Supporting Information

"Honeycomb Catalytic Strategy" for Carbonylation Reaction Based on the Structural Evolution of Cobalt Species

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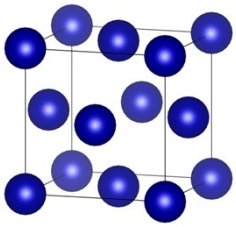
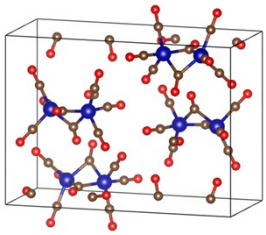
Content

1. Computational Section

In this section, we chose FCC-Co bulk and monoclinic $Co_2(CO)_8$ crystals as calculated models, and crystal structures and unit cell parameters are shown in the table below.



FCC-Co



$Co_2(CO)_8$

	Space group	**Lattice parameters (Å)**	**Angles (°)**
FCC-Co	Fm3m(225)	a=b=c=3.51	α=β=γ=90
$Co_2(CO)_8$	$P2_1/m$(11)	a=6.48 b=15.35 c=11.09	α=γ=90 β=90.54

2. Supplementary Figures

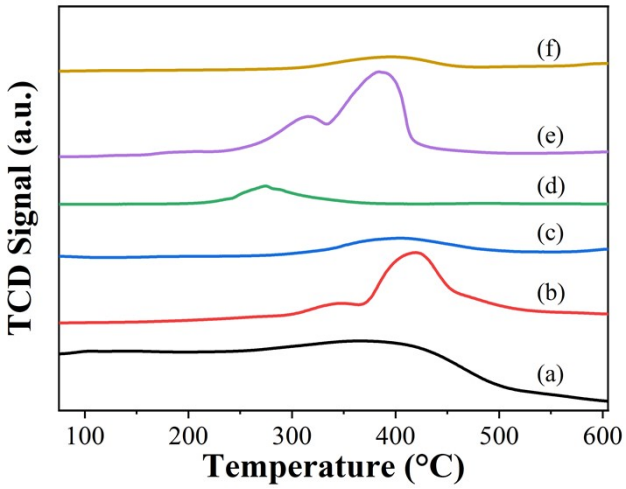


Figure S1. H_2-TPR profiles of the supported cobalt catalysts (a)Co/C, (b) Co/γ-Al_2O_3, (c) Co/S1-Silicalite, (d) Co/SiO_2, (e) Co/TiO_2, and (f) Co/CeO_2.

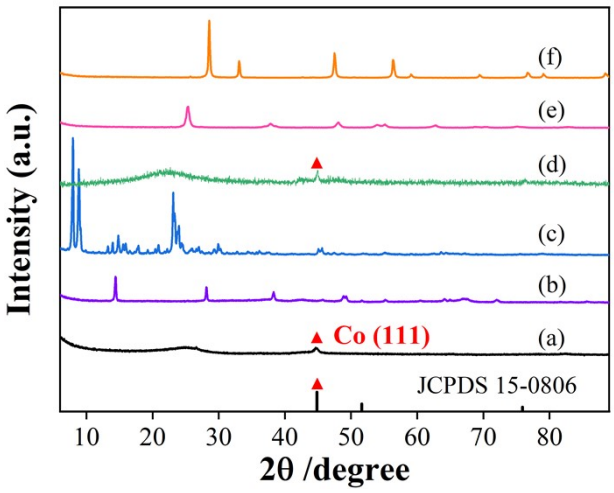


Figure S2. XRD patterns of the supported cobalt catalysts (a)Co/C, (b) Co/γ-Al_2O_3, (c) Co/S1-Silicalite, (d) Co/SiO_2, (e) Co/TiO_2, and (f) Co/CeO_2.

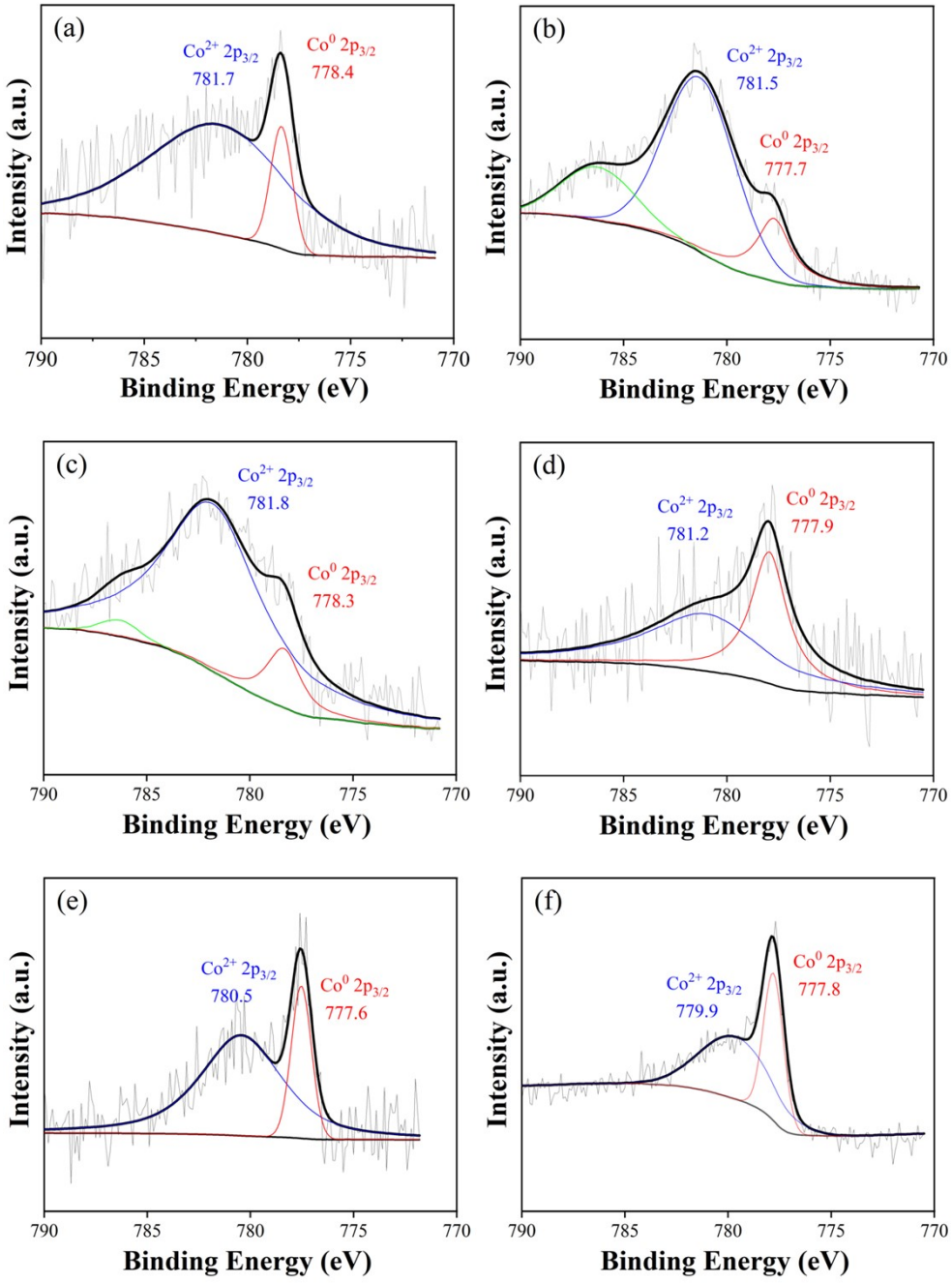


Figure S3. XPS spectra of the supported cobalt catalysts (a)Co/C, (b) Co/γ-Al_2O_3, (c) Co/S1-Silicalite, (d) Co/SiO_2, (e) Co/TiO_2, and (f) Co/CeO_2.

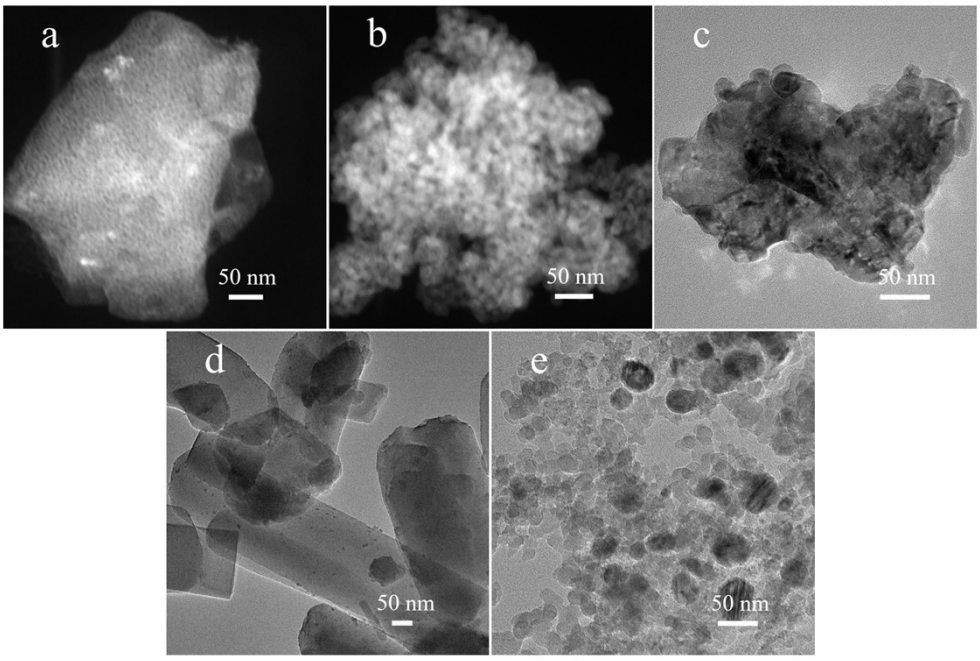


Figure S4. TEM images of the supported cobalt catalysts (a) γ-Al_2O_3, (b) TiO_2, (c) CeO_2, (d) S1-Silicalite, and (e) SiO_2.

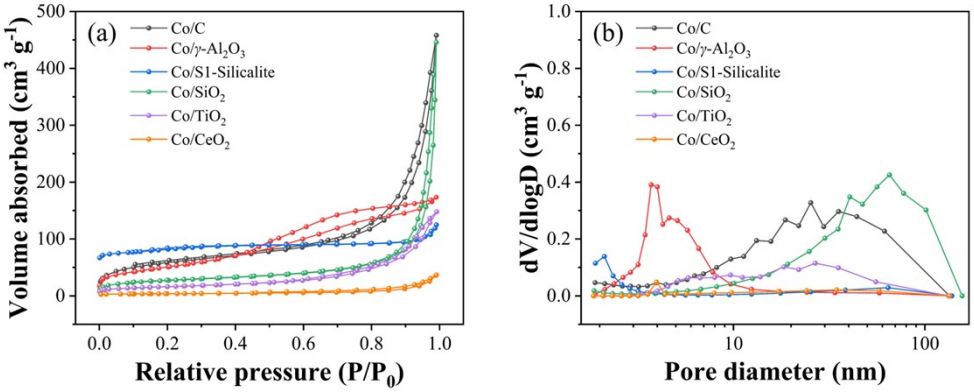


Figure S5. (a) N_2 adsorption-desorption isotherms and (b) BJH desorption pore size distributions of the supported cobalt catalysts.

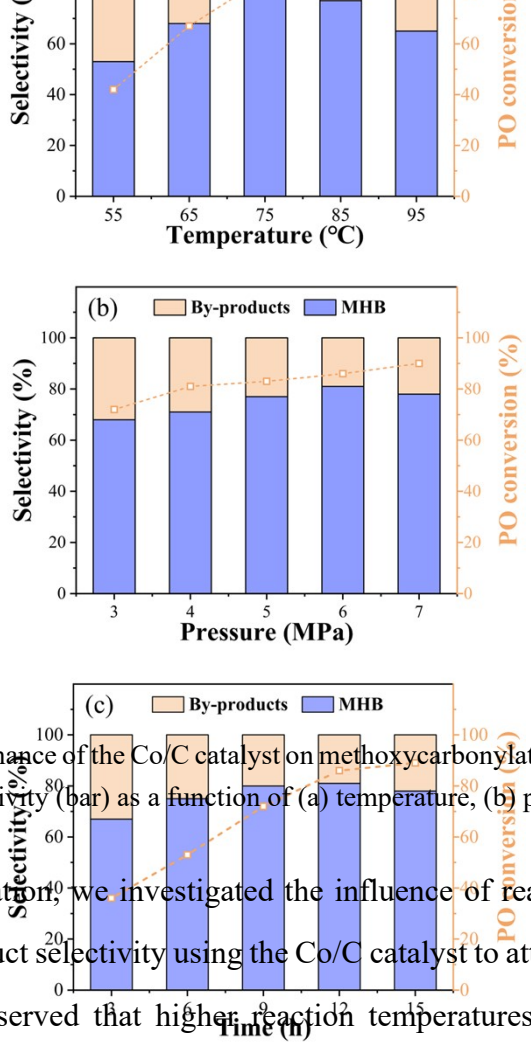


Figure S6. Catalytic performance of the Co/C catalyst on methoxycarbonylation of propylene oxide. Conversion (line) and selectivity (bar) as a function of (a) temperature, (b) pressure, and (c) time.

In the initial investigation, we investigated the influence of reaction conditions on PO conversion and product selectivity using the Co/C catalyst to attain optimal reaction performance. It was observed that higher reaction temperatures in this exothermic reaction were not conducive to achieving a high equilibrium yield and resulted in increased formation of by-products. While the PO conversion increased from 42% to 92% as the temperature rose from 55°C to 95°C, the highest yield of 70% MHB was obtained at 75°C. Hence, 75°C was selected as the optimal reaction temperature. Further optimization indicated that 6 MPa was sufficient, and a reaction time of 12 hours was advisable.

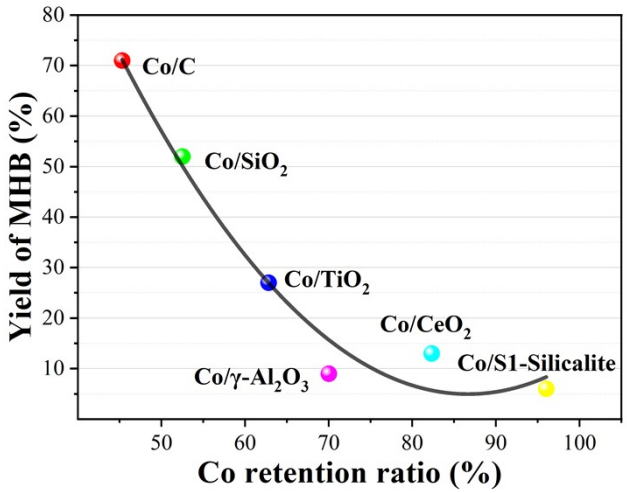


Figure S7. The yield of MHB and Co retention ratio for different catalysts after the reaction.

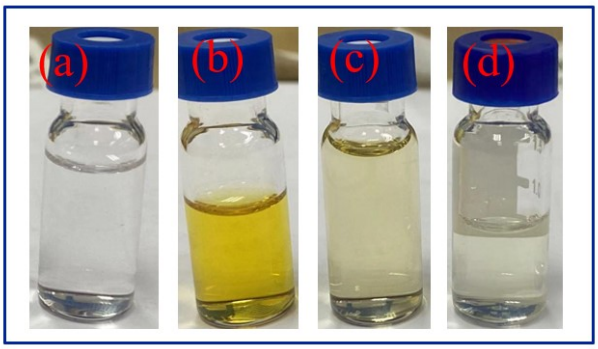


Figure S8. Photographs of supernatant of the Co/C catalyst under different post-treatment temperatures. (a) fresh reactants; (b) without post-treatment; (c) 75°C; (d) 190°C.

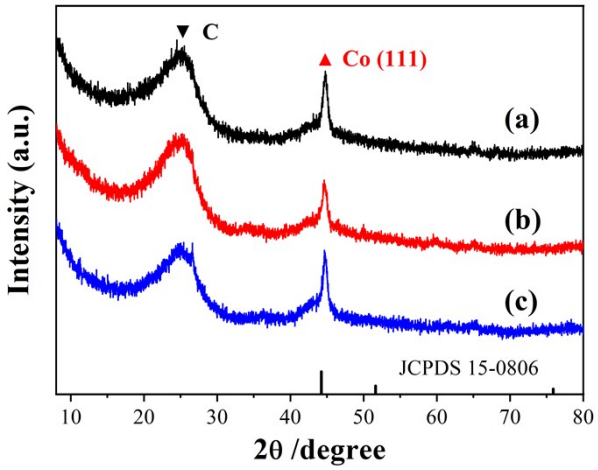


Figure S9. XRD patterns of the Co/C catalyst (a) fresh, (b)used, and (c) recycled 4 times through the “honey catalytic process”.

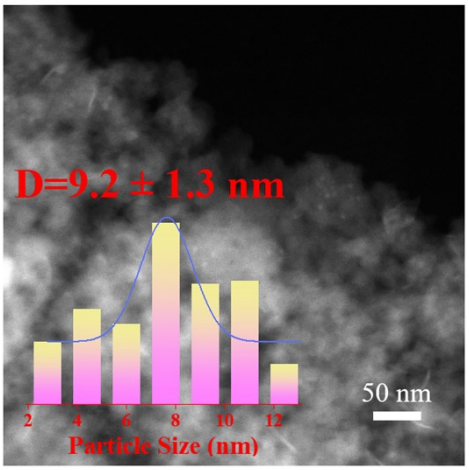


Figure S10. HRTEM and the cobalt nanoparticles size distribution of the used Co/C catalyst.

3. Supplementary Tables

Table S1. BET specific surface area and cobalt loading amount of the supported catalyst.

Sample	Catalyst	Specific surface area (m^2/g)	Co loading (wt%)
1	Co/C	231.0	3.01
2	Co/SiO_2	97.6	3.04
3	Co/TiO_2	57.5	2.67
4	Co/CeO_2	13.3	2.72
5	$Co/\gamma\text{-}Al_2O_3$	186.8	2.63
6	Co/ S1-Silicalite	278.6	2.84
7	Co/C-1	217.9	10.40
8	Co/C-2	201.7	20.79

Table S2. ICP-OES results of cobalt leaching from catalysts.

Entry	Catalyst	Co content of supernatant (μg/g) [a]	Co retention ratio (%) [a]	Co content of supernatant (μg/g) [b]	Co retention ratio (%) [b]
1	Co/C	660.1	45.3	13.3	98.9
2	Co/SiO_2	573.4	52.5	9.5	99.2
3	Co/TiO_2	449.1	62.8	13.7	98.9
4	Co/CeO_2	213.6	82.3	15.4	98.7
5	Co/γ-Al_2O_3	362.2	70.0	7.2	99.4
6	Co/S1-Silicalite	48.3	96.0	19.3	98.4
7	Co/C-1	649.2	46.3	32.6	97.3
8	Co/C-2	602.1	50.2	35.7	96.2

Standard reaction conditions: propylene oxide, 6 mmol; n[Co]/n[3-hydroxypyridine] = 1:3; methanol, 9 mL; initial pressure of CO, 6 MPa; reaction time, 12 hours; temperature, 75°C; catalyst, n[Co]/n[PO] = 1:40; stirring rate, 600 rpm.

[a] Without post-treatment. [b] With post-treatment.

Post-treatment conditions: Venting CO slowly and charging N_2 with an initial pressure of 6 MPa; temperature, 190°C; time, 12 hours; stirring rate, 150 rpm.

Table S3. Catalytic run of recycled Co/C catalyst in the methoxycarbonylation of propylene oxide.

Entry	Run	Conversion (%)	Selectivity (%)	Yield (%)	Co retention ratio (%)
1	1 [a]	89	80	71	45.3
2	2 [a]	53	65	34	23.7
3	3 [a]	37	56	21	14.6
4	4 [a]	24	13	3	8.9
5	1 [b]	91	78	71	98.9
6	2 [b]	86	76	65	97.1
7	3 [b]	87	77	67	96.7
8	4 [b]	84	75	63	95.2

Standard reaction conditions: propylene oxide, 6 mmol; n[Co]/n[3-hydroxypyridine] = 1:3; methanol, 9 mL; initial pressure of CO, 6 MPa; reaction time, 12 hours; temperature, 75°C; catalyst, n[Co]/n[PO] = 1:40; stirring rate, 600 rpm. Determined by gas chromatograph with diphenyl as an internal standard.

[a] Without post-treatment. [b] With post-treatment.

Post-treatment conditions: Venting CO slowly and charging N_2 with an initial pressure of 6 MPa; temperature, 190°C; time, 12 hours; stirring rate, 150 rpm.