Electronic Supporting Information

A magnetic CoRu-CoO$_X$ nanocomposite efficiently hydrogenates furfural to furfuryl alcohol under ambient H$_2$ pressure in water

Yongxing Wang,[a] Yaowei Lu,[a] Qiue Cao[ab] and Wenhao Fang[*ab]

[a] School of Chemical Science and Technology, Key Laboratory of Medicinal Chemistry for Natural Resource - Ministry of Education, Functional Molecules Analysis and Biotransformation Key Laboratory of Universities in Yunnan Province, Yunnan University, 2 North Cuihu Road, 650091 Kunming, China. wenhao.fang@ynu.edu.cn

[b] National Demonstration Center for Experimental Chemistry and Chemical Engineering Education, Yunnan University.

1. Experimental details

Materials and reagents

All the chemicals were used as received without further purification or treatment. Cobalt(II) nitrate hexahydrate (98%) from Alfa Aesar, ruthenium(III) chloride (37−40% on Ru basis) from Innochem, and sodium borohydride (98%) from Acros Organics were used for catalyst preparation. The pure phase Co_3O_4 and CoO nanoparticles were purchased from Alfa Aesar. Furfural (FF, 99%), furfuryl alcohol (FA, 99%), 2-methylfuran (2-MF, 99%), tetrahydrofurfuryl alcohol (THFA, 99%), and furan (99%) from Acros Organics were used for catalytic reaction and quantitative analysis.

Catalyst preparation

0.09 mmol ruthenium(III) chloride and 3.0 mmol cobalt(II) nitrate hexahydrate were first dissolved in 250 mL deionized water and stirred for 15 min. Then 160 mL freshly made sodium borohydride solution (4 g/mL) was dropwise added, and the slurry was stirred by mechanical agitation (350 rpm) at ambient temperature for 2 h. The solid was recovered by filtration and washed by excessive deionized water to completely remove Na^+ and Cl^- ions. The solid was afterwards oven-dried at 100 °C overnight. Finally, the solid was reduced in H_2 at 350 °C (5 °C/min) for 30 min to obtain the magnetic catalysts donated as CoRu-CoO$_X$. This protocol was also applicable to prepare the reference catalysts Co-CoO$_X$ (without Ru) and CoM-CoO$_X$ (M = Au, Pd, Pt or Ir).

Catalytic reaction

Hydrogenation of furfural (FF) was performed in a batch-type Teflon-lined stainless-steel autoclave. The volumes of the autoclave and the Teflon container are 50 mL and 40 mL, respectively. Typically, 1 mmol FF, 30 mg catalyst and 5 mL deionized water (reaction solvent) were added into the reactor. After evacuation of the remaining air and purge with Ar, H_2 was introduced till the pressure was stabilized at 0.1 MPa. The reactor was placed in an oil bath pre-heated at 120 °C with magnetic stirring at 900 rpm. After a fixed reaction time (typically 4 h unless otherwise specified), the reactor was quickly put into ice water. And then the used catalyst was separated by magnet and completely washed by ethanol and water three times followed by drying at 80 °C under vacuum for 12 h and H_2 treatment at 350 °C for 0.5 h before

the next use.

The reactant and products were analyzed on an Agilent 1260 Infinity high performance liquid chromatography (HPLC) armed with a photodiode array detector (DAD) and a C18 column using CH_3CN/H_2O solution (v/v=1) as mobile phase. The quantification was based on the external standard method using FF, FA, 2-MF, THFA and furan as standard chemicals. Conversion of FF and selectivity of each product were defined as the molar percentage of FF converted and the molar percentage of each product formed in FF converted, respectively. Both conversion and selectivity were calculated on a carbon basis. Each reaction was repeated twice at least to guarantee a reproducible result, and the error of the data must be no more than 2%.

$$\text{Conv.}\,(\%) = \frac{n_{FF,0} - n_{FF,t}}{n_{FF,0}}$$

$$\text{Select.}\,(\%) = \frac{n_{product}}{n_{FF,0} - n_{FF,t}}$$

$$\text{Yield}(\%) = \frac{n_{product}}{n_{FF,0}}$$

Characterization methods

The loadings of Ru and Co were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) technique using an Agilent 7500a apparatus. The solid sample was thoroughly dissolved by a mixed solution of HCl and HNO_3 and the obtained solution was placed at room temperature overnight. X-ray diffraction (XRD) analysis was carried out on a Rigaku TTR III Diffractometer provided with Cu Kα radiation (λ = 1.5418 Å) and a beam voltage of 40 kV. The patterns were registered in the 2θ domain (10−90°) with a measured step of 0.02° and a time integration of 0.2 s. Transmission electron microscopy (TEM) measurement was conducted on a Philips-FEI TECNAI F30 field-emission electron microscope operated at an acceleration voltage of 300 kV. Samples for TEM measurements were suspended in ethanol and dispersed ultrasonically. Drops of the suspension were applied on a lacey support film. X-ray photoelectron spectroscopy (XPS) analysis was performed under ultra-high vacuum on a Thermo Scientific Escalab 250Xi system provided with Al Kα radiation. The binding energy shift due to the surface charging was adjusted using a reference to the C 1s line at 284.6 eV. Hydrogen temperature-programmed reduction

(H_2-TPR) was carried out on a Micromeritics Autochem II Chemisorption analyzer. The sample was treated in a 5% H_2/Ar (in vol.) mixed gas with a flow rate of 30 mL/min. The temperature was increased to 800 °C at a rate of 10 °C/min. The CO-adsorbed *in situ* diffuse reflectance Fourier transform infrared (DRIFT-IR) spectra were obtained on a PerkinElmer Frontier FT-IR Spectrometer equipped with MCT detector and 10-cm Demountable Gas Cell (resolution: 4 cm^{-1}, scan number: 32). The catalyst was pre-treated in H_2 flow (20 mL/min) at 350 °C (5°/min) for 30 min and then cooled down to 30 °C. Afterwards the solid was purged by Ar at 30 °C for 20 min and the DRIFT-IR background spectrum was recorded. The solid was further treated in pure CO flow (99.99%) at 30 °C for 60 min and subsequently purged by Ar to remove the free CO before the DRIFT-IR spectra were collected.

2. Complementary data

Table S1 Comparison of the catalytic performances of CoRu-CoO$_X$ catalyst to Co- and Ru-based benchmark catalysts for hydrogenation of FF to FA in water.

Entry	Catalyst	FF (mmol)	$W_{Catal.}$ (mg)	$P H_2$ (MPa)	T (°C)	Time (h)	Conv. FF (%)	Select. FA (%)	Reuse time	Ref.
1	Co/ZrLa$_{0.2}$O$_Y$	6.24	50	2	40	10	98	97	4	1
2	Co/NCNTs	1.0	30	4	80	8	100	100	6	2
3	RuSn$_{0.4}$/C	5.43	250	1.25	90	5	95	91	2[a]	3
4	CoRu-CoO$_X$	1.0	40	0.1	120	4	100	100	5	–

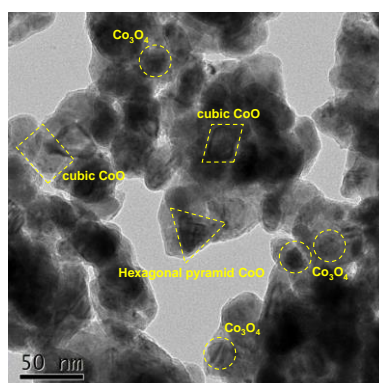[a] Catalyst was deactivated.

Fig. S1 TEM image of the CoRu-CoO$_X$ catalyst with the schematic mark of the representative morphologies for CoO and Co$_3$O$_4$.

References

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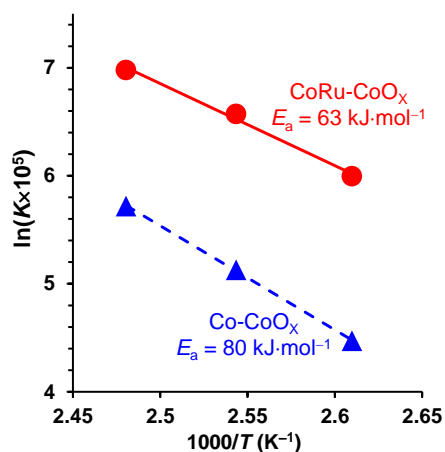3 J. J. Musci, A. B. Merlo and M. L. Casella, *Catal. Today*, 2017, **296**, 43.

Fig. S2 Arrhenius plot of FF conversion in H_2. Reaction conditions: FF, 1 mmol; catalysts, 30 mg; H_2O, 5 mL; H_2, 0.1 MPa; temperature, 100–120 °C; time, 4 h.
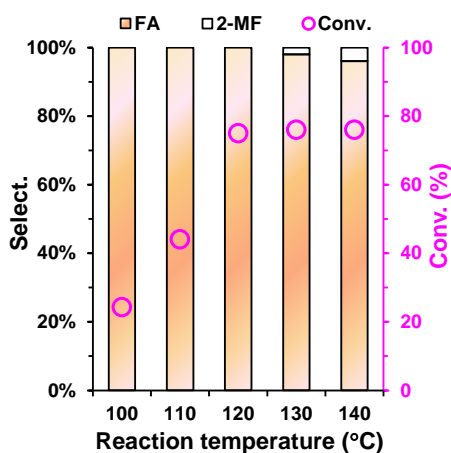

Fig. S3 Conversion of FF and selectivity distribution of products during hydrogenation of FF over the CoRu-CoO$_X$ catalyst *versus* reaction temperature. Reaction conditions: FF, 1 mmol; catalysts, 30 mg; H_2O, 5 mL; H_2, 0.1 MPa; time, 4 h.
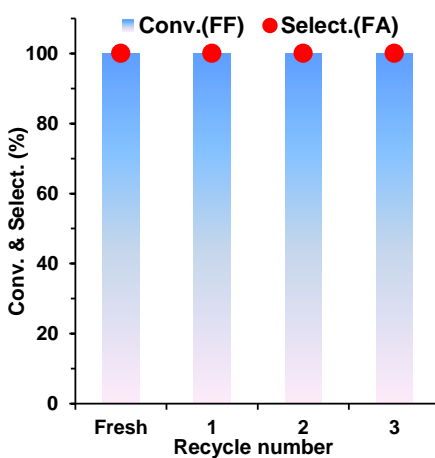

Fig. S4 Recycling test of the CoRu-CoO$_X$ catalyst for hydrogenation of FF to FA. Reaction conditions: FF, 1 mmol; catalyst, 40 mg; H_2O, 5 mL; H_2, 0.1 MPa; temperature, 120 °C; time, 4 h.