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Introduction

As we all know, the survival and development of mankind cannot be separated from energy. With the rapid growth of the world's energy demand, conventional energy such as coal, oil and natural gas will eventually be exhausted. Therefore, the search for renewable resources to provide fuels and chemicals has received widespread attention.^{1,2} Among many renewable resources, only biomass can provide a steady stream of fuels and chemicals.^{3,4} As a result, much effort has been devoted to the development of suitable catalytic processes to produce a variety of platforms and valuable chemicals from sugars or directly from lignocellulose.⁵⁻¹⁰ Among the chemicals derived from biomass, carboxides (furfural (FUR),^{11,12} 5-hydroxy-methylfurfural (5-HMF),¹³⁻¹⁶ levulinic acid (LA) or its esters,^{17,18} ketone compounds,¹⁹ etc.) are an important class of chemicals with broad applications, because they can be further converted into more valuable chemicals such as furfuryl alcohol (FFA), 20,21 γ -valerolactone (γ -GVL), $^{22-24}$ 2,5-bia (hydroxymethyl)fural (BHMF)²⁵⁻²⁷ and so on.

Simple basic zirconium carbonate: low temperature catalysis for hydrogen transfer of biomass-derived carboxides*

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A simple basic zirconium carbonate (BZC), which can be produced on a large scale in industry, was studied for hydrogen transfer of biomass-derived carboxides and exhibited excellent catalytic properties at low temperatures, especially for the conversion of furfural (FUR) to furfuryl alcohol (FFA). With the catalyst, the reduction reaction of FUR was efficiently performed at low temperatures (below 100 °C) and an FFA yield of 98.66% was obtained even at room temperature. When the temperature reached 180 °C, the yield of FFA quickly reached 90.29% within 15 minutes. During the reaction, the changes of the functional groups of the reactants and products were monitored by in situ ATR-IR spectroscopy in real time, which provided a basis for the proposed reaction mechanism. Further, the ATR-IR spectroscopy and XPS results of the different catalysts showed that BZC has the strongest acidity among all the comparative catalysts, which is consistent with its best catalytic performance. In addition, reaction kinetics were also studied.

> Different approaches and catalysts are used in the hydrogenation of biomass-derived carboxides to achieve their conversion to valuable chemicals.²⁸⁻³¹ An efficient strategy for the hydrogenation of the carboxides has been developed using molecular hydrogen (H_2) as a hydrogen source in the presence of zero-valent precious or nonprecious metal-based catalysts (such as: Pd, ^{32,33} Ru, ^{34,35} Rh, ³⁶ Pt, ^{37,38} Re, ³⁹ Ni, ^{40,41} Co, ^{42,43} Cu^{44,45} and so on). However, the safety of storage and transportation of H₂, the hardness of the reaction conditions (high temperature and pressure), encourage us to explore alternative synthetic methods. The Meerwein-Ponndorf-Verley (MPV) reaction, one of the catalytic transfer hydrogenations (CTH) reactions, is an efficient synthetic route for the selective reduction of carboxides using secondary alcohols instead of hydrogen as a source of hydrogen, 46-48 and different types of catalysts are used in the reaction, including metal alkoxides,⁴⁹⁻⁵¹ metal oxides or hydroxides,^{52,53} metal complexes,^{4,54} various zeolites,^{55,56} etc. Among these catalysts, zirconium-based catalysts are widely applied due to their acidbase characteristics (Zr^{4+} and O^{2-} , respectively) which play a key role in the MPV reduction,⁵⁷ such as ZrO₂, Zr(OH)₄, zirconium complexes, Zr-containing zeolites, etc.4,52,53,55,58 And an overview on the hydrogen transfer of biomass-derived carboxides using various catalysts in recent years is provided in Table S1.[†] Zhang et al., Yang et al., etc. found that above 150 °C, metal oxides, metal hydroxides and metals, etc. (ZrO₂, Zr(OH)₄, Al-Zr oxides, Al₂O₃, Ru/C, γ-Fe₂O₃@HAP, etc.) have high activity for the hydrogen transfer of biomass-derived

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carboxides (FUR, HMF, LA or it esters).^{48,59–63} Han *et al.*, Yang *et al.*, *etc.* explored the catalytic performance of zirconium complexes (Zr-PhyA, ZrPN, *etc.*) for the reaction at a lower reaction temperature (Yang *et al.*: 90% yield of FFA, 100 °C, 12 h.) or a shorter reaction time (Han *et al.*: 93.3% yield of FFA, 100 °C, 2 h.).^{64–66} Liu *et al.* researched that Zr-HAs has a high catalytic activity for the hydrogen transfer of FUR to FFA at 50–70 °C (96.9% yield of FFA), which is the lowest temperature for reducing FUR.⁶⁷

A simple basic zirconium carbonate (BZC) catalyst conforming to the concept of green sustainable development is prepared in aqueous solution by adjustment of pH and room temperature agitation without energy input (Scheme S1[†]). As a vital commercial solid base, it is used in the preparation of zirconia and zirconium-based catalyst carrier,68,69 and is also widely applied in textile, paint, paper and other industries. Here, the commercialized BZC was applied to the hydrogen transfer of biomass-derived carboxides at low temperatures, which has better catalytic performance than catalysts such as ZrO₂ and Zr(OH)₄, etc., even is superior to most zirconium complexes. With the catalyst, the reduction reaction of FUR was efficiently performed at very low temperatures (below 100 °C). When the temperature is 180° C, FUR is quickly and almost completely converted to FFA in a very short time (15 min). Further, with in situ ATR-IR and ATR-IR tests, more information about the reaction process was acquired by monitoring changes in functional groups in the reaction and surface chemistry of the catalyst. In addition, reaction kinetics and a possible mechanism were also studied.

Experimental section

Materials

Furfural (FUR), furfuryl alcohol (FFA), levulinate esters, γ -valerolactone, 5-hydroxymethylfurfural (5-HMF), 2,5-bis (hydroxymethyl)furan, cyclohexanone, cyclohexanol, citral, citrate, cinnamaldehyde and cinnamyl alcohol were purchased from TCI Chemical Reagent Company (Shanghai, China). Basic zirconium carbonate, basic nickel carbonate and p-(+)-xylose were purchased from Aladdin Industrial Corporation. Zr(OH)₄, ZrO₂, basic copper carbonate, Mg(NO₃)₂·6H₂O, Zn(NO₃)₂·6H₂O, Na₂CO₃, benzoic acid, pyridine, isopropanol, NaCl, tetrahydrofuran (THF), and AlCl₃·6H₂O were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). All chemicals were used without further purification.

Hydrogen transfer reaction of biomass-derived carboxides and sample analysis

Hydrogen transfer reaction of biomass-derived carboxides was carried out in a stainless-steel autoclave (40 mL) with a magnetic stirrer which was heated in a temperature-controlled oil bath. Typically, FUR (0.67 mmol), isopropanol (2-PrOH) (20 mL), and catalyst (0.1 g) were charged into the reactor which was then sealed and heated to a designed temperature



Fig. 1 Schematic diagram of an autoclave with in situ ATR-IR monitoring.

for an intended reaction time. After the reaction, the autoclave was taken out and cooled to ambient temperature. The hydrogen transfer reactions of xylose-derived FUR and other carboxides were also carried out under the same conditions. Besides, a scaled-up hydrogen transfer experiment of FUR was performed in 300 ml stainless steel autoclave (JULABO) with heating jacket (Fig. 1). Typically, FUR (15 mL), 2-PrOH (135 mL), and catalyst (1 g) were charged into the autoclave, then sealed and heated to 120 °C for an intended reaction time.

Identification of liquid products in the reaction mixture was achieved by the TRACE ISQ GC-MS (Thermo Scientific Co, TR-WAX-MS column 30.0 m × 320 μ m × 0.25 μ m). The temperature program started at 60 °C for 1 min, then increased from 60 °C to 230 °C at a rate of 15 °C min⁻¹ and held for 2 min.

Catalyst characterization

X-ray diffraction (XRD) was carried out via a Rigaku D/max-2550 diffractometer using Cu-Kα radiation. The wavelength of X-ray source was set at 0.154 nm, and the step width was 0.02° with a scanning speed of 6° per minute between two thetas of 10° and 80°. Fourier transform infrared (FT-IR) spectra were recorded between 400 to 4000 cm⁻¹ by using Bruker VERTEXV 80 V spectrometer. The NH₃-IR and HCOOH-IR spectra were recorded on a Bruker 80 v with a range of 600-4000 cm⁻¹ for the MCT detector (detailed information on ESI[†]). The thermogravimetric (TG) analysis was performed using a thermogravimetric analysis system (TG: PerkinElmer Instruments) under air atmosphere at a heating rate of 10 $^{\circ}$ C min⁻¹. Brunauer-Emmett-Teller (BET) surface area was measured on an Asap 2420 surface adsorption apparatus. The elemental compositions of catalysts were determined by inductively coupled plasma (ICP) on an Optima 3300 DV (PerkinElmer Instruments). X-ray photoelectron spectroscopy (XPS) measurements were performed using ESCALAB250 photoelectron spectrometer equipped with a charge neutralizer and an Mg Kα X-ray source. The morphology of the samples was investigated by transmission electron microscopy (TEM; Tecnai F20) and scanning electron microscopy (SEM; Jeol JSM-6700F).

In situ ATR-IR measurements and ATR-IR measurements

The *in situ* ATR-IR measurements were carried out on a VERTEXV 80 V FT-IR spectrometer (Bruker) equipped with a liquid nitrogen-cooled MCT detector. The equipment is an *in situ* mid-infrared based system that monitors the reactions in real time for further reaction information. And it is connected to a 300 ml stainless steel autoclave (JULABO) for catalytic reaction through an optical fiber with a high temperature diamond ATR probe (Bruker). From the Fig. 1, the fiber optic probe is placed near the magnet at the bottom of the autoclave for better monitoring of the reaction.

Since the concentration of FUR in the solution was too low, its infrared peak was masked by the peak of 2-PrOH. Typically, FUR (60 mmol), 2-PrOH (150 mL), and catalyst (1 g) were charged into the autoclave and then stirred with 500 rpm at 120 °C. During the reaction, ATR-IR spectra were recorded every 1 min for 2 h with averaging 32 scans at the resolution of 2 cm⁻¹ in the 3500–600 cm⁻¹. And air was used as the background for the test.

The surface chemistry of zirconium-based catalyst was also studied with ATR-IR spectroscopy on the VERTEXV 80 V FT-IR spectrometer (Bruker) equipped with a Platinum-ATR A225/Q accessory (Bruker).

Typically, 6 mol FUR and 0.1 g BZC catalyst were mixed for 10 min in ultrasound and then placed in a 60 °C water bath for 30 min. One or two drops of the suspension were taken out and placed on the diamond of the accessory for testing. During the measurements, ATR-IR spectra were collected by averaging 64 scans at the resolution of 2 cm⁻¹ in the 4000–390 cm⁻¹. And air was also used as the background for the test.

Results and discussion

Characterization of catalysts

XRD patterns of BZC, Zr(OH)₄ and ZrO₂ are given in Fig. 2a. It can be seen that both BZC and Zr(OH)₄ are amorphous. For ZrO₂, the XRD pattern shows the characteristic peaks of ZrO₂ $(2\theta = 30.2^{\circ}, 34.8^{\circ}, 35.2^{\circ}, 50.3^{\circ}, 59.6^{\circ}, 60.2^{\circ}, 62.9^{\circ} \text{ and } 74.5^{\circ}.$ PDF, 50-1089). In addition, FT-IR is used to analyse the characteristic absorption peaks of these samples. From the Fig. 2b, for the BZC, the typical band at 3252 cm⁻¹ is ascribed to stretching modes of O-H with wide absorbance. The peaks at 1538 and 1385 cm⁻¹ are assigned the asymmetric stretching vibration of CO_3^{2-} . The peaks at 1066 and 847 cm⁻¹ can be attributed to the symmetric stretching and out of plane bending vibrations of CO_3^{2-} , respectively. And the bands at 664 and 473 cm⁻¹ are attributed to the stretching vibration of Zr-O. For the $Zr(OH)_4$, it has the same stretching modes of O-H (3404 cm⁻¹) and stretching vibration of Zr-O (664 and 473 cm^{-1}) as BZC. And the peaks at 1580 cm⁻¹ and 1330 cm⁻¹ corresponding to O-H bending vibration of water and Zr-OH



Fig. 2 The characterization of different Zr-based catalysts. XRD patterns (a). FT-IR spectra (b). N₂ adsorption–desorption isotherm and pore size distribution of the BZC catalyst (c). XPS spectra of Zr 3d (d).

can be perceived, respectively. For ZrO_2 , the bands at 664 and 473 cm⁻¹ belong to the stretching vibration of Zr–O.

The N₂ adsorption-desorption isotherm and pore size distribution reveal that the commercialized BZC is micro mesopores, and the surface area and average pore diameter are 202.4 m^2 g⁻¹ and 2.1 nm, respectively (Fig. 2c and Table 1). The surface area and pore volume for the BZC (202.4 m² g⁻¹, 0.11 cm³ g⁻¹) and Zr(OH)₄ (260.9 m² g⁻¹, 0.19 cm³ g⁻¹) are significantly higher than ZrO_2 (39.2 m² g⁻¹, 0.10 cm³ g⁻¹), but the pore size is smaller than it. From the TG analysis (Fig. S2[†]), due to the desorption of water, the catalyst has a lower weight loss of about 15% before 170 °C, which manifests an excellent stability on the reaction temperatures (below 140 °C).67 And the weight loss of the catalyst from 200 °C to 500 °C is attributed to the decomposition of BZC. Therefore, the CO2-TPD and NH3-TPD tests could not be carried out to achieve the analysis of acid/base strength and amount of the catalysts. However, some information about the Lewis acidity can be obtained by XPS analysis (Fig. 2d). The result shows that the binding energy values of Zr 3d in BZC are higher than that of Zr(OH)₄ and ZrO₂, implying that the highest positive charge exists on the Zr atoms in BZC, which results in the strongest Lewis acidity of BZC, in good accordance with the best catalytic activity of the BZC catalyst observation. In addition, three samples are further investigated for acid-base sites by the tests of the NH₃-IR and HCOOH-IR spectroscopy (Fig. 3). For the NH_3 -IR spectrum (Fig. 3a and b), the peaks at 1620 cm⁻¹ and 3332 cm⁻¹ represent the Lewis acid sites, while the peak at 1460 cm⁻¹ represents the Brønsted acid sites, which is similar to that reported in the literature.^{70,71} Obviously, no peak at 1460 cm⁻¹ testifies that no Brønsted acid sites exist in the catalysts. For the peaks of Lewis acid sites, there is a tendency that the peak intensity of BZC is greater than $Zr(OH)_4$ and ZrO_2 ,

Table 1 Physicochemical properties of catalyst

Entry	Catalyst	BET surface area $(m^2 g^{-1})$	Pore volume $(cm^3 g^{-1})$	Pore size (nm)	Zr content ^a (wt%)	Zr amount of 0.1 g catalyst ^{b} (mmol)
1	BZC	202.4	0.11	2.2	32.6	0.357
2	$Zr(OH)_4$	260.9	0.19	2.9	38.9	0.426
3	ZrO_2	39.2	0.10	11.2	72.5	0.794

^a The content of Zr was determined by ICP. ^b It is calculated by ICP results.



Fig. 3 $\,$ NH_3-IR (a and b) and HCOOH-IR (c and d) spectra of different Zr-based catalysts.

indicating that BZC has more Lewis acid sites. From HCOOH-IR spectrum (Fig. 3c), the peak at 1368 cm⁻¹ is ascribed to the symmetric stretching vibration of CO O⁻. While the peak at 1562 cm⁻¹ and its shoulders were divided into multi-peaks displayed in Fig. 3d. Among the multi-peaks, the peaks at 1565 cm⁻¹ and 1653 cm⁻¹ are attributed to the stretching vibration and bending vibration of C-H, respectively, while the peaks at 1615 cm⁻¹ and 1716 cm⁻¹ are respectively assigned to strong basic and weak basic sites on the catalyst surface,⁷²⁻⁷⁴ which demonstrates that the basic sites of the BZC sample is the strongest among the three samples. Therefore, the conclusion is drawn that the BZC catalyst has the most acid-base sites than $Zr(OH)_4$ and ZrO_2 , which makes it have the best catalytic activity in the hydrogen transfer reactions of biomass-derived carboxides.

SEM and TEM images of BZC demonstrate that the BZC is composed of particles with no uniform shape (Fig. 4 and S3†). Elemental mapping reveals a homogeneous distribution of Zr, O and C elements on the surface of the BZC (Fig. 4a). EDS analysis by selecting two points from the BZC sample shows that there are four elements of Zr, O, C and Si (caused by silica slice for dispersing catalyst) in the catalysts, and the mass percentage and atomic percentage of each element at two points are basically the same, which also demonstrates the uniformity of the element distribution of the catalyst (Fig. 4b). Among



Fig. 4 Elemental mapping images (a) and SEM-EDS data (b) of the BZC catalyst.

them, the mass percentage of Zr content is approximately the same as the result of ICP test (Table 1).

ATR-IR studies of FUR absorbed on different catalyst at 60 °C

In order to get detailed information about the surface-bonding state of FUR adsorbed on catalysts, ATR-IR spectroscopy was used to investigate the interactions between FUR and the different Zr-based catalysts (Fig. 5). Compared with the IR spectrum of FUR (Fig. 5a), no peak position change occurs in the different Zr-based catalysts adsorbing FUR except the peak near 1668 cm⁻¹. The changed peak is assigned to the stretching vibration of the C=O bond (FUR) has undergone a significant red shift from 1668 cm⁻¹ to 1666 cm⁻¹ after mixed with BZC (Fig. 5b). The result indicates a stronger interaction exists between the BZC and the C=O band of FUR, compared with Zr(OH)₄ and ZrO₂. According to the relevant literature,^{4,47,52} C=O is activated by the Lewis acid (Zr⁴⁺) to achieve the purpose of hydrogen transfer reaction. Thus, the red shift of



Fig. 5 ATR-IR spectra of FUR adsorbed on different Zr-based catalysts in the complete investigated region (a) and 1625-1705 cm⁻¹ region (b).

the C==O peak position is caused by Zr^{4+} , and the red shift induced by BZC is the largest, proving that it has the strongest or most Lewis acidity among the three catalysts. This allows the BZC catalyst to exhibit the best catalytic performance for hydrogen transfer of biomass-derived carboxides and is consistent with the results of XPS and NH₃-IR. In addition, influenced by the electronic effect of Zr^{4+} on the C==O group, the vibrational peak of the C–H bond on the aldehyde group disappears, further indicating that the Zr^{4+} (Lewis acid) can activate the C==O group (Fig. S4⁺).

In situ ATR-IR studies of the hydrogen transfer of FUR

To gain insight into the reaction mechanism, *in situ* ATR-IR was used to monitor the reaction progress. Under normal reaction conditions (5.03 mmol FUR, 150 mL 2-PrOH, 0.75 g catalyst), due to the excess of 2-PrOH, no significant peak position change is observed in the IR spectrum of 600–3500 cm⁻¹ at 80 °C for 5 h (Fig. S5†).

The progress of the reaction is continuously monitored after enlarging the amount of FUR (60 mmol FUR, 150 mL 2-PrOH, 1 g catalyst) through infrared spectroscopy at 120° C for 2 h. At this time, although isopropanol is in excess, changes in the characteristic peaks of the functional groups of FUR, FFA and acetone (CP) can still be observed in the range of 600–3500 cm⁻¹ (Fig. 6a). For the hydrogen transfer reaction of FUR, it is most important to monitor the changes of carbonyl functional groups of FUR and CP. From Fig. 6b, that the intensity of the absorption peak at 1675 cm⁻¹ corresponding to the stretching vibration of C=O of FUR decreases with time until it disappears, suggests that the aldehyde group of FUR is gradually reduced in the reaction. The two absorption peaks at 1715 and 1224 cm⁻¹ are attributed to the stretching vibration and bending vibration of C=O of CP, respectively, and their

intensity is gradually increased, illustrating the formation of CP. As a result, it is found that in the hydrogen transfer reaction, the reduced reaction of FUR proceeds simultaneously with the formation of CP. Further analysis of Fig. 6c, the peak at 1367 cm⁻¹ is attributed to the C-H bending vibration of the aldehyde group, and its intensity gradually decreases with time due to the reduction of the aldehyde group. Meanwhile, since the aldehyde group is reduced, the effect of the conjugation effect of C=O bond on the C=C bond of furan ring disappears, which causes a change in the stretching vibration peak of the C=C bond, including a weakening of the peak intensity at 1569 cm⁻¹ (C=C double bond stretching vibration of FUR), and an enhancement of the peak intensity at 1505 cm^{-1} (C=C double bond stretching vibration of FFA). From Fig. 6d, the enhancement of the bending vibration of the O-H (731 cm⁻¹) and the stretching vibration of the C-O (hydroxyl) (1011 cm^{-1}) belonging to the FFA is also observed. Similarly, the bending vibration of the C-H in the olefin of FUR/FFA also shifts from 758 to 742 cm⁻¹ due to the effect of the conjugation effect. In summary, the monitoring of the above reaction process helps us understand the reaction mechanism.

Catalytic activity of the various catalysts for hydrogen transfer of FUR

In our research, FUR, representative of biomass-derived carboxides, was used as a model reactant to examine catalytic activity of various catalysts for the production of FFA through the hydrogen transfer reaction with 2-PrOH as a hydrogen donor (Table 2). The reaction did not occur without catalyst (Table 2, entry 1). Among the tested catalysts, BZC showed the highest activity with a FFA yield of 96.67% at 80 °C with 5 h (Table 2, entry 2). For comparison, ZrO_2 only displayed a rela-



Fig. 6 In situ ATR-IR spectra during the hydrogen transfer of FUR in 2-PrOH over the BZC at 120 °C (FUR (60 mmol), 2-PrOH (150 mL) and catalyst (1 g)). The complete investigated region (a). Partial magnification of the investigated region (b, c and d).

Table 2 Hydrogen transfer reaction of FUR to FFA with isopropanol as solvent over various	catalysts
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		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	OH Catalyst	T, t OH + OH			
Entry	Catalyst	Conversion (%)	Yield (%)	Selectivity (%)	Formation rate ^{<i>a</i>} (mmol $g^{-1} h^{-1}$ )	$\begin{array}{c} \text{TOF}^b\\ (h^{-1}) \end{array}$	
1 ^c	0	<1	0	0	0	0	
2	BZC	97.69	96.67	98.95	1.29	0.366	
3	$ZrO_2$	4.15	3.36	80.96	0.04	0.007	
4	$Zr(OH)_4$	65.04	63.65	97.86	0.85	0.204	
$5^d$	BZC	71.99	68.65	95.36	0.92	0.270	
6 ^e	BZC	46.97	31.25	66.53	0.42	0.176	
$7^{f}$	BMC-Mg	4.94	2.14	43.31	0.03	_	
$8^g$	BZC-Zn	3.35	1.12	33.53	0.02	_	
$9^h$	BNC-Ni	28.40	23.08	81.26	0.3	_	
$10^{i}$	BCC-Cu	5.45	2.24	41.10	0.03	—	

Conditions: Catalyst (0.1 g), FUR (0.67 mmol), 2-PrOH (20 mL), 80 °C, 5 h. ^{*a*} The FFA formation rate is defined as mmol (formed FFA)/[g (catalyst amount) × h (time)]. ^{*b*} TOF is defined as mmol (converted FUR)/[mmol (total metal is measured by ICP) × h (time)]. ^{*c*} Reaction without any catalyst. ^{*d*} 5 mmol of pyridine was added additionally. ^{*e*} 5 mmol of benzoic acid was added additionally. ^{*f*} BMC-Mg is basic magnesium carbonate. ^{*g*} BZC-Zn is basic zinc carbonate. ^{*h*} BZC-Ni is basic nickel carbonate. ^{*i*} BZC-Cu is basic copper carbonate.

tively poor activity with a FFA yield of 3.36% (Table 2, entry 3), and Zr(OH)₄ also exhibited a low activity with a FFA yield of 63.65% (Table 2, entry 4), which are consistent with the ATR-IR studies, the XPS analysis, NH3-IR and HCOOH-IR of the Zr-based catalysts (Fig. 2d, 5 and 3). In order to further confirm the effect of the acid-base sites on the reaction, pyridine/benzoic acid was added to the reaction system to poison the acid/base sites of the catalyst, respectively (Table 2, entries 5 and 6). And the results demonstrated that the yield of FFA decreased from 96.67% to 68.65%/31.25% after addition of pyridine/benzoic acid, which directly proved that the acid-base sites of the catalyst had a great influence on the catalytic activity. Other basic carbonates (BMC-Mg, BZC-Zn, BNC-Ni and BCC-Cu) showed a similar lower activity (2.14%, 1.12%, 23.08% and 2.24% yields, respectively) under the same reaction conditions (Table 2, entries 7-10). In addition, the FFA formation rate and TOF value of the different catalysts were calculated. Moreover, the same reactions were carried out with oxides and hydroxides of magnesium, nickel, copper and zinc as catalysts (Table S2[†]), and the results indicate that among the three types of compounds (oxides, hydroxides and basic carbonates), the basic carbonates have the best catalytic performance.

# Effect of reaction temperature and time on the performance of BZC catalyst and reaction kinetics study

The influence of reaction temperature and time on the performance of BZC catalyst was studied, and all experiments were conducted at different temperatures from room temperature (about 22 °C) to 180 °C within a certain period of time (Fig. 7). To our delight, the BZC catalyst exhibited superior catalytic performance at room temperature (Fig. 7a), and the yield was more than 90% over 5 d while maintaining a very high selectivity (close to 100%). In order to verify this result, we carried out a reaction without any catalyst at room temperature for 7 d, no FFA product was produced here, indicating that the catalyst has good catalytic activity for the hydrogen transfer of FUR at room temperature. As the reaction temperature increased (from 40 °C, 60 °C, 80 °C up to 100 °C), the time to maintain the yield of FFA more than 90% and an exclusive selectivity to FFA was shortened gradually from 48 h to 2 h. When the temperature was 180 °C, the catalyst exhibited a high activity with 90% yield of FFA in 15 minutes. Taking into account the reaction temperature and reaction time, moderate temperature and time (80 °C and 5 h) were chosen as the optimal reaction conditions for the series of reactions herein.

To further research the hydrogen transfer reaction of FUR through the BZC catalyst, kinetic studies were explored at 40 °C, 60 °C and 80 °C. Since the amount of catalyst was fixed and there was a large excess of isopropanol, the reaction was assumed to be a first-order reaction as a function of FUR concentration. It is apparent that  $\ln(C_t/C_0)$  was linear with the reaction time t of hydrogen transfer of FUR (Fig. 8a). By calculating the slope of the curve, the reaction rate constants (k)were determined to be 0.0597, 0.2491 and 0.6022  $h^{-1}$ , corresponding to temperatures of 40 °C, 60 °C and 80 °C, respectively. According to the Arrhenius plot (Fig. 8b), the activation energy  $(E_a)$  of the hydrogen transfer of FUR to FFA over the BZC catalyst in 2-PrOH was calculated to be 53.55 kJ mol⁻¹. close to or lower than the reported  $E_a$  value for the reaction by other catalysts.^{52,64,75} The low activation energy should be related to the acid-base sites of the BZC catalyst.

#### Effect of the catalyst dosage

The effect of the catalyst dosage on the hydrogen transfer of FUR was researched in 2-PrOH at 80 °C for 5 h (Fig. 9). It can be seen that the yield of FUR increases as the amount of catalyst increases. When the amount of the catalyst is 0.1 g, a yield of 90% or more is obtained. Continue to increase the amount of catalyst to 0.2 g, the yield of FFA slowly increases to nearly



Fig. 7 Effect of different reaction temperatures on the performance of BZC catalyst. Room temperature (a), 40 °C (b), 60 °C (c), 80 °C (d), 100 °C (e) and 180 °C (f). Reaction condition: Catalyst (0.1 g), FUR (0.67 mmol), 2-PrOH (20 ml).



**Fig. 8** First-order kinetic fit (a) for the hydrogen transfer of FUR to FFA at different temperatures and the corresponding Arrhenius plots (b) for the BZC catalyst. Reaction condition: Catalyst (0.1 g), FUR (0.67 mmol), 2-PrOH (20 ml).

100%. And throughout the range from 0.01 g to 2 g, the catalyst exhibits extremely high selectivity to FFA. Therefore, 0.1 g of catalyst is selected as the most appropriate amount.

### Reusability and heterogeneity of the catalyst

The reusability and heterogeneity of the BZC catalyst were also investigated. Upon completion of each cycle, the catalyst was separated from the liquid by filtration, washed twice with each 5 ml of fresh acetone and 2-PrOH, and then involved in the next cycle. The conversion of FUR and the yield of FFA and selectivity to FFA for seven cycles are shown in Fig. 10a. There is no considerable decrease in the conversion, yield and selectivity after seven cycles, proving that the catalyst is very stable. Leaching test of the catalyst was also explored (Fig. 10b). The reaction was stopped after 1.5 h, the catalyst was filtered out and the solution continued to react under same conditions. The yield of FFA did not further increase



Fig. 9 Effect of different amount of BZC on the hydrogen transfer of FUR (F). Reaction condition: FUR (0.67 mmol), 2-PrOH (20 mL), 80  $^{\circ}$ C, 5 h.

after removal of the catalyst. After 4 hours, the BZC catalyst was re-added to the reaction system, and the yield of FFA continued to increase to over 90%, demonstrating the heterogeneity and stability of the catalyst. Meanwhile, trace of zirconium ions (0.09 ppm) in the solution after the reaction also proved that the catalyst is heterogeneous and stable.

The stability of the catalyst was further analyzed by XRD, FT-IR and SEM-EDS. The XRD pattern of the fresh catalyst is similar to that of the spent catalyst with two broad and weak peaks, suggesting no new phase formation after seven cycles (Fig. 11a). From the FT-IR spectra (Fig. 11b), compared with the



Fig. 10 Reusability (a) and leaching test (b) of the catalyst for the hydrogen transfer of FUR. Reaction condition: Catalyst (0.31 g), FUR (0.67 mmol), 2-PrOH (20 mL), 80  $^{\circ}$ C, 5 h.



**Fig. 11** The characterization of the BZC catalyst after 7 cycles. XRD patterns (a), FT-IR spectra (b), elemental mapping images (c) and SEM-EDS data (d).

fresh catalyst, the new absorption peaks at about 1480, 1370 and 1200 cm⁻¹ appears in the infrared spectrum of the spent catalyst, from which it can be inferred that some nonvolatile organic compounds are present on the surface of the spent catalyst. The compounds are responsible for the slight decrease in catalytic activity after the first run, and the new peaks at 1480 and 1370 cm⁻¹ are attributed to bending vibration of C–H. In addition, from elemental mapping and SEM-EDS (Fig. 11c and d), on the surface of the catalyst, the elemental content of the spent catalyst is not much different from that of the fresh catalyst (Fig. 4a and b), and Zr, O and C elements are uniformly dispersed on the surface of the spent catalyst. In summary, the catalyst is quite stable after seven cycles.

# Hydrogen transfer of carboxides and xylose-derived FUR over the BZC catalyst

Inspired by the excellent catalytic performance of the BZC catalyst for hydrogen transfer of FUR at low temperature, the conversions of other carboxides were subject to the similar conditions and the results are shown in Table 3. The BZC catalyst has remarkable catalytic performance for hydrogen transfer of different carboxides. It is noteworthy that ketones or aldehydes with long chains or complex structures need a longer reaction time or harsh conditions to achieve good conversions and yield as compared to simple aldehydes, caused by steric hindrance and electron-donating nature of the alkyl groups in these molecules.

In order to make the catalytic performance of the BZC catalyst more complete for biomass conversion, xylose-derived FUR (a true biomass-derived carboxide) is researched as a representative. The related research on the catalytic conversion from xylose to FUR has been widely studied and even industrialized.^{76,77} Here, a two-phase reaction system was established to synthesize FUR from xylose (Scheme S2[†]). After the reaction, the organic phase was fractionated to get FUR with a purity of 85.14% (containing a small amount of water, THF, by-products, etc.) (Fig. S6 and S7[†]). The impure xylosederived FUR was used as a model carboxide to verify the true catalytic performance of the BZC catalyst. From the results (Fig. 12a), the yield of FFA reached 94.81% at 80 °C for 5 h, indicating that high conversion and high yield are also received with the biomass-derived FUR as feedstock. For reusability test of the catalyst (Fig. 12b), the activity of the catalyst decreased a little bit, but the selectivity of the product remained constant after five cycles. Compared with the hydrogen transfer of pure FUR, the catalytic activity and reusability of the catalyst using the xylose-derived FUR as feedstock are slightly decreased due to more carbon accumulation (Fig. S8[†]).

#### A scaled-up hydrogen transfer experiment of FUR

In order to estimate the industrial application potential of BZC catalyst for hydrogen transfer of FUR to FFA, a scaled-up experiment of FUR was examined in 135 mL of 2-PrOH at 120 °C for 4 h using 15 mL of FUR with 1 g of BZC as catalyst. The results display that a FUR yield of 88.72% is obtained, revealing an industrial prospect for the BZC catalyst.

#### Mechanism analysis

According to previous reports,^{61,78,79} the amphoteric nature of the catalysts is the major reason for catalyzing the hydrogen transfer of carboxides. For Zr-containing catalysts, the acid and basic sites mainly originate from the Zr⁴⁺ and O²⁻, respectively. The preceding ATR-IR and in situ ATR-IR tests verify that Zr4+ of BZC can activate C=O and clarifies the hydrogen transfer process of FUR. In addition, the NH₃-IR and HCOOH-IR spectra also demonstrate that BZC catalysts contain a large amount of acid-base sites. Combined with relevant literature,65,67 a possible mechanism based on the catalyst for hydrogen transfer of carboxides is proposed (Scheme 1). First, isopropanol adsorbed on the surface of the BZC catalyst interacts with the acid-base sites (Zr⁴⁺-O²⁻) on the surface of the catalyst, resulting in dissociation of isopropanol to form the corresponding alkoxide and hydrogen. Meanwhile, the carbonyl group of the substrate molecule is also adsorbed and

 Table 3
 Hydrogen transfer reaction of carboxides over the BZC catalyst

Entry	Reactant	Main product	Temperature (°C)	Time (h)	Conv. (%)	Yield (%)
1		OH	80	7	>99	>99
2	OH OF	OH OH	80	9	>99	98.66
3		ОН	80	15	>99	98.85
4		ОН	80	15	95.14	94.63
5	o	ОН	120	8	>99	>99
6			140	14	97.75	91.32

Conditions: Catalyst (0.1 g), substrate (0.67 mmol), 2-PrOH (20 mL).



**Fig. 12** Different reaction time (a) and reusability test (b) of the catalyst for the hydrogen transfer of FUR on the performance of BZC catalyst. Reaction condition (a): Catalyst (0.31 g), FUR (0.67 mmol), 2-PrOH (20 mL), 80 °C. Reaction condition (b): Catalyst (0.31 g), FUR (0.67 mmol), 2-PrOH (20 mL), 80 °C, 5 h.



**Scheme 1** Plausible reaction mechanism for hydrogen transfer of carboxides with the BZC catalyst. activated by the acid-base sites. Further, a hydrogen transfer reaction occurs between the dissociated alkoxide and the activated carbonyl group through a six-membered ring transition state to form the product and acetone. Finally, the product and acetone are desorbed from the surface of the catalyst and acidbase sites on the surface of the catalyst are regenerated.

## Conclusions

A simple basic zirconium carbonate (BZC) catalyst was applied for catalyzing the hydrogen transfer reaction of carboxides derived from biomass, which exhibits high catalytic activity at low temperatures, especially for the conversion of FUR to FFA. At room temperature (about 24 °C), the yield of FFA reaches 98.08% with nearly complete conversion. As the reaction temperature increases to 180 °C, and the yield of FFA reaches 90.29% with 91.02% conversion within 15 minutes. The results of ATR-IR spectroscopy and XPS indicate that BZC possesses the strongest lewis acidity of the three catalysts, which are the reasons why BZC has the best catalytic performance. Similarly, the NH₃-IR and HCOOH-IR spectra also demonstrate that BZC catalysts contain the largest amount of acid-base sites among the three. Kinetic studies reveal that with the BZC as the catalyst, the  $E_{\rm a}$  value of the reaction is lower in the same type of catalysts, which is 54.77 kJ mol⁻¹. In addition, the characterization of in situ ATR-IR provides a clearer understanding for the real-time dynamics of the FUR hydrogen transfer reaction, further contributing to the proposed mechanism of the reaction. Overall, combined with the advantages of cost-effectiveness and simple synthesis, *etc.*, the BZC catalyst has a good application prospect for the hydrogen transfer of biomass-derived carboxides.

## Conflicts of interest

There are no conflicts to declare.

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