

## **Supporting Information**

### **Generating abundant $\text{Co}^{3+}$ species via $\text{H}_2\text{O}/\text{N}_2$ mixed atmosphere pyrolysis of CoZn-ZIF for catalytic transfer hydrogenation**

Honghao Song, Chaosheng Bao and Tong-Liang Hu\*

School of Materials Science and Engineering, Nankai University, Tianjin 300350, China.

E-mail: tlhu@nankai.edu.cn

## 1. Experiment Section

### 1.1 Chemicals

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (99%) and 2-Methylimidazole (98%) was purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd.  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (99%) was purchased from Beijing Mreda Technology Co., Ltd. Levulinic acid was purchased from Heowns (Tianjin) Technology Co., Ltd. Isopropyl alcohol (GC) was purchased from Tianjin Bohua Chemical Reagent Co., Ltd. All of the reagents were used without further purification.

### 1.2 Catalyst Preparation

#### 1.2.1 Preparation of CoZn-ZIF

The CoZn-ZIF precursor was synthesized in bulk according to the reported work.<sup>1</sup> Typically, 9mmol  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 9mmol  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were dissolved in 450 mL of methanol, referred to as solution A. Solution B consisted of 72 mmol of 2-Methylimidazole (2-meim) in another 450 mL of methanol. Then, the two solutions were mixed rapidly under stirring, which continued for 30 minutes. The product was collected by centrifugation, rinsed three times with methanol, and dried at 80 °C for 12 h.

#### 1.2.2 Preparation of CoZn/CN- $\text{H}_2\text{O}$ and CoZn/CN- $\text{N}_2$

CoZn-ZIF (500 mg) was placed in the ceramic boat. Then the ceramic boat was transferred into a tube furnace.  $\text{N}_2$  (30 mL/min) was bubble through a 50 mL tube containing 20 mL of deionized water, which was placed in a temperature-controlled water bath. The  $\text{H}_2\text{O}$  content in the mixed atmosphere was changed by adjusting the water bath temperature. Unless otherwise specified, the water bath temperature was maintained at 30 °C. The precursor was pyrolyzed at 600 °C for 1.5 h, with a heating rate of 5 °C/min. CoZn/CN- $\text{N}_2$  was synthesized following the same procedure as CoZn/CN- $\text{H}_2\text{O}$ , with the only difference being the use of a pure  $\text{N}_2$  atmosphere.

### 1.3 Characterization

Powder X-ray diffraction spectra of the prepared samples were obtained on the Rigaku MiniFlex 600 diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Nitrogen adsorption-desorption isotherms were measured on the BSD-PM2 physical adsorption instrument. Prior to use, the samples were degassed under vacuum at 150 °C for 12 h. The Barrett-Joyner-Halenda (BJH) method was employed to obtain the pore size distribution and pore volume of the samples. The Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface area of the

samples. The morphology and elemental mapping of the samples were demonstrated by transmission electron microscopy (TEM) using a JEM-2800 electron microscope. The chemical states of C, N, Co and Zn were characterized by X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific K-Alpha.

NH<sub>3</sub> temperature-programmed desorption (TPD) was performed using a BSD-Chemc200. Firstly, the sample was pretreated by heating to 300 °C for 30 min under He flow (30 mL/min). After cooling to 30 °C, NH<sub>3</sub> (30 mL/min) was introduced for 90 min. The NH<sub>3</sub> desorption signal was obtained by heating the sample to 800 °C (10 °C/min) under a He flow (30 mL/min).

Pyridine-adsorbed FTIR was measured on a BRUKER FTIR spectrometer (Tensor II) with a MCT detector cooled by liquid nitrogen. The catalysts were pretreated by heating to 200 °C (10 °C/min) for 30 min under Ar flow (30 mL/min). After cooling to 25 °C, the background was collected and the pyridine was introduced with Ar flow (30 mL/min) to saturate the catalysts. After raising the temperature to 100 °C (10 °C/min) and removing physically adsorbed pyridine under Ar flow (30 mL/min), the IR spectrum was continuously recorded.

#### 1.4 Evaluation of Catalytic Performance

The transfer hydrogenation of LA to GVL was performed in a 100 mL high-pressure autoclave. In a typical reaction, 50 mg of catalyst and 10 mL of i-PrOH containing 0.15 M LA were added to an autoclave. Following four cycles of N<sub>2</sub> purging, the autoclave was pressurized to 1 MPa and heated under magnetic stirring at 500 rpm. After the reaction, the autoclave was cooled to room temperature in a water bath. Furthermore, the solution was filtered and analyzed using gas chromatography (GC-2014C) with an autosampler (AOC-20i). In the reusability test, the spent catalyst was rinsed with ethanol, and dried under an N<sub>2</sub> atmosphere at 80 °C for subsequent reuse.

The conversion of LA, the yield of GVL and the reaction rate were calculated by:

$$\text{LA conversion} = \frac{\text{Mole of LA converted}}{\text{Mole of LA added}} \times 100\% \quad (1)$$

$$\text{GVL yield} = \frac{\text{Mole of GVL}}{\text{Mole of LA added}} \times 100\% \quad (2)$$

$$\text{Reaction rate} = \frac{\text{Mole of GVL}}{\text{Reaction time} \times \text{Quantity of catalyst}} \times 100\% \quad (3)$$

## 2. Supporting Figures and Tables

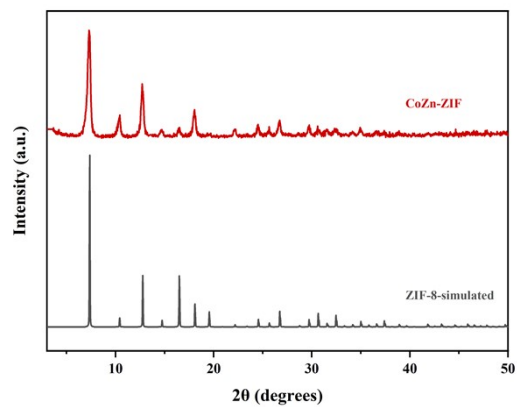


Fig. S1 PXRD patterns of CoZn-ZIF and ZIF-8-simulated.

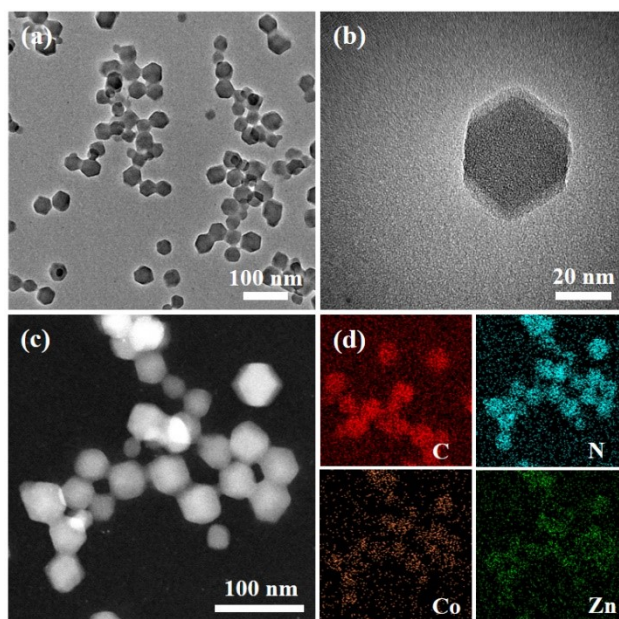


Fig. S2 (a-c) TEM images and (d) EDS elemental mappings of the CoZn-ZIF.

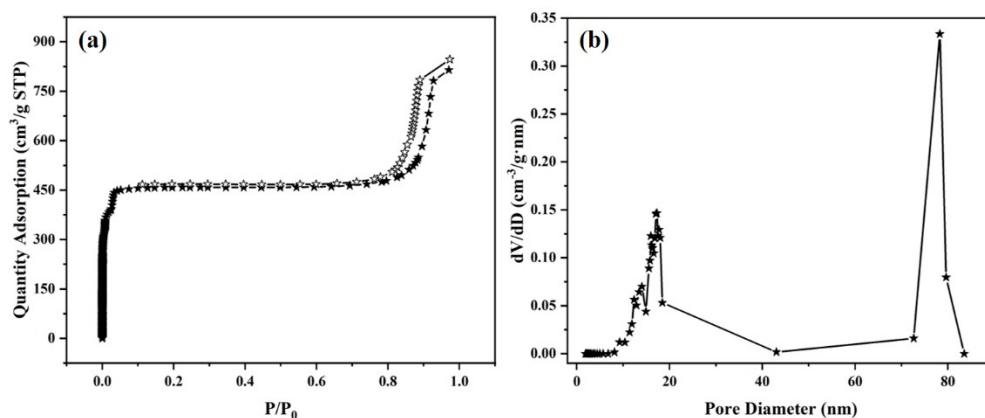


Fig. S3 (a)  $N_2$  adsorption-desorption isotherms and (b) pore diameter distribution of the CoZn-ZIF.

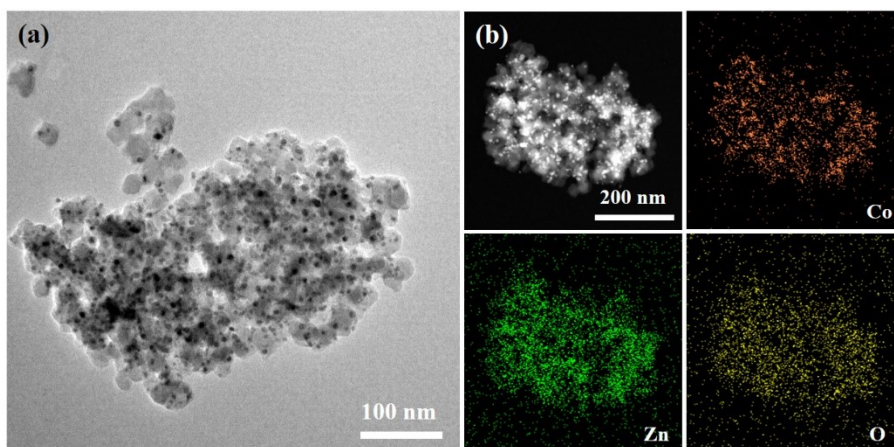


Fig. S4 (a) TEM and (b) EDS elemental mappings of the CoZn/CN-H<sub>2</sub>O.

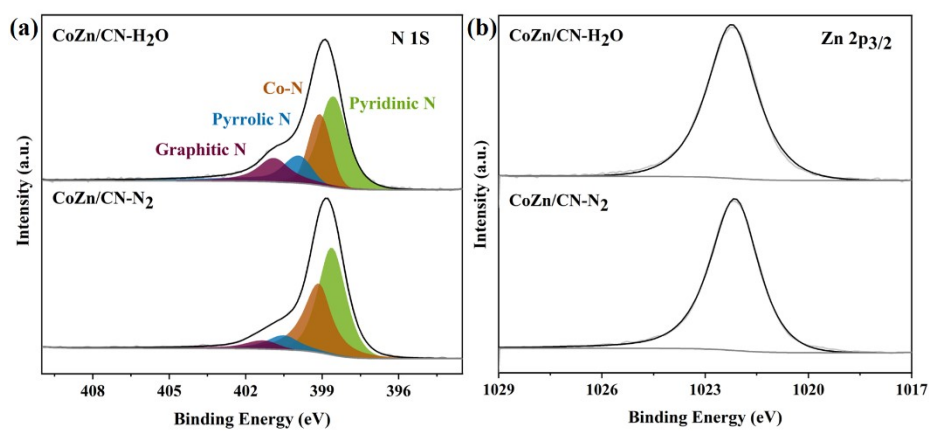


Fig. S5 High-resolution XPS of (a) N 1S and (b) Zn 2p<sub>3/2</sub> for CoZn/CN-H<sub>2</sub>O and CoZn/CN-N<sub>2</sub>.

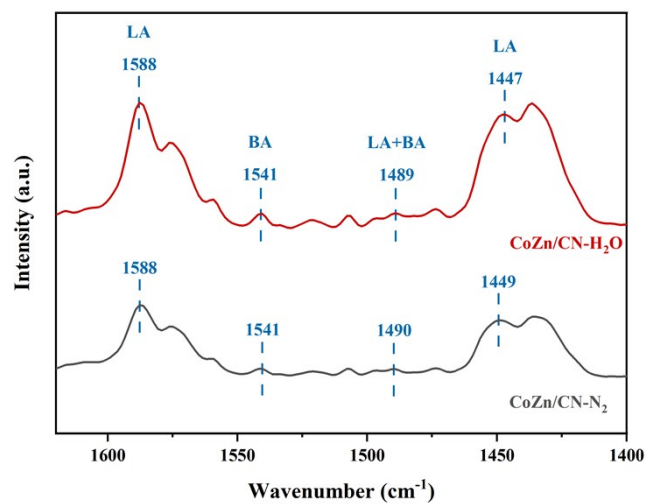


Fig. S6 Pyridine-adsorbed FTIR spectra of CoZn/CN-H<sub>2</sub>O and CoZn/CN-N<sub>2</sub>.

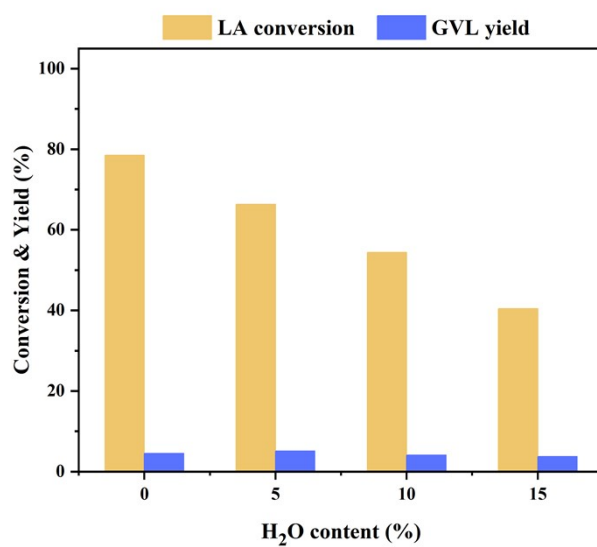


Fig. S7 Catalytic performance of CoZn/CN-N<sub>2</sub> at different H<sub>2</sub>O content. Reaction conditions: LA (1.5 mmol), catalyst (50 mg), i-PrOH + H<sub>2</sub>O (10 mL), N<sub>2</sub> pressure (1 MPa), reaction time (1 h), reaction temperature (180 °C).

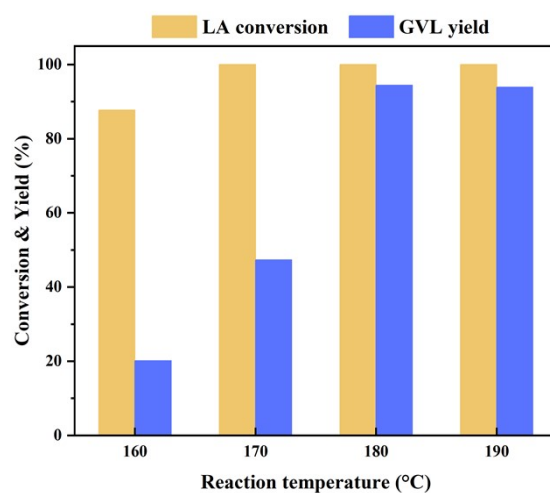


Fig. S8 Catalytic performance of CoZn/CN-H<sub>2</sub>O at different reaction temperatures. Reaction conditions: LA (1.5 mmol), catalyst (50 mg), i-PrOH (10 mL), N<sub>2</sub> pressure (1 MPa), reaction time (1 h).

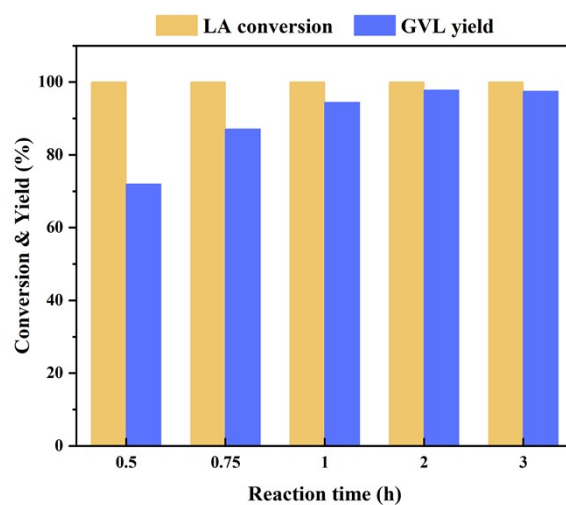


Fig. S9 Catalytic performance of CoZn/CN-H<sub>2</sub>O at different reaction time. Reaction conditions: LA (1.5 mmol), catalyst (50 mg), i-PrOH (10 mL), N<sub>2</sub> pressure (1 MPa), reaction temperature (180 °C).

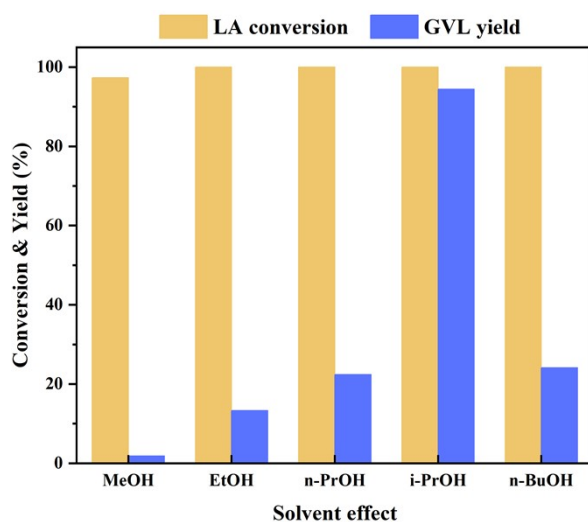


Fig. S10 Catalytic performance of CoZn/CN-H<sub>2</sub>O at different solvents. Reaction conditions: LA (1.5 mmol), catalyst (50 mg), reaction time (1 h), N<sub>2</sub> pressure (1 MPa), reaction temperature (180 °C).

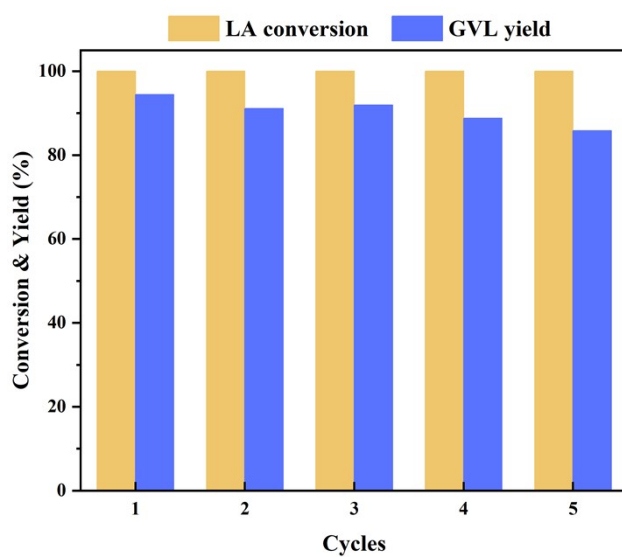


Fig. S11 Catalyst reusability test of CoZn/CN-H<sub>2</sub>O. Reaction conditions: LA (1 mmol), catalyst (50 mg), reaction time (1 h), N<sub>2</sub> pressure (1 MPa), reaction temperature (180 °C), i-PrOH (10 mL).



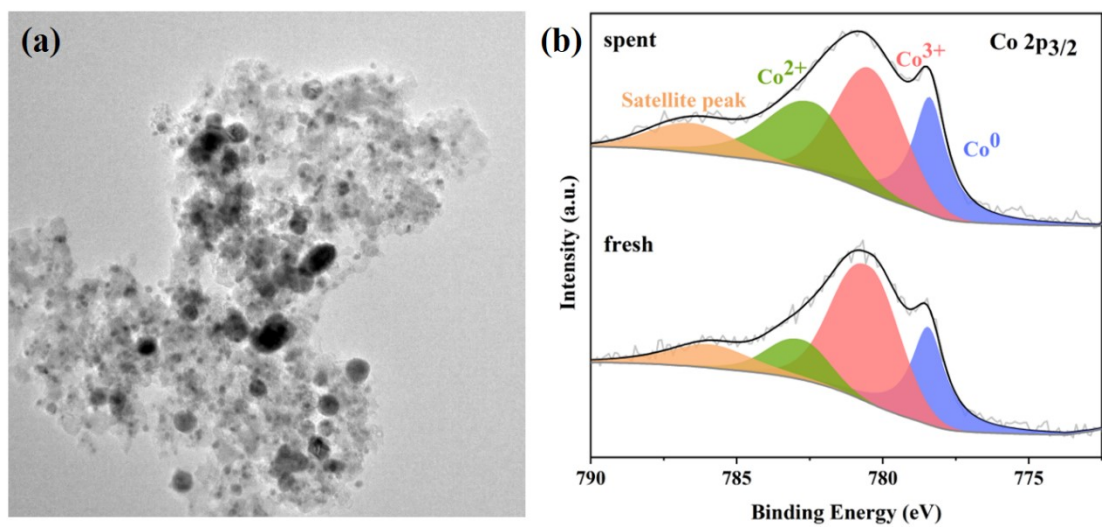


Fig. S12 (a)TEM and (b) High-resolution XPS of Co 2p<sub>3/2</sub> of spent catalyst.

Table S1 Surface area, pore volume and average pore diameter of CoZn-ZIF and CoZn/CN.

Samples	BET surface area (m <sup>2</sup> ·g <sup>-1</sup> )	Pore volume (mL·g <sup>-1</sup> )	Average pore diameter (nm)
CoZn-ZIF	1398.08	1.95	5.57
CoZn/CN-H <sub>2</sub> O	80.75	0.92	45.56
CoZn/CN-N <sub>2</sub>	340.92	0.74	8.63

Table S2 Relative abundance ratio of Co species valence states of CoZn/CN.<sup>a</sup>

Catalyst	Co <sup>0</sup> (%)	Co <sup>3+</sup> (%)	Co <sup>2+</sup> (%)	Satellite (%)
CoZn/CN-H <sub>2</sub> O	25.4	49.8	13.4	11.4
CoZn/CN-N <sub>2</sub>	28.0	15.0	50.0	7.0
CoZn/CN-H <sub>2</sub> O-spent	25.3	37.2	26.4	11.1

<sup>a</sup>The values were determined from the XPS peak area ratios.

Table S3 Comparison of catalytic performance for the CTH reaction of LA to GVL over recent reported catalysts.

Entry	Catalyst	Reaction conditions	GVL yield (%)	Reaction rate (mmol/h/g)	Ref.
1	CoZn/CN-H <sub>2</sub> O	180 °C, 2 h	97.8	14.67	This work
2	Co-MnO/SPCE-C	200 °C, 3 h	93.5	6.23	2
3	Zr/Fe <sub>2</sub> Al <sub>2</sub> -SP	170 °C, 1 h	89.2	44.60	3
4	MCM-ZrP1	160 °C, 8 h	89.6	0.62	4
5	Hf(1.7)@HNTs	160 °C, 4 h	97.8	4.21	5
6	ZrP(15)/SBA-15	200 °C, 2 h	60.1	5.17	6
7	ZrOH (7)	200 °C, 2 h	71.0	6.11	7
8	TY700	175 °C, 12 h	94.0	0.67	8
9	15% PTA/UiO-66@PI	240 °C, 3 h	93.2	62.13	9
10	CoAl NT <sub>160-H</sub>	160 °C, 2 h	93.5	9.35	10

## References

- 1 Y.-T. Li, L. Zhou, G.-N. Han, W.-G. Cui, W. Li and T.-L. Hu, *Int. J. Hydrogen Energy*, 2024, **51**, 452-461.
- 2 H. Zhang, Z. Yu, Y. Liang, T. Gan, Z. Huang, H. Hu and Y. Zhang, *J. Cleaner Prod.*, 2025, **503**, 145417.
- 3 X. Chen, H. Tian, L. Deng, S. Zhou, X. Yu, Z. Wang, Y. Li and Y. Tian, *Chem. Eng. J.*, 2025, **508**, 160796.
- 4 P. Hou, H. Su, K. Jin, Q. Li and W. Yan, *Molecules*, 2024, **29**, 3779.
- 5 R. Huang, Y. Wang, F. Chen, H. Liu, R. Zhang, W. Jia, L. Peng, Y. Sun and J. Zhang, *Chem. Eng. J.*, 2024, **497**, 154537.
- 6 R. Zhao and J. W. Bae, *Catal. Today*, 2024, **435**, 114718.
- 7 R. Zhao, S. Kasipandi, C.-H. Shin and J. W. Bae, *ACS Catal.*, 2023, **13**, 12711-12722.
- 8 M. T. Jayakumari and C. Kanakkampalayam Krishnan, *Appl. Catal., A*, 2023, **663**, 119318.
- 9 H. Tan, S. Rong, Z. Zong, P. Zhang, R. Zhao, F. Song, H. Cui, Z.-N. Chen, W. Yi and F. Zhang, *Phys. Chem. Chem. Phys.*, 2023, **25**, 18215-18223.
- 10 Y.-R. Shao, F. Zhao, Z.-C. Wei, Y.-F. Huo, J.-J. Dai and T.-L. Hu, *ACS Appl. Mater. Interfaces*, 2023, **15**, 26637-26649.