Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supplementary Information

Zirconium-cyanuric acid coordination polymer: Highly efficient catalyst for conversion of levulinic acid to γ-valerolactone

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Catalyst characterization:

The scanning electron microscopy (SEM) measurements were performed on a Hitachi S-4800 Scanning Electron Microscope operated at 15 kV.

The transmission electron microscopy (TEM) images were obtained using a TEM JeoL-1011 with an accelerating voltage of 120 kV.

X-ray diffraction (XRD) measurements were conducted on an X-ray diffractometer (D/MAX-RC, Japan) operated at 40 kV and 200 mA with Cu Kα (λ=0.154 nm) radiation.

N_2 adsorption-desorption isotherms were obtained using the Micromeritics ASAP 2020 V3.00 H (USA) surface area analyzer at 77 K at high vacuum.

The XPS measurements were carried out on an ESCAL Lab 220i-XL specrometer at a pressure of ~3×10^{-9} mbar (1 mbar=100 Pa) using Al Kα as the excitation source ($h\nu$=1486.6 eV) and operated at 15 kV and 20 mA. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon.

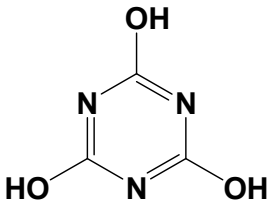
The contents of Zr in Zr-CA and the concentration of Zr in the reaction solution were determined by ICP-AES (VISTA-MPX). The content of C and N in Zr-CA were obtained from elemental analysis by using the FLASH EA1112 analyzer.

FT-IR spectra were recorded on Bruker Tensor 27 IR spectrometer.

Temperature-programmed desorption of carbon dioxide (CO_2-TPD) was performed on Micromeritics' AutoChem 2950 HP Chemisorption Analyzer. In the experiment, the catalyst was charged into the quartz reactor, and the temperature was increased from room temperature to 150 ^oC at a rate of 10 ^oC/min under a flow of He (50 cm^3/min), and then the catalyst was kept at 150 ^oC for 4 h. After that, the temperature was decreased to 60 ^oC. CO_2 (50 cm^3/min) was pulsed into the reactor at 60 ^oC under a flow of He (10 cm^3/min) until the basic sites were saturated with CO_2. The adsorbed CO_2 was removed by a flow of He (50 cm^3/min). When the baseline was stable, the temperature was increased from 60 ^oC to 500 ^oC at a rate of 10 ^oC/min.

Temperature-programmed desorption of ammonia (NH_3-TPD) was performed on Micromeritics' AutoChem 2950 HP Chemisorption Analyzer. The catalysts were charged into the quartz reactor, and the temperature was increased from room temperature to 150 ^oC at a rate of 10 ^oC/min under a flow of He (50 cm^3/min), and then the catalyst was kept at 150 ^oC for 4 h. After that, the temperature was decreased to 60 ^oC. NH_3/He (10/90, 50 cm^3/min) was pulsed

into the reactor at 60 °C under a flow of He (10 cm^3/min) until the acid sites were saturated with NH_3. The adsorbed NH_3 was removed by a flow of He (50 cm^3/min). When the baseline was stable, the temperature was increased from 60 °C to 500 °C at a rate of 10 °C/min.



Scheme S1. The structure of cyanuric acid.

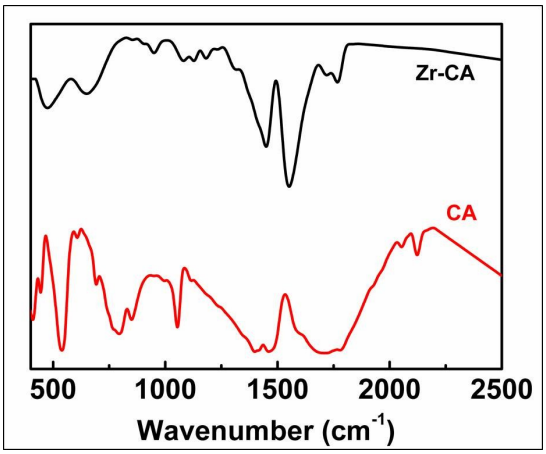


Figure S1. The FT-IR spectra of Zr-CA and CA.

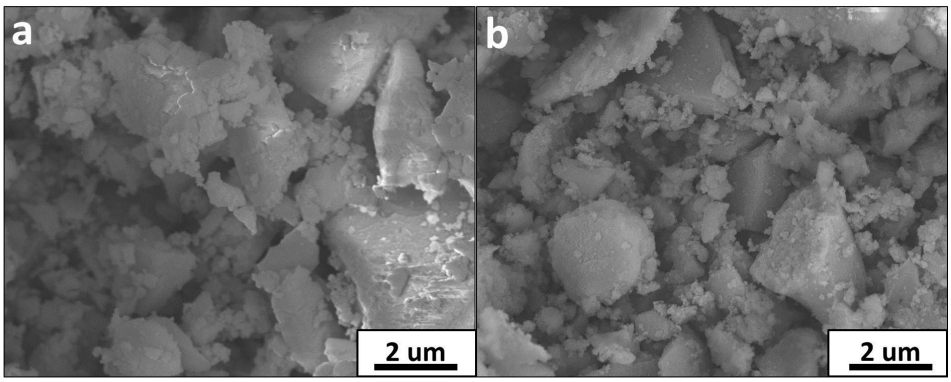


Figure S2. SEM images of other metal-CA catalysts. Zn-CA (a) and Sn-CA (b).

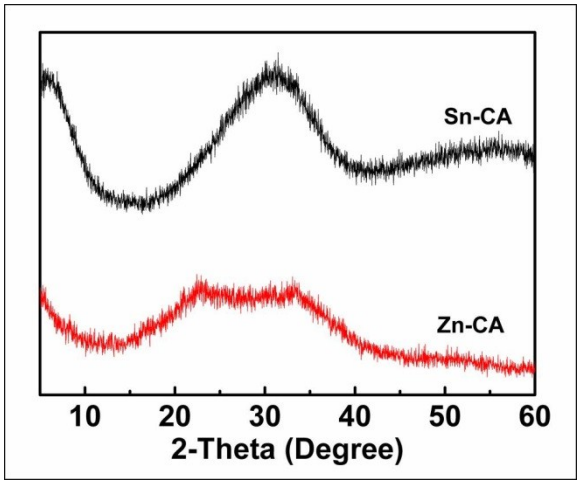


Figure S3. XRD patterns of other metal-CA catalysts. These XRD patterns indicated that the metal-CA catalysts prepared were poorly ordered and amorphous. At the same time, their crystallinity was very low.

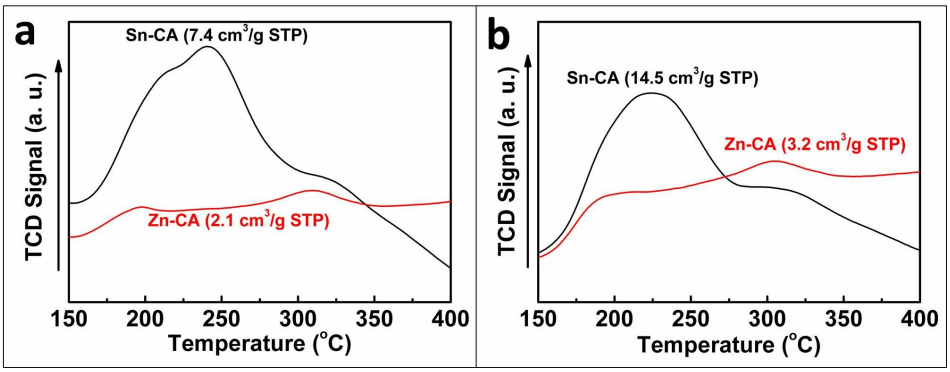


Figure S4. NH_3-TPD (a) and CO_2-TPD (b) examinations for Sn-CA and Zn-CA.

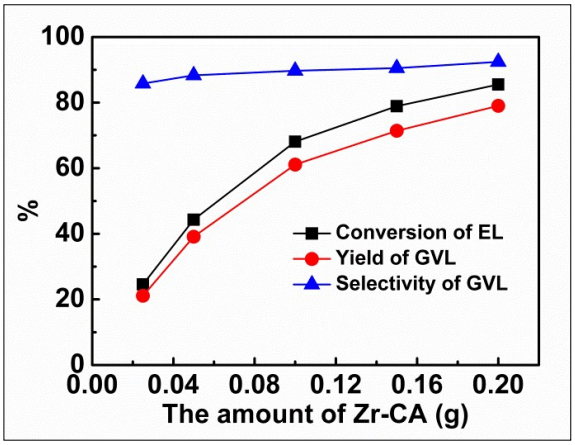


Figure S5. The influence of the Zr-CA amount on the TH reaction. Reaction conditions: EL, 1 mmol; isopropanol, 6 g; reaction time, 4 h; reaction temperature, 130 °C; a stainless reactor of 15 mL.

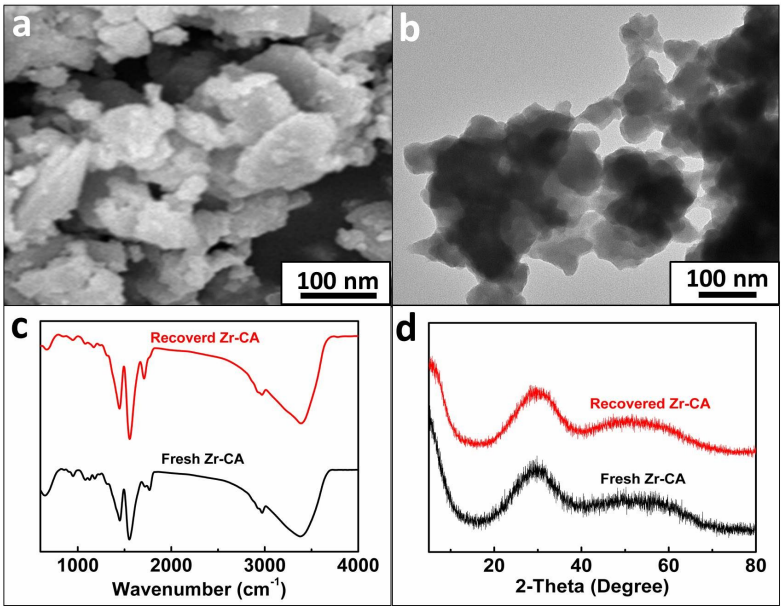


Figure S6. The characterization of the Zr-CA after reused for five times. SEM image (a), TEM image (b), FT-IR spectrum (c), and XRD pattern (d).

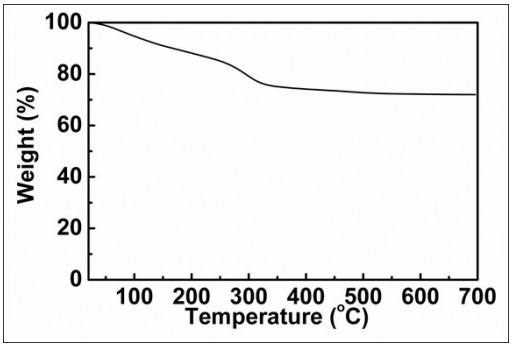


Figure S7. Thermogram of the prepared Zr-CA.

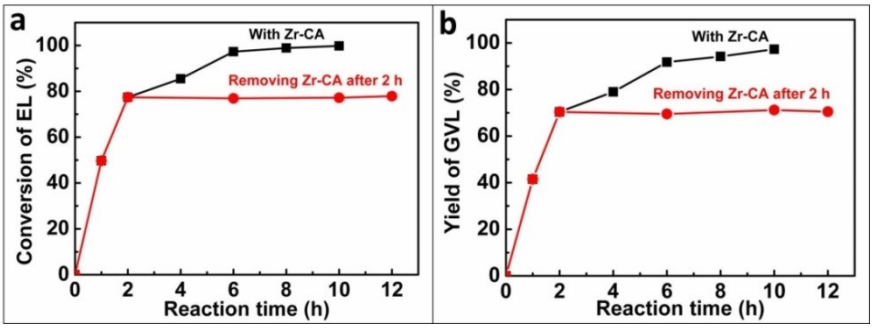


Figure S8. Time-conversion (a) and time-yield (b) plots for transfer hydrogention reaction of EL with Zr-CA (Black line) or removing Zr-CA after 2h (Red line). Reaction conditions: EL 1 mmol; isopropanol 6 g; Zr-CA 0.2 g; reaction time 10 h; reaction temperature, 130 °C.

Table S1. Properties of other metal (Zr, Sn, Zn)-CA catalysts.

Entry	Sample[a]	BET surface area (m^2/g)[b]	Pore volume (cm^3/g)[c]	Pore diameter (nm)[d]
1	Zr-CA	108	0.13	3.5
2	Sn-CA	104	0.14	3.2
3	Zn-CA	125	0.11	3.0
4[e]	Zr-CA	102	0.11	2.8
5	ZrO_2	21	0.01	0.53

[a]The samples were degassed at 120 °C for 24 h. [b]Surface area based on multipoint BET method. [c]Pore volume based on BJH method. [d]Pore diameter based on BJH method. [e]The Zr-CA was the recovered one after reused for five times.

Table S2. The influence of the isopropanol/EL mole ratio on the TH of EL to GVL.[a]

Entry	Isopropanol/EL mole ratio	Conversion of EL (%)[b]	Yield of GVL (%)[b]	Selectivity of GVL (%)[c]
1	1:1	38.3	21.8	56.9
2	1:5	66.4	46.9	70.6
3	1:10	80	61.8	77.3
4	1:17	86.7	72.3	83.4
5	1:33	88.5	77.7	87.8
6	1:67	89.6.	81.8	91.2
7	1:100	89.3	82.1	91.9

[a]Reaction conditions: a stainless reactor of 15 mL, 0.2 g catalyst, 1 mmol EL. [b]Conversion and GVL yield were determined by GC. [c]The other products were mainly isopropyl levulinate by transesterification with minute by-products from aldol condensation between EL and in-situ generated acetone in entries 1-5.

Table S3. The contents of various elements on the surface of Zr-CA determined by XPS examination.

Element	Content of various elements on the surface (Atomic%)[a]	
	Fresh Zr-CA	Spent Zr-CA
Zr	9.56	9.4
N	1.12	0.93
C	54.36	54.22
O	34.96	35.45