-H<sub>3</sub>IDC-T with high selectivity: (1) The Hf-H<sub>3</sub>IDC-T catalyst exhibited high activity, with conversion (100%) and selectivity (99.2%) in the MPV reduction for the conversion of FUR to FFA using 2-propanol as the hydrogen source under mild conditions compared to most solid catalyst. (2) Poisoning experiments authenticated that the catalyst with high content of basic sites was crucial to improve the catalytic activity for MPV reduction. Therefore, we chose 4,5-imidazoledicarboxylic acid with a basic group as an organic ligand. There are the amino groups on the imidazole ring structure in the catalyst Hf-H<sub>3</sub>IDC-T, and the interaction between the amino groups (as the base site) and the hydroxyl group can also activate the dissociation of 2-propanol into the corresponding alkoxide and proton, which is conducive to the MPV reaction. (3) BET experiments and catalytic experiments indicated that we introduced surfactants (CTAB) as template agents to modify metal organic structures. It can enhance the binding of carboxylate to Hf and enlarge surface areas, and facilitate the diffusion and mass transfer of the substrate, therefore improve the catalytic performance. From the viewpoint of the reaction conditions and the design for catalyst preparation, the Hf-H<sub>3</sub>IDC-T catalyst had obvious advantages and showed excellent catalytic activity.

 $\mathbf{r} = -\mathbf{d}\mathbf{c}_{t} / \mathbf{d}\mathbf{t} = \mathbf{k} \cdot [\mathbf{F}\mathbf{U}\mathbf{R}]^{\gamma}, \ \mathbf{k} = \mathbf{k}_{0} \cdot [\mathbf{C}\mathbf{a}\mathbf{t}]^{\alpha} \cdot [2 \cdot \mathbf{p}\mathbf{r}\mathbf{o}\mathbf{p}\mathbf{a}\mathbf{n}\mathbf{o}\mathbf{l}]^{\beta}$ (1)

 $r = -dc_t/dt = k$ [FUR]

 $\ln(c_t/c_0) = -k \cdot t$ 

$$E_a = (lnA - lnk) \cdot RT$$
(4)

# 3.5. Effects of the catalyst dosage, heterogeneity and recyclability for the MPV of FUR to FFA

The effect of the dosages of Hf-H<sub>3</sub>IDC-T catalyst on the reaction activity was researched at 120 °C for 1 h. As shown in Fig. 7a, the FUR conversion and FFA selectivity increased rapidly with an increase in Hf-

 $\rm H_3IDC$ -T dosages (25–100 mg). It was found that the hemi-acetalization of FUR with 2-propanol is the main reaction pathway for the consumption of substrates [50], thus resulting in low to moderate FFA selectivity at relatively high FUR conversions for relatively low catalyst dosages (25–75 mg). Although a large dosage of 150 mg of Hf-H\_3IDC-T could promote complete conversion of FUR (Fig. 7a) without the production of hemiacetal by-products, the downstream product (IPMA) was formed by the etherification of FFA and 2-propanol by excessive acid and base sites. Experimental results proved that the 100 mg (21 mol% Hf) would be an appropriate dosage under this reaction condition.

To investigate the catalytic behavior of Hf-H<sub>3</sub>IDC-T in MPV reaction from FUR to FFA, two parallel experiments were performed using a solid catalyst at an optimal dosage of 100 mg, with or without separation of the catalyst from the thermal reaction mixture after 30 min in 2propanol at 120 °C (Fig. 7b). After stirring for an additional 1.5 h under the same conditions, Hf-H<sub>3</sub>IDC-T continued to smoothly catalyze the conversion of FUR to FFA, while almost no reaction was observed for the reaction system with the filtered catalyst. Inductively coupled plasma optical emission spectroscopy (ICP-OES) indicated that both filtrates contained very low Hf species, clearly proved the heterogeneity of Hf-H<sub>3</sub>IDC-T catalysis in the MPV reaction.

The recyclability of solid catalysts is one of the most important characteristics for evaluating its potential applications in industrial production [49,51]. In six consecutive cycles of experiments, Hf-H<sub>3</sub>IDC-T catalyst could be simply recovered by washing with DMF and ethanol, and remained capable of producing FFA in yields of 91-99% at almost complete FUR conversion under the same reaction conditions (Fig. 8). In addition, the concentration of Hf immersed in the reaction mixture was extremely low as detected by ICP-OES. These results confirmed the high durability of Hf-H<sub>3</sub>IDC-T for the MPV of FUR to FFA. The structural changes in Hf-H<sub>3</sub>IDC-T before and after MPV for sixth cycle was characterized by SEM (Fig. S7), FT-IR, XRD, TG, N<sub>2</sub> adsorption-desorption, and NH<sub>3</sub>/CO<sub>2</sub>-TPD (Fig. S8). There was only a slight change of the structural and textural for the used catalysts, (BET surface area: 153.5 vs 133.77  $m^2/g$ ), which could be attributed to the adsorption of organic substances into the cavities of Hf-H<sub>3</sub>IDC-T during the reaction [30]. The acidic/basic properties (acidity: 1.41 vs 1.38 mmol/g; basicity: 0.78 vs 0.72 mmol/g; base/acid ratio: 0.55 vs 0.52) of the used Hf-H<sub>3</sub>IDC-T catalysts had no significant change after six consecutive cycles. It was worth noting that the slight weight loss of the recovered Hf-H<sub>3</sub>IDC-T catalyst compared to the fresh catalyst indicated a small adsorption of organic matter, which might partially hinder the entry of the active site, resulting in a marginal decrease in catalytic activity [49].



(2)

(3)

Fig. 7. Effect of Hf-H<sub>3</sub>IDC-T dosage on conversion of FUR to FFA (a); and time-yield plots for MPV reaction of FUR with Hf-H<sub>3</sub>IDC-T (21 mol% Hf) or removing Hf-H<sub>3</sub>IDC-T after 0.5 h (b). Reaction conditions: 1 mmol FUR, 10 ml 2-propanol, 120 °C, and 1 h.



Fig. 8. Recyclability of Hf-H<sub>3</sub>IDC-T from FUR to FFA (Reaction conditions: 1 mmol FUR, 100 mg Hf-H<sub>3</sub>IDC-T (21 mol% Hf), 10 ml 2-propanol, 120  $^{\circ}$ C, and 1 h).



**Fig. 9.** Reaction kinetics study from FUR to FFA hydrogenation in cosolvent tert-butanol and isotopic 2-propanol-d8 with a molar ratio of 3:1 using <sup>1</sup>H NMR; other unmarked major bonds in <sup>1</sup>H NMR spectra belonged to the solvent, and in situ-formed acetone with constant chemical shifts.

# 3.6. Reaction mechanism study and MPV reduction of other carbonyl compounds

To clarify the reaction mechanism, the MPV reaction from FUR to FFA in the cosolvent tert-butanol and 2-propanol-d8 with a molar ratio of 3:1 was monitored by ex situ NMR spectroscopy at different reaction times. As shown in <sup>1</sup>H NMR spectrum (Fig. 9), the protons in the FUR (1a) aldehyde group (–CHO) gradually disappeared as the amount of deuterium (D) gradually increased from 2-propanol-d8 to its C=O bond, which resulting in the formation of a  $-CH_2-$  moiety in FFA (1b). However, due to the non-selective addition of D, it was not clear whether the reaction route was the direct hydrogen transfer or the metal hydride route. In order to clearly distinguish the two hydrogenation routes, tert-butanol cannot be used as an H-donor due to the

absence of the  $\beta$ -H, but it can exchange most D of -OD group in the isotopic 2-propanol with -OH and replace the D on the metal surface with H (Scheme S4). By GC-MS analysis, an additional 1 amu (m/ z = 99) of the molecular ion peak of FFA was detected, whereas D could not be used for the metal hydride route, thus confirming that the reaction undergoes direct hydrogen transfer with the Hf-H<sub>3</sub>IDC-T (Scheme S4, Fig. S10). As noted above, the Lewis acid-base coupling sites and the Brønsted acid sites were critical for the MPV reaction from the carbonyl compounds to the corresponding alcohols. Fig. 10 shown the rational reaction mechanism for Hf-H<sub>3</sub>IDC-T catalytic reduction of carbonyl compounds. Firstly, 2-propanol was adsorbed on Hf-H<sub>3</sub>IDC-T, resulting in its dissociation to alkoxide and hydrogen by the acid-basic coupled sites  $(Hf^{4+} - O^{2-})$ . Meanwhile, the deprotonation of 2-propanol was increased by the basic  $O^{2-}$  atoms and amino groups. The carbonyl group in the substrate molecules was activated by Lewis acidic Hf<sup>4+</sup> species. Next, the six-membered ring transition state was formed with carbonyl groups and 2-propanol, leading to direct hydride transfer via β-H elimination and yielding corresponding alcohols and acetones [31,49].

In the process of FUR conversion to produce FFA, Hf-H<sub>3</sub>IDC-T catalyst showed excellent catalytic performance, and the target product with higher yield was obtained. Inspired by this reaction, we researched the probability of the MPV reactions of other carbonyl compounds using the Hf-H<sub>3</sub>IDC-T catalyst (Table 3). All chosen aldehydes could be efficiently catalyzed by Hf-H<sub>3</sub>IDC-T to produce their corresponding alcohols in high yields. For example, the developed Hf-H<sub>3</sub>IDC-T exhibited superior catalytic performance for 5-methylfurfural and 5-hydroxymethylfurfural, resulting in high conversions (more than 90%) and high selectivities (96% and 98%, Table 3, entry 3-4). In addition, Hf-H<sub>3</sub>IDC-T was also widely applicable to MPV of other bio-derived aldehydes, the conversions of bio-derived aldehydes exceeding 95%, and the selectivity to the corresponding alcohol also exceeding 95% (Table 3, entry 5–8). These corresponding alcohols are important chemical intermediates widely used in the preparation of pharmaceuticals, perfumes and cosmetics in the industries. In addition to testing catalytic biomass-derived chemicals, other commercial aldehydes and ketones were tested to assess their catalytic potential. As expected, the aliphatic and aromatic aldehydes could be effectively hydrogenated to corresponding alcohols under the moderate conditions (100 °C) in 2 h (Table 3, entry 9-10). The wide substrate scope indicates that the Hf-H<sub>3</sub>IDC-T catalyst was a highly versatile catalyst for MPV reduction of both biomass-based platform compounds and other commercial aldehydes to alcohols.

### 4. Conclusions

In summary, the porous heterogeneous nitrogen-containing acidbase bifunctional catalyst Hf-H<sub>3</sub>IDC-T hybrids were synthesized by a facile surfactant-assisted route. These catalysts possessed high surface area and the strong Lewis acid-base couple sites  $(Hf^{4+} - O^{2-})/mod$ erate basic sites (the inherent amino groups), which exhibited excellent catalyst activity, with conversion of 100%) and selectivity of 99% in the MPV reduction for the conversion of FUR to FFA. There are two special points about the catalyst: (1) The interaction between the amino groups on the imidazole ring (as basic sites) and the hydroxyl group can activate the dissociation of hydrogen source into the corresponding alkoxide and proton, which is conducive to the MPV reaction. (2) The surfactant (CTAB) as template agents for preparation of Hf-H<sub>3</sub>IDC-T can enhance the binding of carboxylate to Hf and enlarge surface areas, and facilitate the diffusion and mass transfer of the substrate, therefore improve the catalytic performance of Hf-H<sub>3</sub>IDC-T. The E<sub>a</sub> of the MPV reaction of FUR was as low as 50.89 kJ/mol, indicating that the MPV reaction is a high reaction rate. The direct hydrogen transfer from  $\alpha$ -C of 2-propanol to the  $\alpha$ -C of FUR was verified to be the dominant reaction pathway and the rate-determining step. In addition, the as-prepared Hf-H<sub>3</sub>IDC-T hybrid has high thermal stability and chemical

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Fig. 10. Plausible reaction pathway involved in the MPV reduction of FUR to FFA over Hf-H<sub>3</sub>IDC-T.

Table 3	
MPV of different biomass-derived carbonyl compounds to alcoho	ols <sup>a</sup> .

Entry	Substrate	Product	Temperature (°C)	Time (h)	Conversion (%) <sup>b</sup>	Yield (%) <sup>b</sup>	Selectivity (%) $^{\rm b}$
1	~ [)	HO	120	1	100	99	99
2	$\sim$	HO	100	3	97	92	95
3			100	4	97	93	96
4	€ C>OH	и Сулон	100	4	94	92	98
5	$\langle \cdot \rangle$	HO HO	120	4	95	91	95
6		HO	120	3	98	94	97
7	Ž	$\sim$	120	4	95	90	95
8		HO HO	120	4	95	91	96
9	° on	но	100	2	96	93	97
10	°√⊖`	HO	100	2	98	96	98

 $^{\rm a}\,$  Reaction conditions: 1 mmol substrate; 0.1 g Hf-H\_3IDC-T and 10 ml of 2-propanol.

<sup>b</sup> Conversion, yield and Selectivity were quantified using GC, determined by GC analysis using an internal standard.

stability, and can maintain excellent catalytic performance after six consecutive cycles of reaction. Moreover,  $Hf-H_3IDC-T$  as efficient catalyst for MPV reaction can be extrapolated to other similar lignocellulose-derived substrates for upgrading biomass.

#### **Declaration of Competing Interest**

The authors declare no competing financial interest.

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### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.110611.

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