Cellulose Hydrogenolysis to Alcohol and Ketone Products Using Co@C Catalysts in Phosphoric Acid Aqueous Solution

Haosheng Xin[a,b,c,d], Haiyong Wang[a,b,c], Xiaohong Hu[a,b,c], Xiuzheng Zhuang[a,b,c], Long Yan[a,b,c*], Chenguang Wang[a,b,c], Longlong Ma[e], Qiying Liu[a,b,c*]

[a]Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, P. R. China

[b]CAS Key Laboratory of Renewable Energy, Guangzhou 510640, P. R. China

[c]Guangdong Provincial Key Laboratory of New and Renewable Energy Research and Development, Guangzhou 510640, P. R. China

[d]University of Chinese Academy of Sciences, Beijing 100049, P. R. China

[e]Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing 210096, China

[*]**Corresponding author. Email**: liuqy@ms.giec.ac.cn.

Fax: +86-20-8705-7673; Tel: +86-20-3702-9839

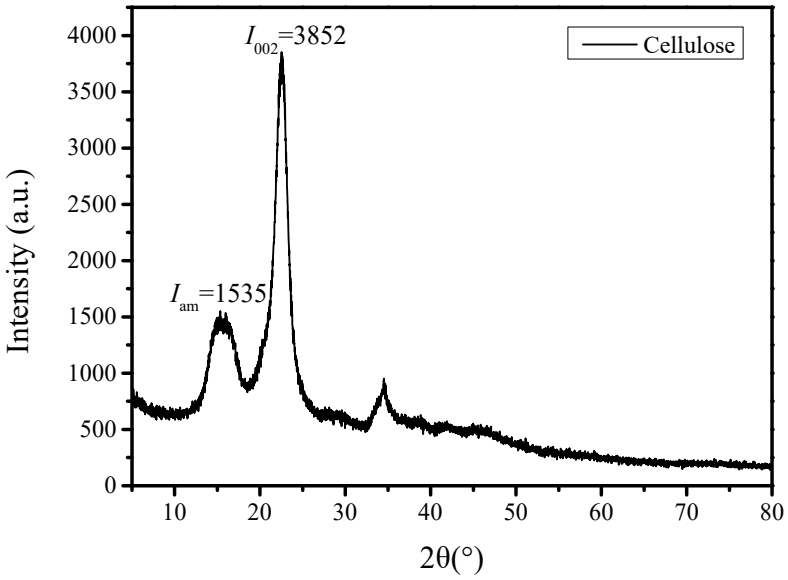
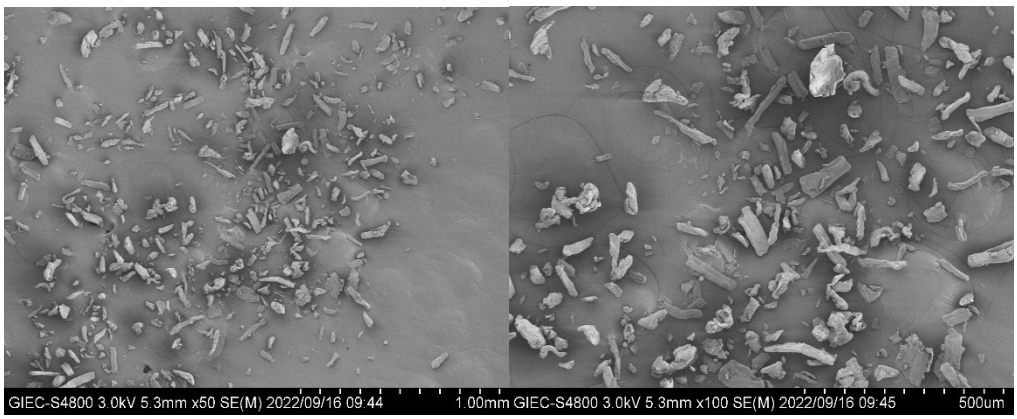


Figure S1. The XRD spectrum of cellulose

$$Cellulose_{crysrallinity} = \frac{I_{002} - I_{am}}{I_{002}} \quad \text{(S1)}$$

Here, I_{002} is the diffraction intensity of 002 crystal face, I_{am} is the diffraction intensity of the amorphous part.



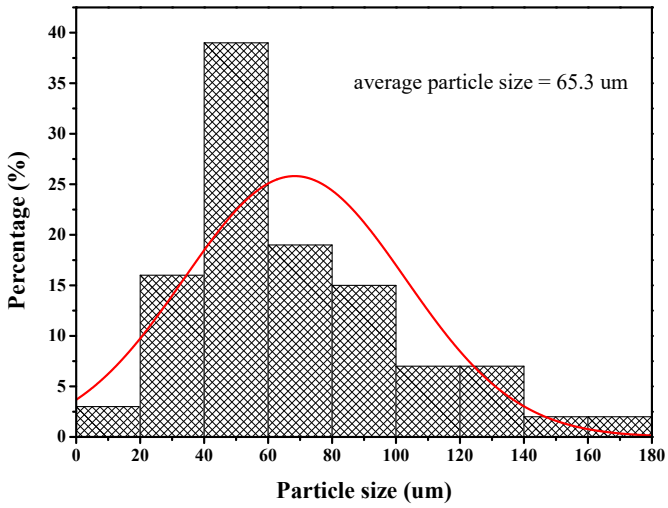


Figure S2. SEM images of cellulose

Here, we take the length of the cellulose particle as the benchmark and measure one hundred units to obtain the data in the Figure S2.

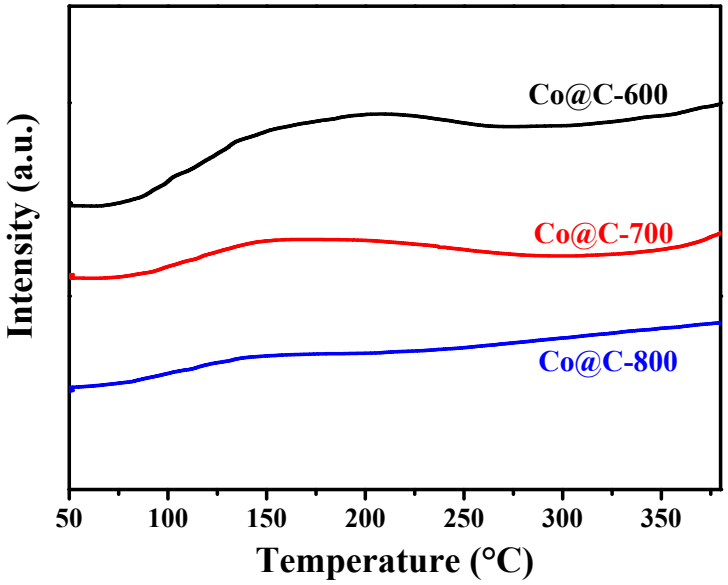


Figure S3. H_2-TPD profiles of Co@C catalyst samples.

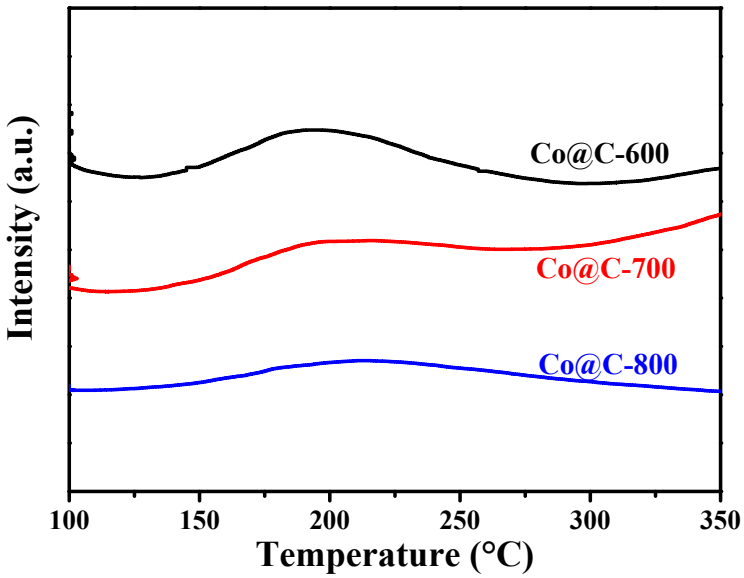


Figure S4. NH_3-TPD profiles of Co@C catalyst samples.

Table S1. Acid mount of Co@C catalysts determined by NH_3-TPD.

Ctalyst	Co@C-600	Co@C-700	Co@C-800
Acid amount (mmol/g)	0.034	0.027	0.019

Table S2. Reaction time to the gas phase distribution of Co@C-700 catalyst for cellulose hydrogenolysis.

Time (h)	Conversion (%)	Gas phase yield (C-mol%)	CH_4 Selectivity (%)	C_2H_6 Selectivity (%)	C_3H_8 Selectivity (%)	C_4H_{10} Selectivity (%)	n-C_6H_{14} Selectivity (%)	CO_2 Selectivity (%)
2	57	2.2	53.5	0	0	0	2.0	44.5
2.5	99	4.4	50.5	0	0	2.8	7.0	39.7
3	100	4.3	56.5	0	1.5	2.0	1.9	38.1
3.5	100	6.3	53.4	0	0	1.7	3.3	41.6
4	100	5.7	53.1	1.5	2.0	2.2	2.5	38.7

Reaction conditions: 210 °C, 0.1 g cellulose, 50 mg Co@C-700, 5.5 MPa H_2, 5 ml 0.06 M H_3PO_4, 800 rpm.

Table S3. The CHN elemental analysis of Co@C catalysts via two parallel tests.

Catalyst	Run	C (%)	H (%)	N (%)
Co@C-600	1	21.00	0.84	0.20
	2	21.19	0.86	0.19
Co@C-700	1	22.89	0.74	0.14
	2	22.47	0.73	0.15
Co@C-800	1	58.44	0.50	0.14
	2	62.89	0.34	0.14

Table S4. Ethanol conversion over Co@C-700 catalyst in H_3PO_4

Entry	Ethanol dosage (g)	Reaction time	Conversion	Gas phase yield (C-mol%)	Gas products selectivity		
					CH_4	C_2H_6	CO_2
1	0.1007	0.5 h	3.2%	2.23	53.4	0.5	46.1
2	0.1003	1.0 h	5.9%	3.74	51.4	3.2	45.4

Reaction conditions: 210°C, 50 mg Co@C-700, 5.5 MPa H_2, 5 ml 0.06 M H_3PO_4, 800 rpm.

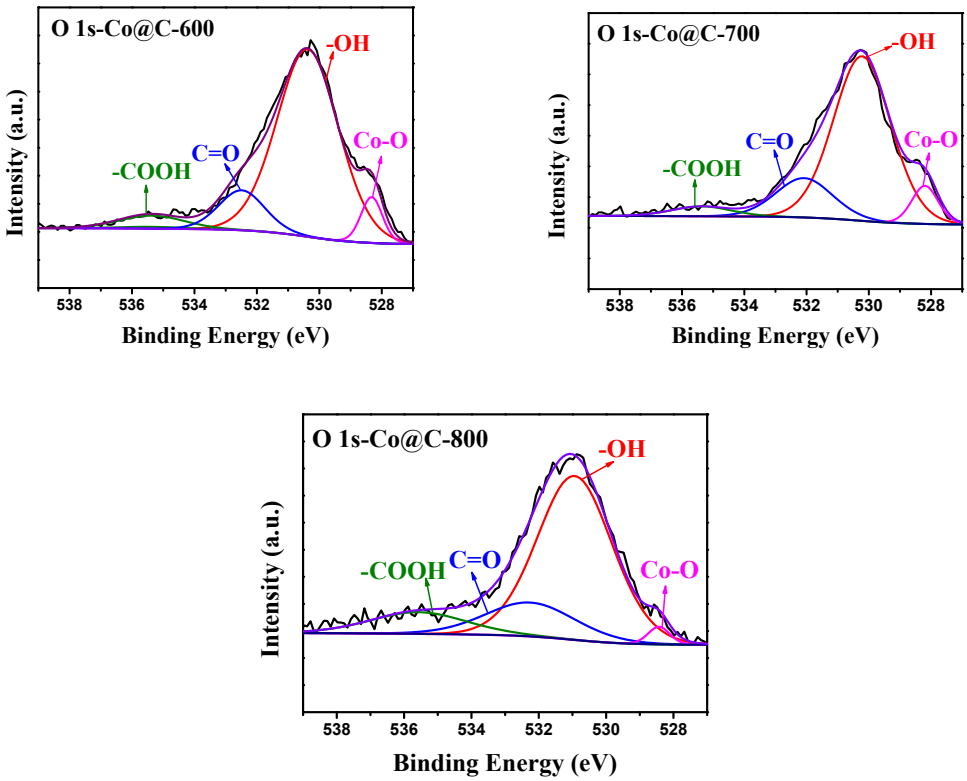


Figure S5. O_{1s} XPS spectra of Co@C catalysts at different calcination temperature

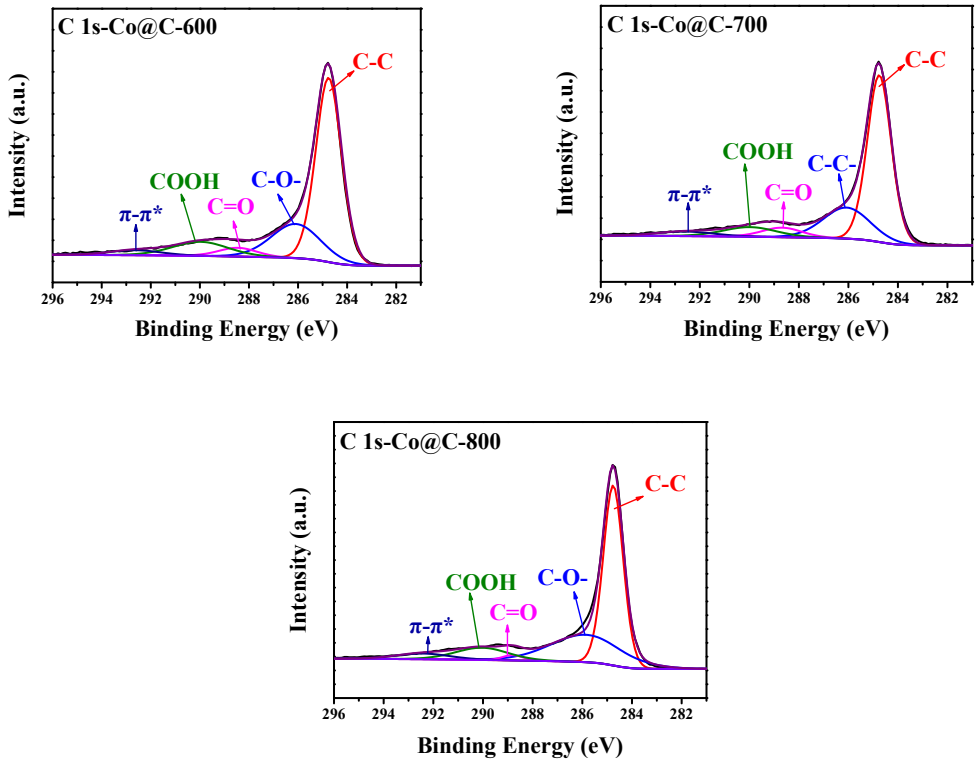


Figure S6. C_{1s} XPS spectra of Co@C catalysts at different calcination temperature

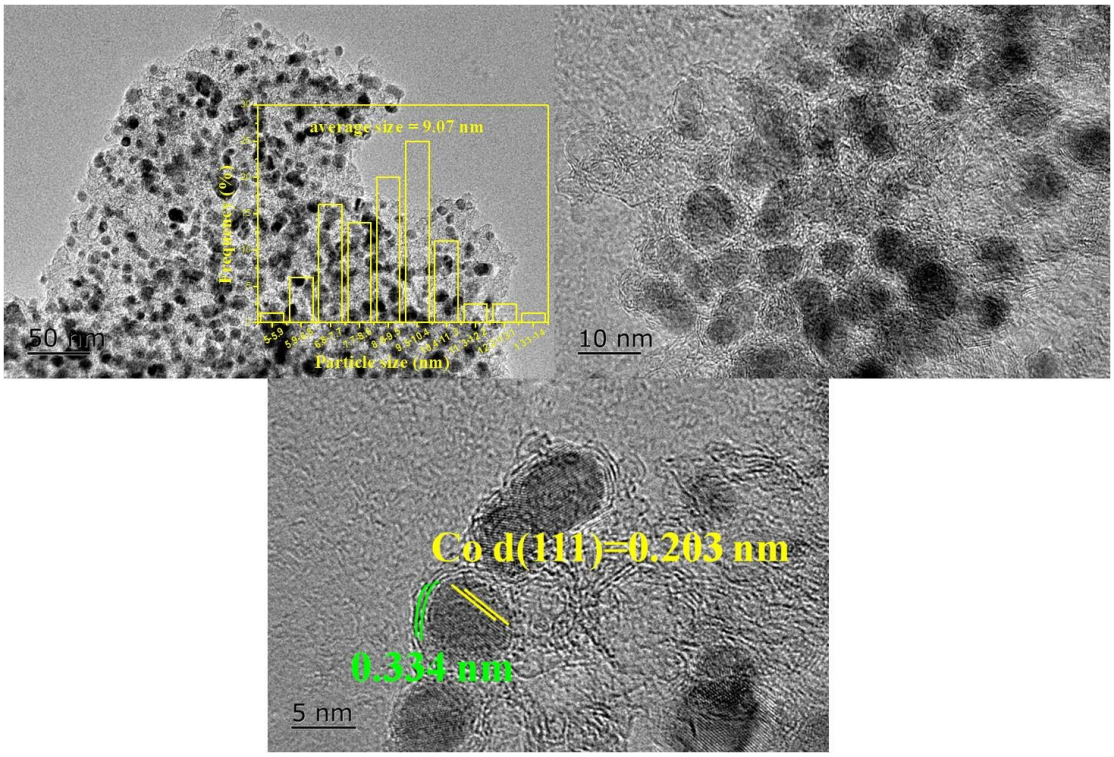


Figure S7. TEM images and statistical distribution of Co@C-700 particle size after 5 runs

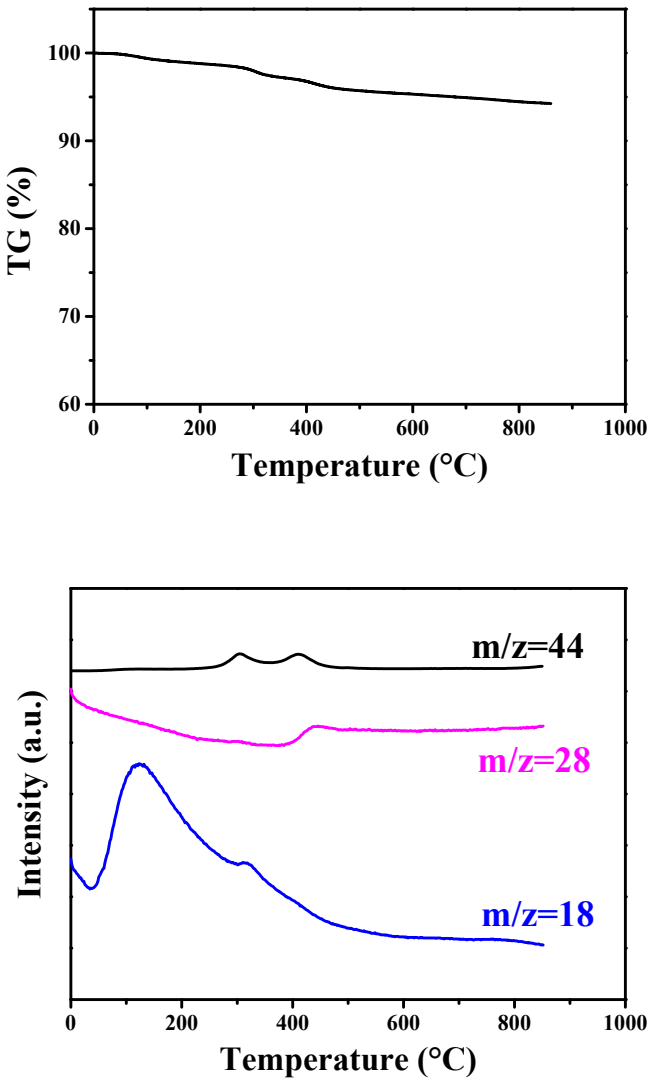


Figure S8. TG-MS analysis of Co@C-700 catalyst.

The experiment was conducted at the heating rate of 10 °C/min under 100 ml/min N_2 flow. The outlet gases from the decomposition was monitored by H_2O (m/z=18), CO (m/z=28), CO_2 (m/z=44). Two main weight losses of about 2.5% and 3.5% were observed in the range of 50 °C - 250 °C and 300 °C -600 °C during the decomposition, respectively. Based on the MS measurements, the weight losses (below 210 °C) were mainly ascribed to the H_2O desorption of Co@C-700 catalyst