Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

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

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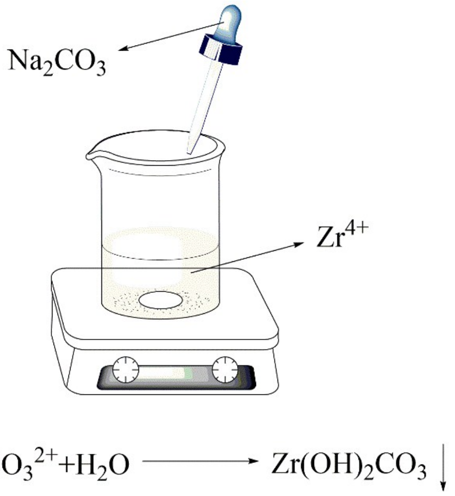
Figure S8. The color change of the BZC catalyst before and after the reaction.

Table S1. The hydrogen transfer reaction of the biomass-derived carboxides using various catalysts in recent years.

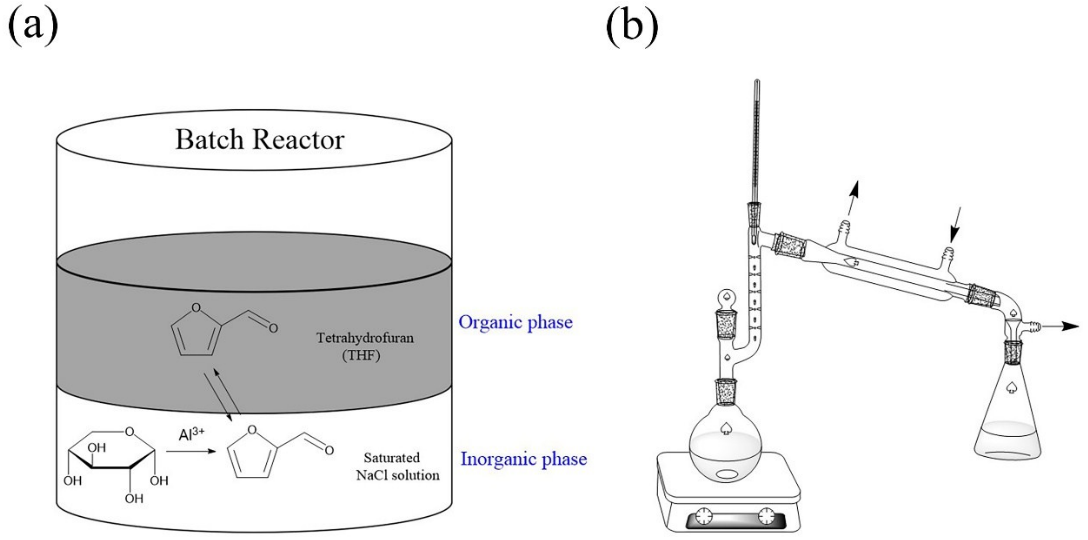
Table S2. Hydrogen transfer reaction of FUR to FFA with isopropanol as solvent over various catalysts

1. The test Conditions of the NH_3-IR and HCOOH-IR spectra.

NH_3-IR spectra were recorded on a Bruker 80 v with a range of 600-4000 cm^{-1} for the MCT detector. The catalyst powder was placed in an in situ IR cell equipped with a ZnSe window. Prior to adsorption, the catalyst in the IR cells was purified in N_2 flow at 150 °C for 0.5 hours. The cells were then cooled to 50 °C. Next, NH_3 gas was introduced into the cells and desorbed in a flow of N_2 at 50 °C to remove excess NH_3 molecules in the stream of N_2. After 0.5 hours, the IR spectra of the catalyst was collected. Similarly, HCOOH-IR spectra was tested by the same method.



Scheme S1. Preparation of the BZC catalyst.



Scheme S2. Process for preparing FUR by two-phase solvent reaction system (a). Organic phase fractionation and purification device (b).

The xylose-derived FUR was prepared by a two-phase solvent reaction system. In detail, the reaction was carried on in a stainless steel autoclave (40 mL) heated in a temperature-controlled oil bath. The mixture of xylose, solvents (biphase: 15 mL THF as extract phase and 15 mL saturated NaCl solution as reaction phase) and $AlCl_3$ were put in the Teflon-lined stainless steel autoclave (40 mL) equipped with a magnetic stirring bar. After reaction, the reactor was cooled to room temperature. The organic phase (extract phase) was moved to a fractionation unit for purification of FUR. The inorganic phase (reaction phase) was added to xylose and filled with 15 mL THF to continue production of FUR.

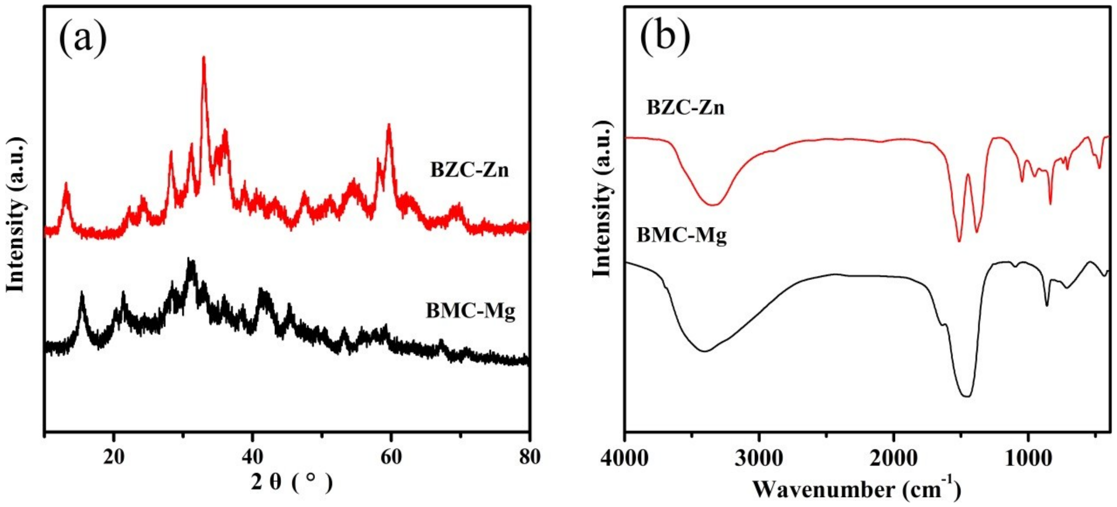


Figure S1. XRD patterns (a) and FT-IR spectra (b) of BMC-Mg and BZC-Zn.

The basic magnesium carbonate (BMC-Mg) catalyst was prepared by the precipitation method. Briefly, $Mg(NO_3)_2 \cdot 6H_2O$ (10 mmol) was dissolved in 60 mL deionized water and was stirred at ambient temperature for 15 mins. With vigorous stirring, 1 M Na_2CO_3 solvent was added dropwise until pH=7. After being aged for 5 h at room temperature, the precipitate was separated by filtration and washed several times with deionized water. The resulting precipitate was dried in the oven at 80 °C for 5 h. Basic zinc carbonate (BZC-Zn) catalysts was also prepared by the same method.

As for Figure S1a, the XRD map shows the characteristic peaks of BMC-Mg (2θ= 15.3°, 21.2°, 30.8°, 33.2°, 41.2°, 52.8°, 59.0 ° and 66.9°. PDF, 29-0857) and BZC-Zn, respectively (2θ= 13.6°, 22.2°, 24.2°, 28.4°, 31.3°, 33.2°, 36.2 , 43.3°, 47.3°, 54.3°, 59.7° and 69.8°. PDF, 19-1458). In addition, from the Figure S1b, it can be also seen the FT-IR spectrum peaks of BMC-Mg and BZC-Zn in good accordance with the XRD observation. Therefore, it can be stated that the synthesized samples are indeed BMC-Mg and BZC-Zn.

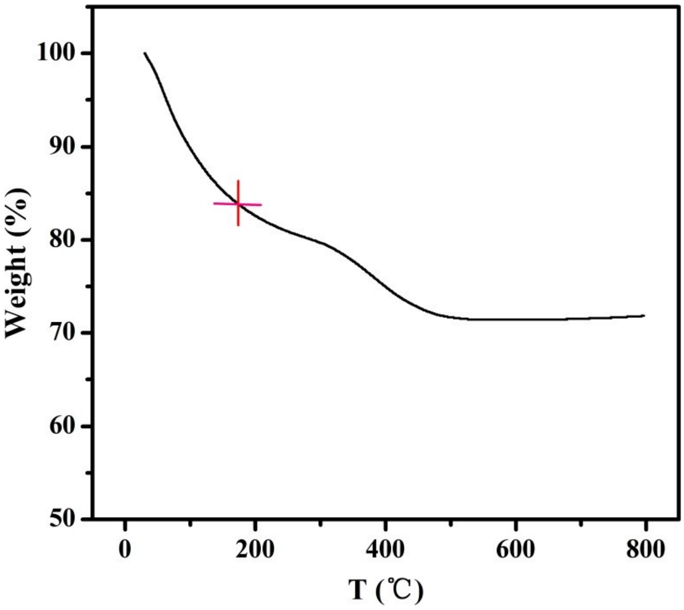


Figure S2.TG analysis of the BZC catalyst.

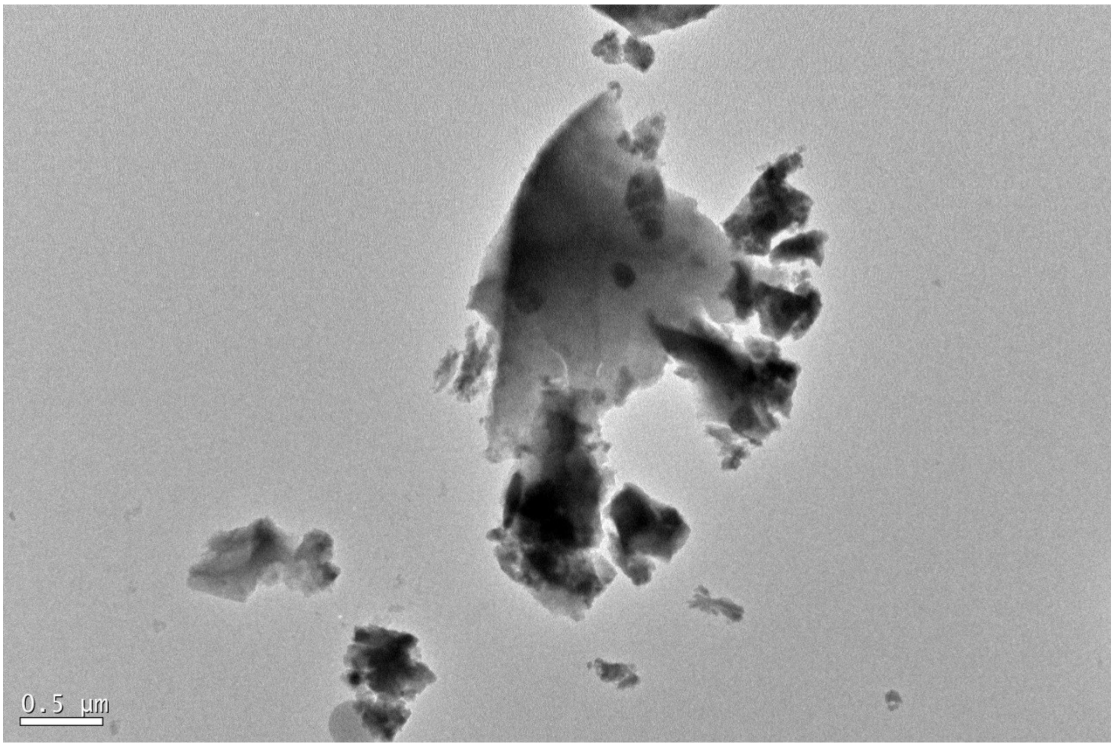


Figure S3. TEM image of the BZC catalyst.

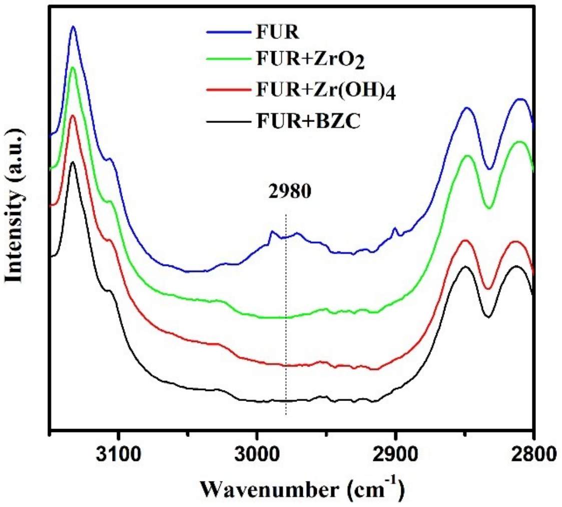


Figure S4. ATR-IR spectra of FUR adsorbed on different Zr-based catalysts in the 2800-3150 cm^{-1} region.

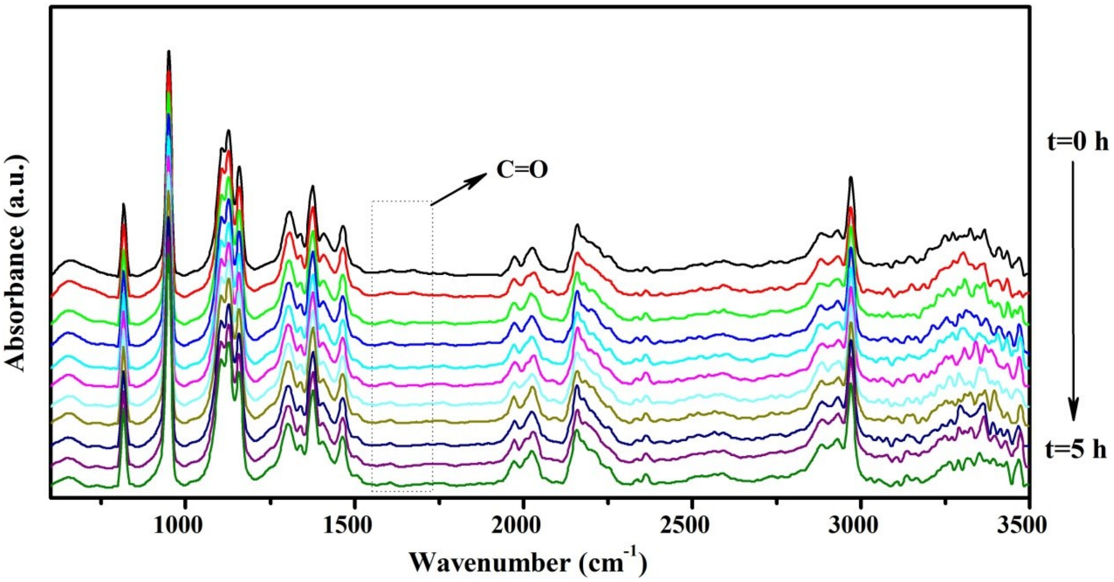


Figure S5. In situ ATR-IR spectra during the hydrogen transfer of FUR in 2-PrOH over the BZC. Reaction condition: FUR (5.03 mmol), 2-PrOH (150 mL) catalyst (0.75 g), 80 °C.

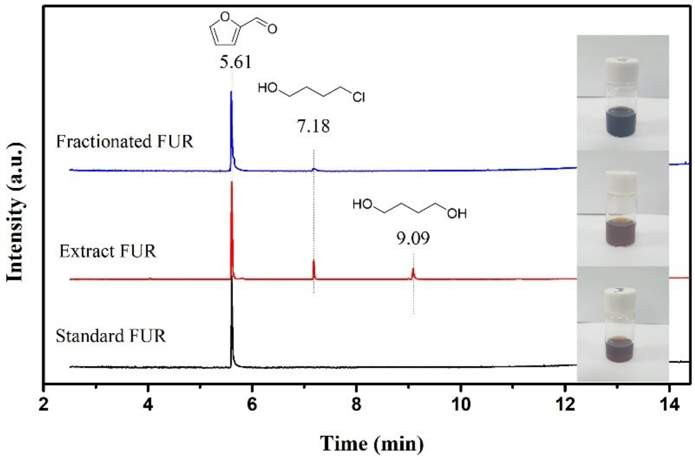


Figure S6. GC-MS spectra of different FUR.

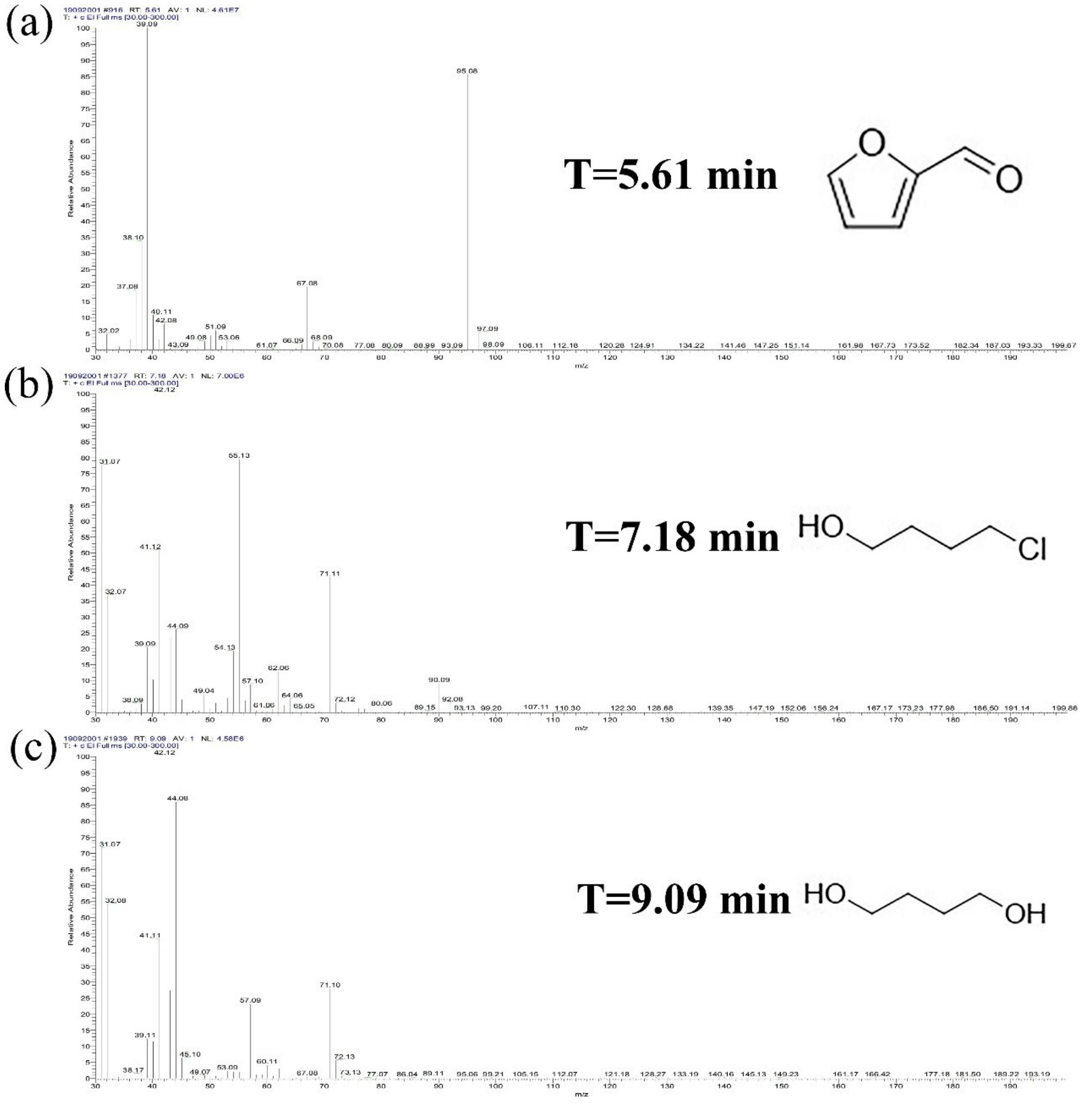


Figure S7. MS spectra of extract phase (extract FUR).

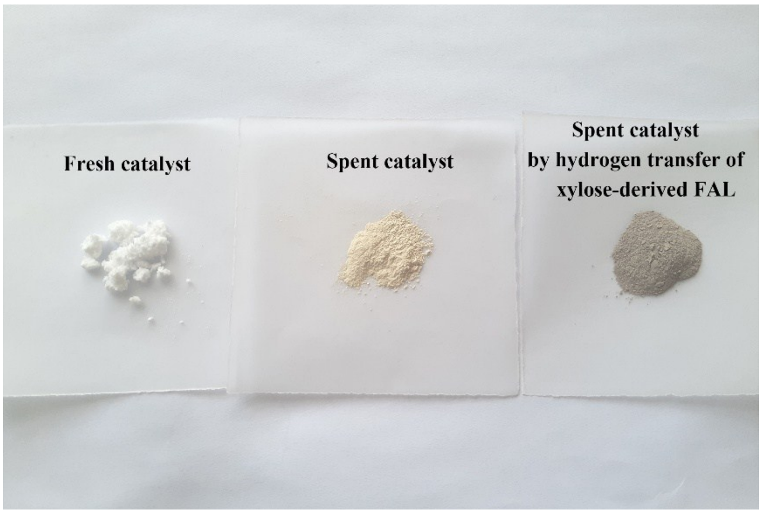


Figure S8. The color change of the BZC catalyst before and after the reaction.

Table S1. The hydrogen transfer reaction of the biomass-derived carboxides using various catalysts in recent years.

Entry	Catalysts	Reactant /product	H-donor	Reaction conditions	C./%	Y./%	S./%	Refs
1	BZC	FUR/FFA	2-PrOH	room temperature， 5d	93.77	92.99	99.16	This work
		FUR/FFA	2-PrOH	80℃，5h	97.69	96.67	98.95	
		FUR/FFA	2-PrOH	180℃，15min	91.02	90.29	99.19	
		HMF/BHMF	2-PrOH	80℃，9h	>99	>99	>99	
		ML/GVL	2-PrOH	140℃，15h	97.61	91.32	93.56	
2	ZrO_2	EL/GVL	ethanol	250℃，3h	95.5	81.5	85.3	1
3	$Zr(OH)_4$	EL/GVL	2-PrOH	200℃，1h	93.6	88.45	94.5	2
4	Al-Zr oxides	EL/GVL	2-PrOH	220℃，4h	95.5	83.2	87.1	3
5	Al_2O_3	FUR/FFA	2-PrOH	150℃，6h	>90	>90	>90	4
6	Ru/C	FUR/FFA	benzyl alcohol	150℃,4h	100	100	100	5
		HMF/BHMF		150℃，10h	90.7	86.89	95.8	
7	γ-Fe_2O_3@HAP	FUR/FFA	2-PrOH	180℃，10h	96.2	91.6	95.3	6
		HMF/BHMF	2-PrOH	180℃，10h	78.2	72.0	92.1	
		EL/GVL	2-PrOH	180℃，12h	41.2	36.0	87.3	
8	$NiFe_2O_4$	FUR/FFA	2-PrOH	180℃，6h	99	94	95	7
9	Al-Zr@Fe	FUR/FFA	2-PrOH	180℃，4h	99.1	90.5	91.3	8
		HMF/BHMF	2-PrOH	180℃，4h	82.7	71.0	85.9	
10	Zr-SBA-15	FUR/FFA	2-PrOH	90℃，4h	65.0	45.0	69.2	9
11	ZrPN	FUR/FFA	2-PrOH	100℃，15h	93.0	90.0	96.8	10
		HMF/BHMF	2-PrOH	140℃，2h	>99	98	98	
		EL/GVL	2-PrOH	160℃，10h	93	92	99	
12	Zr-PhyA	FUR/FFA	2-PrOH	100℃，2h	99.3	99.3	99.3	11
		ML/GVL	2-PrOH	130℃，8h	100	95.8	95.8	
13	Zr-HAs	FUR/FFA	2-PrOH	50℃，15h	97.4	96.9	>99	12
		ML/GVL	2-PrOH	150℃，15	>99	85	85	
14	m-PhPZr	FUR/FFA	2-PrOH	120℃，2h	>99	99	99	13
		HMF/BHMF	2-PrOH	120℃，2h	>99	93	93	
		EL/GVL	2-PrOH	160℃，6h	100	98	98	

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Table S2. Hydrogen transfer reaction of FUR to FFA with isopropanol as solvent over various catalysts

Entry	Catalyst	Conversion (%)	Yield (%)	Selectivity (%)
1	MgO	<1	0	0
2	$Mg(OH)_2$	<1	0	0
3	NiO	<1	0	0
4	$Ni(OH)_2$	<1	0	0
5	CuO	<1	0	0
6	$Cu(OH)_2$	<1	0	0
7	ZnO	<1	0	0
8	$Zn(OH)_2$	<1	0	0

Conditions: catalyst (0.1 g), FUR (0.67 mmol), 2-PrOH (20 mL), 80 °C, 5 h.