

## **Green and efficient catalytic oxidation of ethylbenzene to acetophenone over cobalt oxide supported on carbon material derived from sugar**

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## 2. Experimental section

### 2.1. Catalyst preparation

Table S1 Primary materials in the experiment

Chemicals	Chemical formula	Purity	Sources of Chemicals
cobalt acetate	$(\text{CH}_3\text{COOH})_2\text{Co}\cdot 4\text{H}_2\text{O}$	AR	Sinopharm Chemical Co.,Ltd.
acetic acid	$\text{CH}_3\text{COOH}$	AR	Sinopharm Chemical Co.,Ltd.
acetonitrile	$\text{CH}_3\text{CN}$	AR	Sinopharm Chemical Co.,Ltd.
potassium bromide	KBr	AR	Tianjin Kemiou Chemical Reagent Co., Ltd
alcohol	$\text{C}_2\text{H}_5\text{OH}$	AR	Tianjin Kemiou Chemical Reagent Co., Ltd
hydrochloric acid	HCl	AR	Tianjin Kemiou Chemical Reagent Co., Ltd
ethylbenzene	$\text{C}_6\text{H}_6$	AR	Beijing Energy Engineering Technologies Co.,Ltd.
Hydrogen peroxide	$\text{H}_2\text{O}_2$	30%	Xinxing reagent co., ltd.
sugar			Zuoyuan Group Co., Ltd.
edible sugar (production in February 2022)			Nanchang Economic and Technological Development Zone Hongping Food Factory

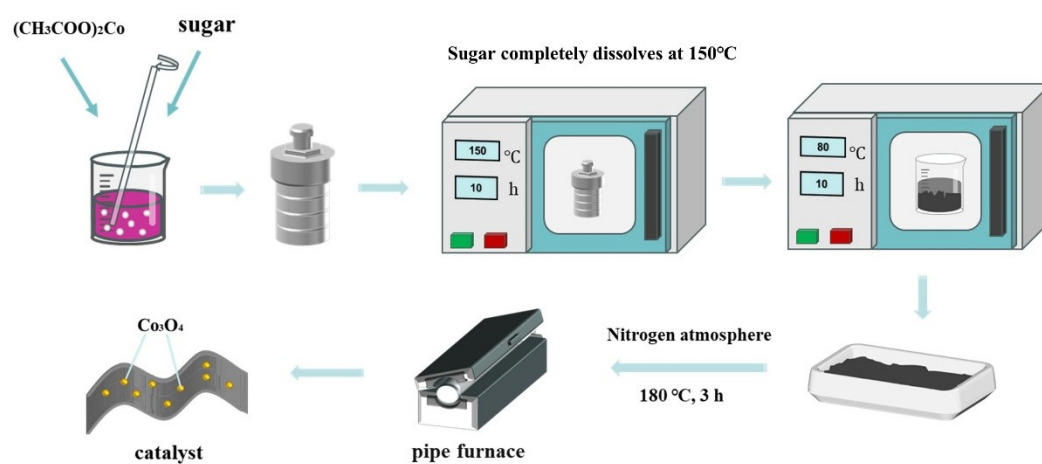


Fig.S1 The preparation process of  $\text{CoO}_x/\text{SC}-10$  *in situ*.

### 3. Results and discussion

#### 3.1. Catalyst characterization

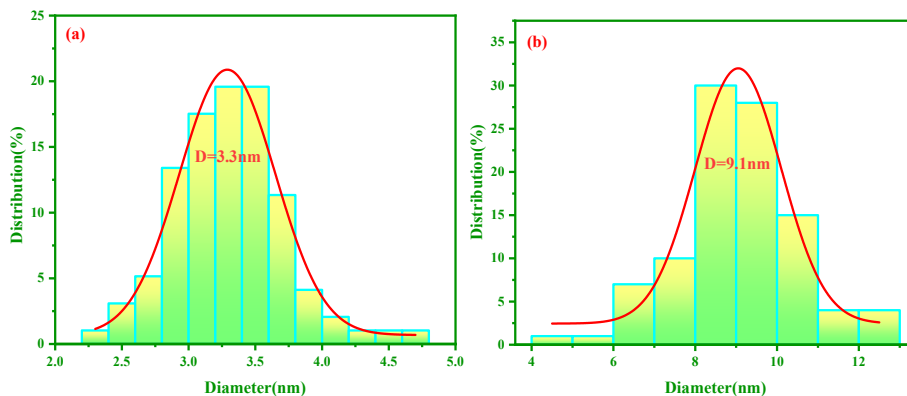


Fig.S2 Particle size distribution of (a)CoO<sub>x</sub>/SC-10-*in situ*, (b)CoO<sub>x</sub>/SC-10-*im*.

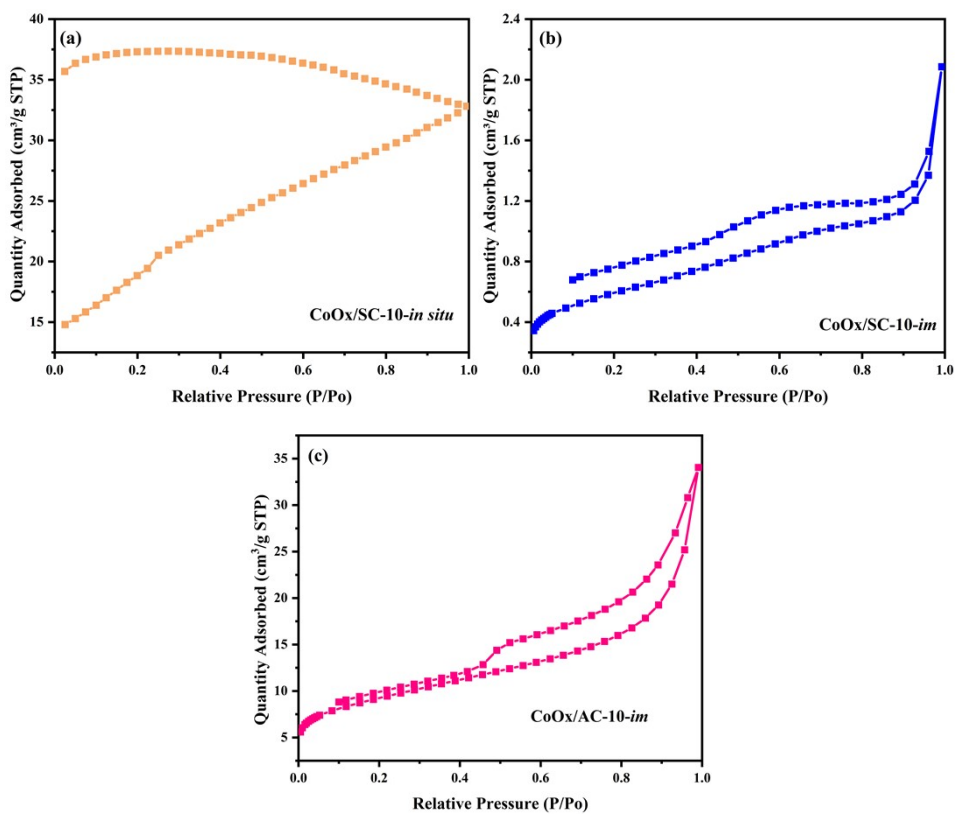


Fig.S3 N<sub>2</sub> adsorption-desorption isotherms of (a) CoO<sub>x</sub>/SC-10-*in situ*, (b) CoO<sub>x</sub>/SC-10-*im*, (c) CoO<sub>x</sub>/AC-10-*im*.

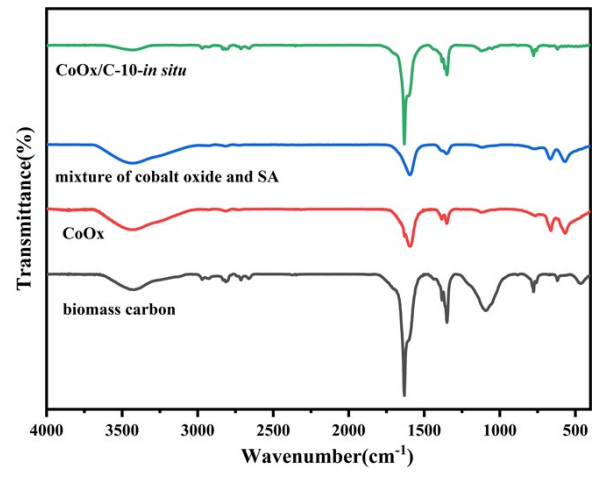


Fig.S4 FT-IR spectra of the samples.

### 3.2. Evaluation of catalytic oxidation performance

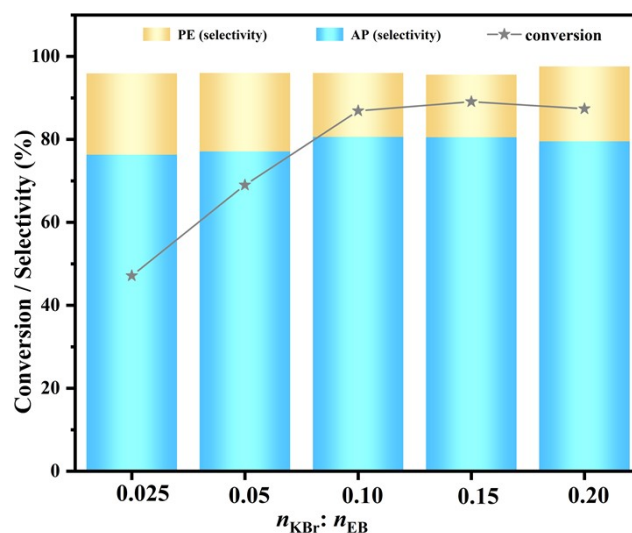


Fig.S5 The effect of the amount of additives (KBr).

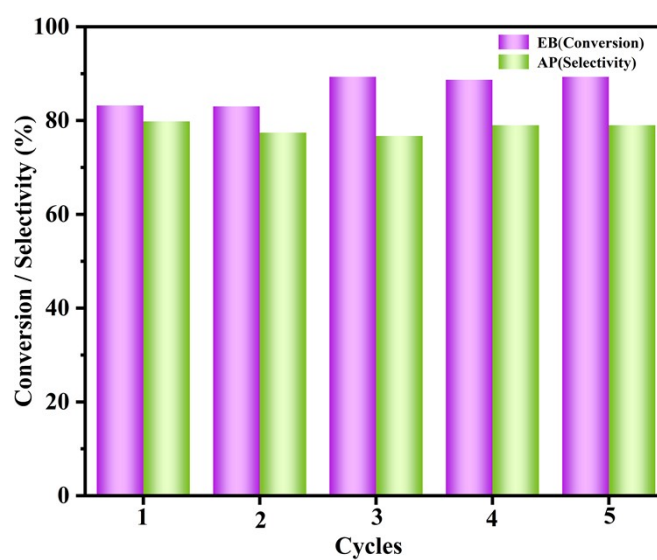


Fig.S6 Reusability of  $\text{CoO}_x/\text{SC-10}$ -*in situ* catalyst for EB oxidation. Reaction conditions:  $T=80\text{ }^\circ\text{C}$ ,  $m_{\text{catalyst}} : m_{\text{EB}}=0.15$ ,  $n_{\text{H}_2\text{O}_2} : n_{\text{EB}} : n_{\text{KBr}}=14.4 : 1 : 0.1$ ,  $t=8\text{ h}$ ,  $V_{\text{EB}} : V_{\text{CH}_3\text{COOH}}=1 : 10$ ,  $n_{\text{EB}}=0.1 : 1$ .

Table S2 Comparison of literature catalysts in the EB oxidation reaction

Entry	Catalyst	solvent	oxidant	Time /h	Temperature/ °C	Con./%(EB )	Sel./%(A P)	Literature
1	Ag/SiO <sub>2</sub>	chlorobenzene	TBHP	12	120	38	33.4	1
2	Mn/MCM-41	50 vol.% acetonitrile	TBHP	6	80	57.7	82.2	2
3	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> -APTMS-BPK-Co		TBHP	24	80	69	92	3
4	CoO-β		O <sub>2</sub>	6	160	34.6	72.9	4
5	Co-N-S-C-700		O <sub>2</sub>	5	120	48	85	5
6	Co/AC-salen-400		TBHP	4	80	47.9	83.5	6
7	Co-MCM-41(100)		TBHP	24	80	26	85	1
8	Ni/13USY		O <sub>2</sub>	5	150	21.4	76.5	7

### 3.3. Reaction mechanism

Table S3 The activity data of EB oxidation in different solvents using CoO<sub>x</sub>/SC-10-*in situ*.

Entry	solvent	Con. <sup>a</sup> (%)	Sel. <sup>b</sup> (%)
1	2.5mL acetic acid	75.12	81.06
2	2.5mL acetic acid and 1.5mL alcohol	73.27	55.82
3	2.5mL alcohol	17.24	12.53
4	2.5mL acetonitrile		
5	2.5mL acetonitrile and 0.02mLHCl(12mol/L)	66.61	73.56

Reaction conditions: T=80 °C, m<sub>catalyst</sub> : m<sub>EB</sub>=0.15, t=4 h, V<sub>EB</sub>:V<sub>CH<sub>3</sub>COOH</sub>=1:10, n<sub>H<sub>2</sub>O</sub>:n<sub>KBr</sub> : n<sub>EB</sub>=0.1 : 1. <sup>a</sup> Conversion of EB. <sup>b</sup> Selectivity of AP.

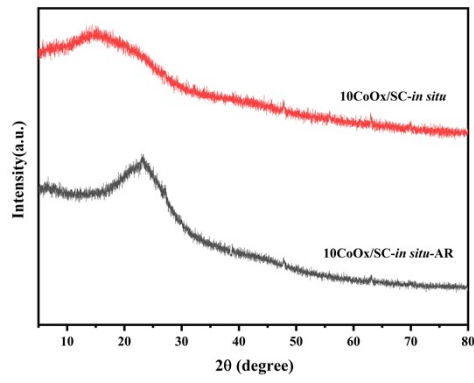


Fig.S7 XRD patterns of  $\text{CoO}_x/\text{SC}$ -10-*in situ* and  $\text{CoO}_x/\text{SC}$ -10-*in situ*-AR.

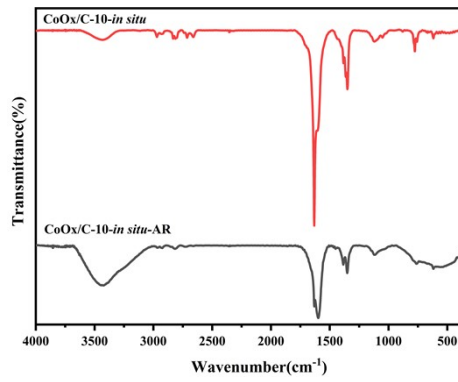


Fig.S8 FT-IR spectra of  $\text{CoO}_x/\text{SC}$ -10-*in situ* and  $\text{CoO}_x/\text{SC}$ -10-*in situ*-AR.

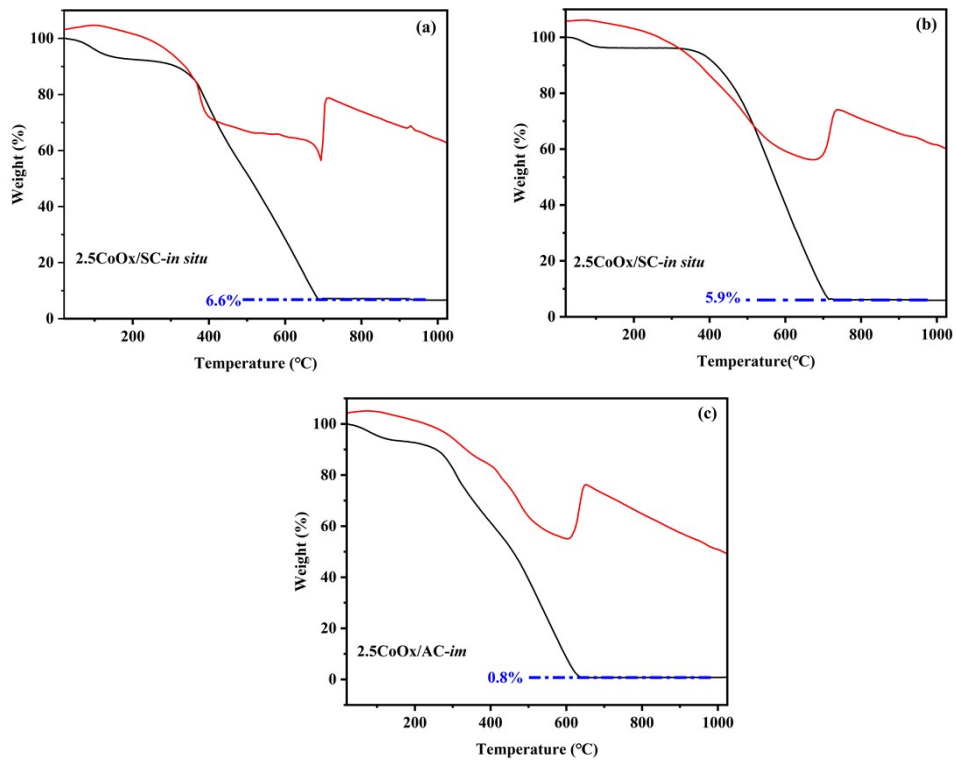


Fig.S9 TG-DSC curves of different samples (a)  $2.5\text{CoO}_x/\text{SC}$ -*in situ*, (b)  $2.5\text{CoO}_x/\text{SC}$ -*im*, (c)  $2.5\text{CoO}_x/\text{AC}$ -*im*.

## Notes and references

- 1 S. S. Bhoware and A. Singh, *J. Mol. Catal. A-Chem.*, 2007, **266**, 118-130.
- 2 K. Parida and S. S. Dash, *J. Mol. Catal. A-Chem.*, 2009, **306**, 54-61.
- 3 D. Habibi and A. R. Faraji, *C.R. Chim.*, 2013, **16**, 888-896.
- 4 G. Zhang, D. Wang, P. Feng, S. Shi, C. Wang, A. Zheng, G. Lü and Z. Tian, *Chinese J. Catal.*, 2017, **38**, 1207-1215.
- 5 W. Yan, Z. H. Chen, J. Huang, G. J. Li, J. L. Cao, B. Zhang, X. Y. Chen, H. L. Zhang and J. Lei, *T. Nonferr. Metal. Soc.*, 2018, **28**, 2265-2273.
- 6 K. Nakatsuka, T. Yoshii, Y. Kuwahara, K. Mori and H. Yamashita, *Phys. Chem. Chem. Phys.*, 2017, **19**, 4967-4974.
- 7 S. U. Nandanwar, S. Rathod, V. Bansal and V. V. Bokade, *Catal. Lett.*, 2021, **151**, 2116-2131.