

## Electronic Supplementary Information

### **Bicontinuous mesoporous Co, N co-doped carbon catalysts with high catalytic performance for ethylbenzene oxidation**

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## 1. General

Tetraethoxysilane (TEOS, 98% purity), Pluronic P123 EO-PO-EO triblock copolymer ( $M_w = 5800$ ), propionic acid, benzaldehyde, pyrrole, ethanol, *N,N*-dimethyl formamide (DMF), cobalt chloride hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), ethylbenzene, sucrose were obtained from commercial sources and used as received without further purification.

## 2. Experimental

### 2.1 Synthesis of 5, 10, 15, 20-tetraphenylporphyrin

The cobalt porphyrin was prepared based on a reported method<sup>1</sup>. First, a mixture containing propionic acid (150 mL) and benzaldehyde (5.56 g) was heated to reflux in 500 mL three-necked flask and kept refluxed for an hour with constant stirring after the distilled and diluted pyrrole was added. Subsequently, 100 mL deionized water was added after the mixture cooled down to ambient temperature and then refrigerated overnight. After that, the resulting product was collected by filtration, wash and purification by column chromatography and marked as TPP. The <sup>1</sup>H-NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) -2.7 (s, 2H, N-H), 7.78 (d, 12H, Ar-H), 8.22(d, 8H, Ar-H),  $\delta$  8.85 (s, 8H, pyrrole-H). UV-vis ( $\lambda$ ) 438, 479, 513, 536, 591 and 650 nm.

### 2.2 Synthesis of 5, 10, 15, 20-tetraphenylporphyrin

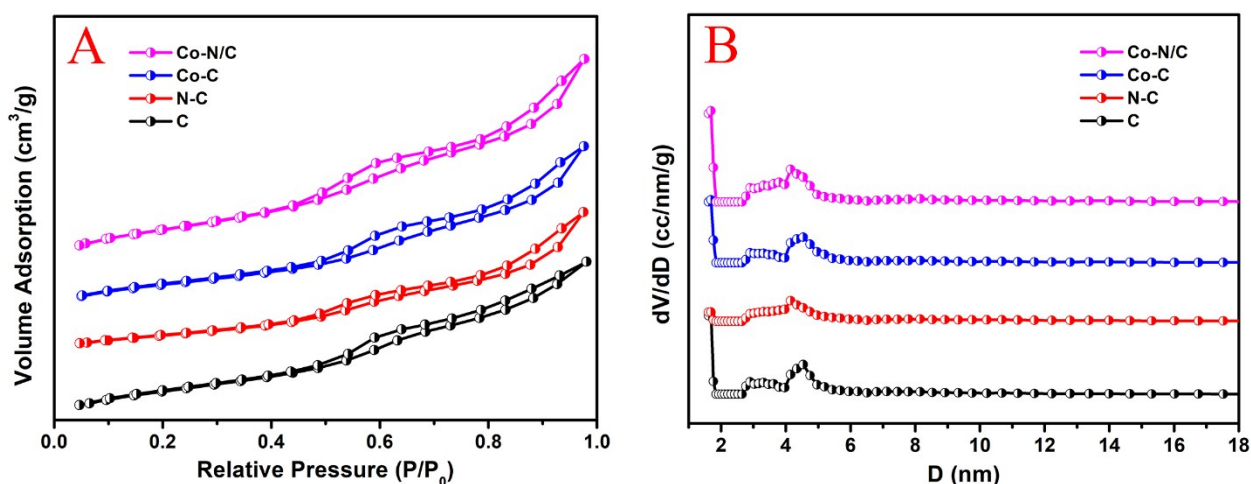
The obtained TPP (1.0 g) was added to a flask containing 100 mL *N,N*-dimethyl formamide and heated to refluxing. Then, 2.5 g  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  was added in batches and 100 mL deionized water was added when cooled to room temperature. The received precipitate was filtered and washed repeatedly with deionized water, and then dried at

80°C for 12 hours in vacuum oven. The finally obtained solid material was marked CoTPP. UV-vis ( $\lambda$ ) 434, 524 and 626 nm.

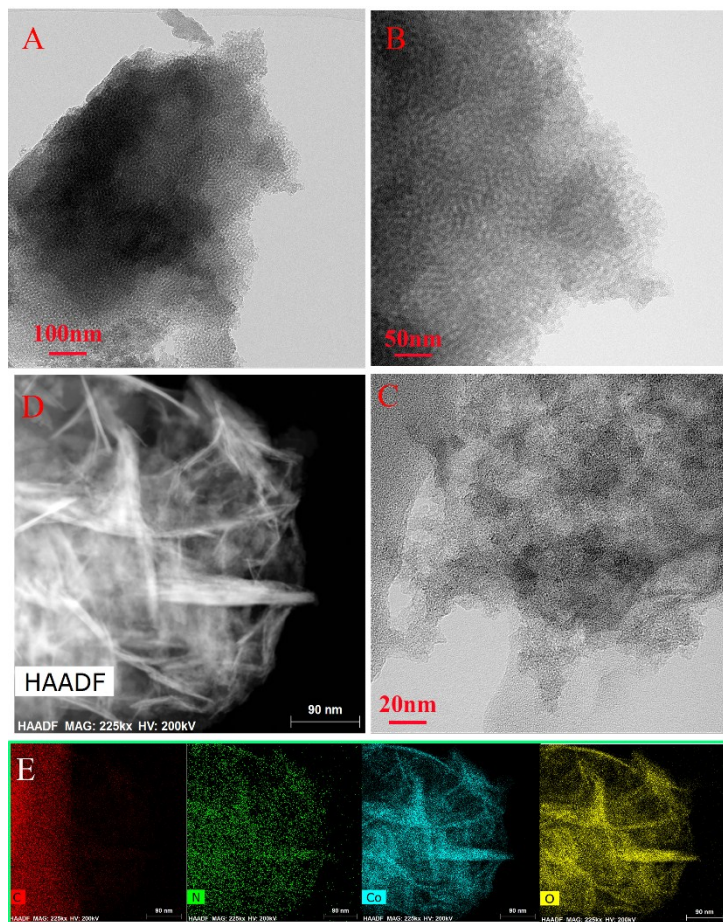
### 2.3 Synthesis of KIT-6

The synthesis of KIT-6 was carried out in a mixed acidic solution of butanol and Pluronic P123. TEOS is recommended as a silica source. In a typical synthesis, 4.0 g of P123 was dissolved in 144 g of distilled water and 7.9 g of concentrated HCl (35%) and then stirred at 35 °C until P123 was entirely dissolved. 4.0 g of butanol was added under stirring at 35 °C. After 1 h stirring, 8.6 g of TEOS was added in the mixture solution, and continues stirring at 35 °C for 24 h. Following, the mixture was transferred to a Teflon-lined autoclave and heated at 100 °C for 24 h. The resulting white precipitates were filtered, and washed with deionized water, and dried at 100 °C for 24 h. Finally, the mesoporous KIT-6 was obtained after calcination at 550 °C in air for 5 h.

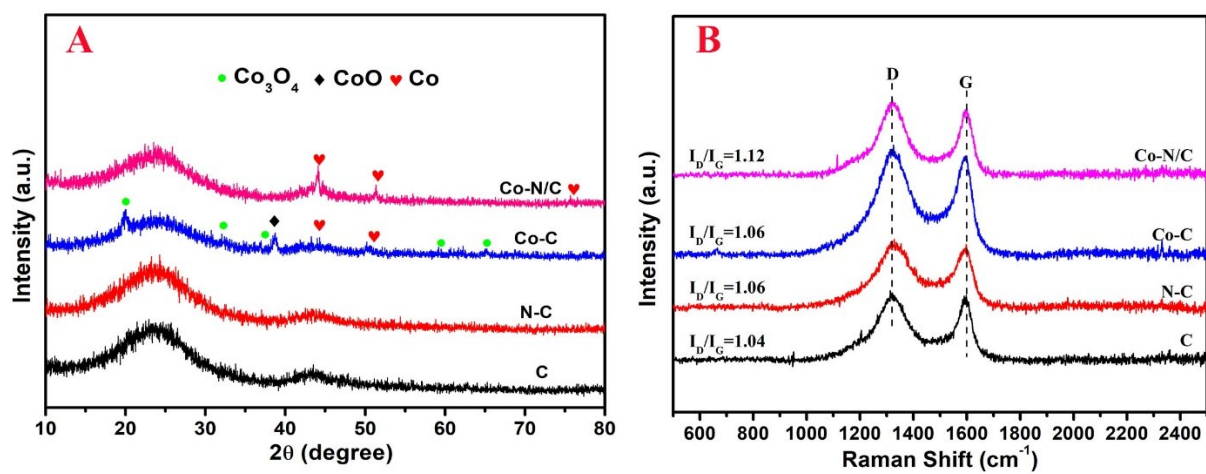
### 3. Characterization and results



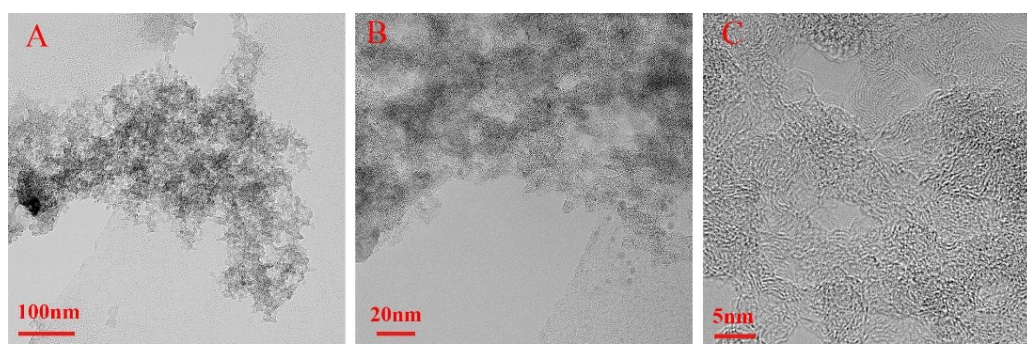
**Fig. S1** A, B) TEM images of KIT-6; C, D) TEM, and E, F, G, H) the corresponding element maps of the Co-C catalyst.



**Fig. S2** A, B) TEM images of KIT-6; C, D) TEM, and E) the corresponding element maps of the Co-C catalyst.



**Fig. S3** XRD analysis and Raman spectra analysis of Co-N/C, Co-C, N-C, C.



**Fig. S4** A, B, C) TEM and HRTEM images of the Co-N-C-10-R.

**Table S1** The results of N<sub>2</sub> adsorption-desorption measurements of Co-N-/C, Co -C, N-C, C and Co-N-C-10-R.

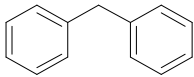
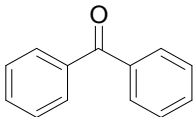
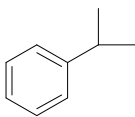
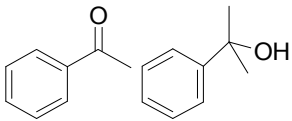
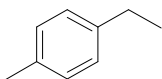
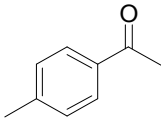
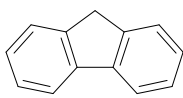
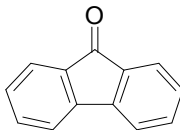
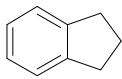
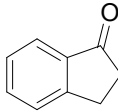
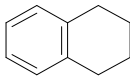
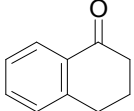
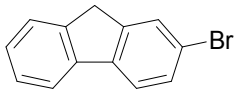
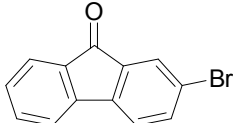
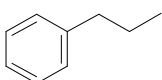
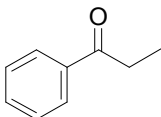
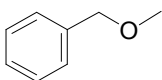
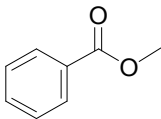
Sample	D <sub>p</sub> (nm)	S <sub>BET</sub> (m <sup>2</sup> /g)			V <sub>p</sub> (cm <sup>3</sup> /g)		
		S <sub>total</sub>	S <sub>micro</sub>	S <sub>meso</sub>	V <sub>total</sub>	V <sub>micro</sub>	V <sub>meso</sub>
Co-N/C	4.70	859	378	481	1.01	0.22	0.79
Co-C	5.05	618	226	392	0.78	0.13	0.65
N-C	8.37	261	-	261	0.55	-	0.55
C	4.22	792	399	393	0.84	0.23	0.61
Co-N-C-10-R	8.66	347	-	347	0.75	-	0.75

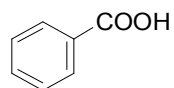
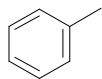
S<sub>BET</sub>: BET surface area; S<sub>total</sub>: BET surface area; S<sub>micro</sub>: micropore surface area; S<sub>meso</sub>: mesopore surface area; S<sub>meso</sub>=S<sub>total</sub>-S<sub>micro</sub>; V<sub>p</sub>: pore volume; V<sub>total</sub>: total pore volume; V<sub>micro</sub>: micropore volume; V<sub>meso</sub>: mesopore volume; V<sub>meso</sub>=V<sub>total</sub>-V<sub>micro</sub>; D<sub>p</sub>: average pore diameter

**Table S2** Elemental composition on Co-N-C-10, Co -C, N-C, Co-N-/C and Co-N-C-10-R.

Sample	N/% (XPS)				Co/% (XPS)				C/% (XPS)	O/% (XPS)
	total	Pyridinic N	Pyrolic N	Graphitic N	total	Co <sup>0</sup>	Co-O	Co-N		
Co-N-C-10	1.52	47.6	35.2	17.2	0.44	6.9	40.6	52.5	79.24	18.80
Co-C	-	-	-	-	1.22	0	21	79	88.99	9.78
N-C	1.34	17.0	58.5	24.5	-	-	-	-	79.29	19.37
Co-N/C	1.55	40.4	27.5	32.1	0.62	22.9	38.7	38.6	78.66	19.17
Co-N-C-10-R	0.94	28.3	34.6	37.1	0.41	8.9	52.1	39.0	84.96	13.68

**Table S3** Catalytic oxidation several of substrates by Co-N-C-10.

Entry	Substrate	Product	Conv./%
1			99
2		 3.6:1	89
3			91
4			99
5			97
6			97
7			>99
8			89
9			>99



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Reaction conditions: substrate (1.0 mmol), TBHP (3.5 mmol, 70 wt% in water), catalyst (15 mg), H<sub>2</sub>O (3 mL), 80 °C, 6 h; the conversion was determined by GC.

## Notes and references

[1] Y. Chen, L. Fu, Z. Liu and Y. Wang, *ChemCatChem*, 2016, **8**, 1782–1787.