

Atmospheric and Efficient Selective Oxidation of Ethylbenzene Catalyzed by Cobalt Oxides Supported on Mesoporous Carbon Nitride

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Preparation of eg-C₃N₄ and FDU-12

eg-C₃N₄: Dicyandiamide (5 g) was added into a crucible with a lid and then heated at a rate of 3 °C·min⁻¹ to reach a temperature of 550 °C and then held for another 4 h. After cooling down to room temperature, the obtained pale yellow solid was labeled as g-C₃N₄.

Exfoliated g-C₃N₄ materials were prepared by a thermal exfoliation method. Briefly, g-C₃N₄ solid (2 g) was placed into a crucible with a lid and then heated at 550 °C for 2 h. After that, the resultant powder with faint yellow was designated as eg-C₃N₄.

FDU-12: FDU-12 material was prepared using a Pluronic F127 (EO₁₀₆PO₇₀EO₁₀₆) triblock copolymer surfactant, and 1,3,5-trimethylbenzene (TMB) as an organic swelling agent. In brief, 2.0 g of F127, and 5.0 g of KCl were dissolved in 120 mL of HCl (a.q. 2 mol·L⁻¹). After that, 2.4 g of TMB and 8.3 g of tetraethyl orthosilicate were added, and the mixture was further stirred at 38 °C for 24 h. The obtained milky solution was transferred into an autoclave and heated in an oven at 140 °C for 24 h. Afterward, the white precipitate was filtered off and then rinsed with distilled water three times to remove KCl. After drying overnight at 60 °C, the resultant solid was calcined at 550 °C for 5 h to remove the surfactant.

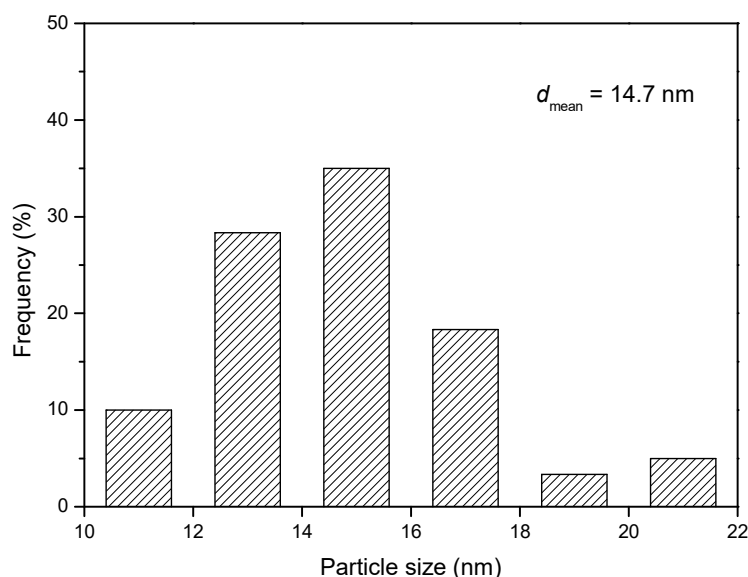


Figure S1. Particle size histogram of CoO_x in 3CoO_x/mpg-C₃N₄-400.

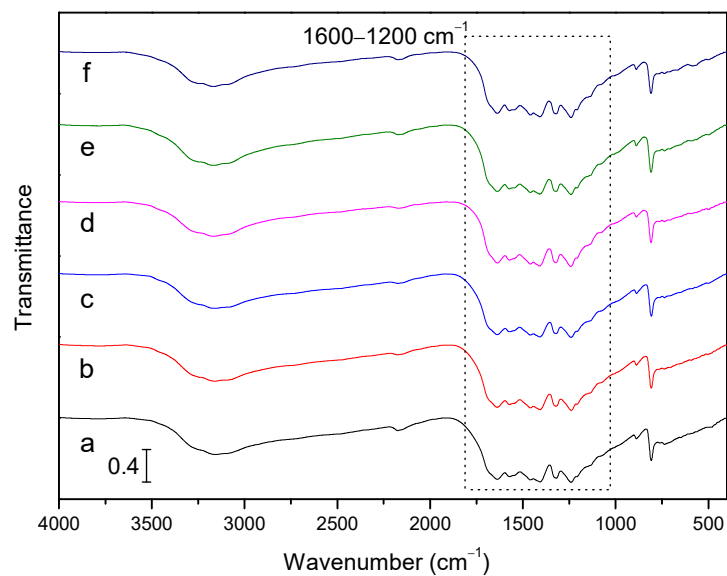


Figure S2. FT-IR spectra of mpg-C₃N₄ (a), 3CoO_x/mpg-C₃N₄-300 (b), 3CoO_x/mpg-C₃N₄-350 (c), 3CoO_x/mpg-C₃N₄-400 (d), 3CoO_x/mpg-C₃N₄-450 (e), and 3CoO_x/mpg-C₃N₄-500 (f) materials.

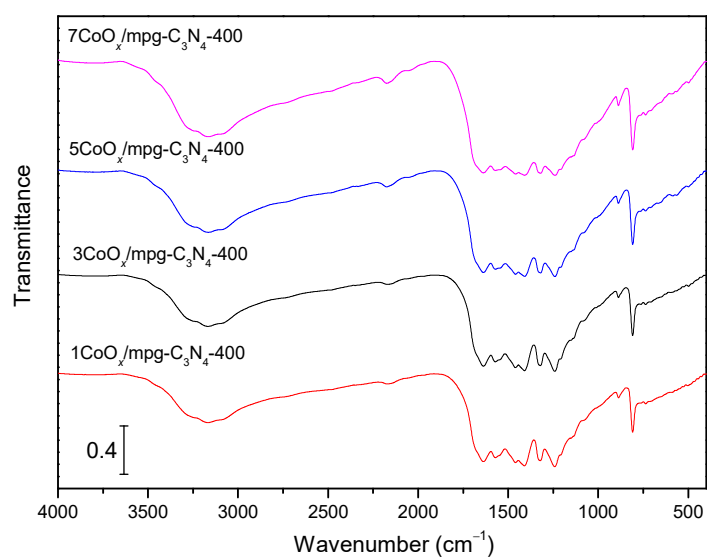


Figure S3. FT-IR spectra of mCoO_x/mpg-C₃N₄ materials.

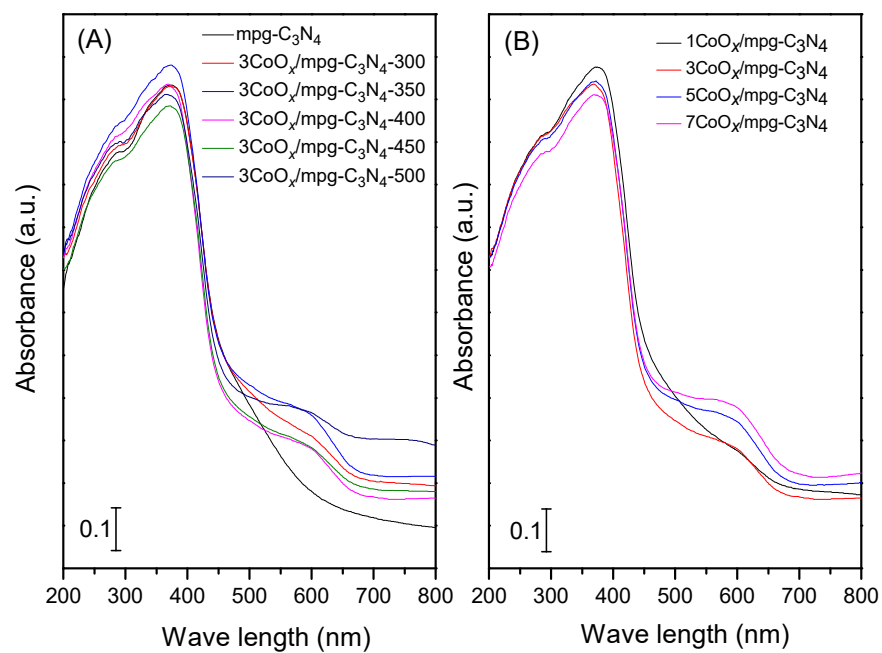


Figure S4. UV-vis spectra of mpg-C₃N₄ (A) and CoO_x/mpg-C₃N₄ materials (B).

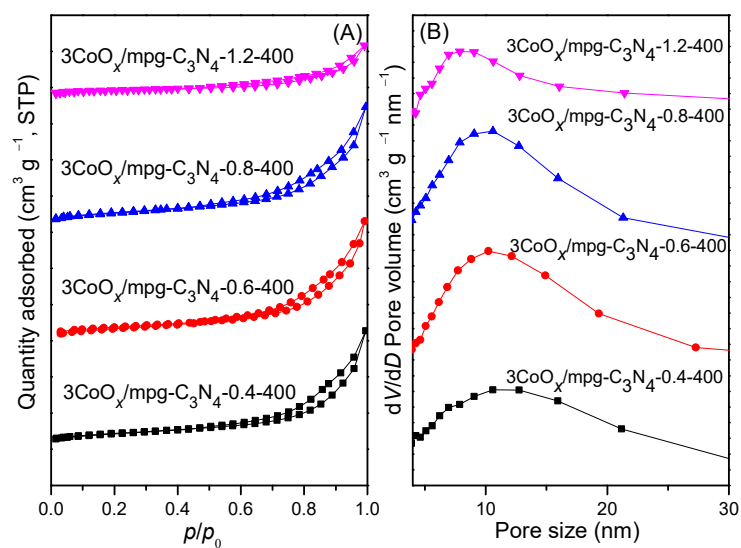


Figure S5. N₂ adsorption-desorption isotherms (A) of 3CoO_x/mpg-C₃N₄-*r* materials and the corresponding pore size distributions (B).

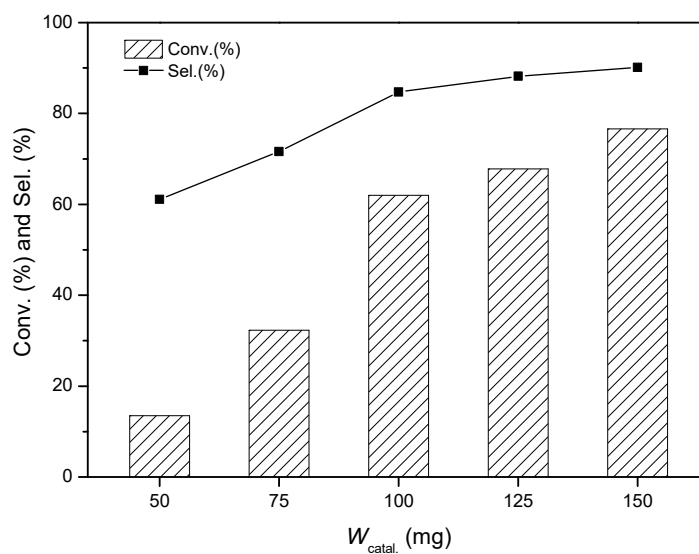


Figure S6. Catalytic performances with various feeding doses of 3CoO_x/mpg-C₃N₄. Reaction conditions: 10 mmol of EB, 30 mmol of TBHP, 4 mL of acetonitrile, $T = 100\text{ }^{\circ}\text{C}$, and $t = 10\text{ h}$.

Table S1. Molar ratios of C/N of mpg-C₃N₄ and 3CoO_x/mpg-C₃N₄- T materials.

Material	$n\text{C}/n\text{N}^{\text{a}}$
mpg-C ₃ N ₄	0.85
3CoO _x /mpg-C ₃ N ₄ -350	0.86
3CoO _x /mpg-C ₃ N ₄ -400	0.84
3CoO _x /mpg-C ₃ N ₄ -450	0.83
3CoO _x /mpg-C ₃ N ₄ -400R	0.83

^a Calculated based on the peaks of XPS survey.

Table S2. Surface areas and porous properties of 3CoO_x/mpg-C₃N₄- r materials.

Sample	S_{BET} (m ² ·g ⁻¹)	Pore size (nm) ^a	Pore volume (cm ³ ·g ⁻¹)
3CoO _x /mpg-C ₃ N ₄ -0.4	65	10.6	0.15
3CoO _x /mpg-C ₃ N ₄ -0.6	70	10.2	0.26
3CoO _x /mpg-C ₃ N ₄ -0.8	74	10.6	0.16
3CoO _x /mpg-C ₃ N ₄ -1.2	34	7.9	0.07

^a Determined by the adsorption branches.

Table S3. Catalytic performances of various $m\text{CoO}_x/\text{mpg-C}_3\text{N}_4$ catalysts in the selective oxidation of EB^a.

Catalyst	Con. (%)	Sel. (%)		
		AP	PE	BA
1CoO_x/mpg-C₃N₄	20.7	75.2	15.0	9.8
3CoO _x /mpg-C ₃ N ₄	62.0	84.7	4.8	10.6
5CoO _x /mpg-C ₃ N ₄	63.7	86.5	10.3	3.2
7CoO _x /mpg-C ₃ N ₄	64.5	90.2	7.0	2.8

^a Reaction conditions: 10 mmol of EB, 30 mmol of TBHP, $W_{\text{catal.}} = 100$ mg, 4 mL of acetonitrile, $T = 100$ °C, and $t = 10$ h.