Unlocking High Selectivity and Stability of Cobalt-based Catalyst in *n*-Butanol Amination Reaction

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Supplementary Tables

Table S1 Textural properties and Co content of cobalt-based catalysts using different supports.

Catalysts	Co content[a] (wt.%)	S_{BET}[b] (m^2/g)	S_{ext} (m^2/g)	V_{total}[c] (cm^3/g)	V_{micro} (cm^3/g)
3Co/SSZ-13	3.2	712	32	0.30	0.26
3Co/USY	3.3	840	127	0.64	0.27
3Co/S1	3.3	432	124	0.30	0.12
$3Co/Al_2O_3$	3.5	204	203	0.53	—
$3Co/SiO_2$	3.3	294	282	0.91	—

[a] Co content was determined by XRF analysis;

[b] Specific surface area calculated by the BET method;

[c] Total pore volume measured at $P/P_0 = 0.99$.

Table S2 Calculated proportions of CoO_x nanoparticles and nanoclusters on nCo/S1 catalysts based on H_2-TPR hydrogen consumption.

Catalysts	Co content[a] (wt.%)	CoO_x nanoparticles[b] (%)	CoO_x nanoclusters[b] (%)
5Co/S1	5.4	97	3
1Co/S1	1.1	26	74

[a] Co content was determined by XRF analysis;

[b] Relative contents of CoO_x nanoparticles and nanoclusters were estimated by deconvoluting the H_2-TPR profiles.

Table S3 Quantitative XPS analysis of surface cobalt oxidation states in nCo/S1 catalysts.

Catalysts	Co^{3+} (%)	Co^{2+} (%)
5Co/S1	49	51
1Co/S1	17	83

Table S4 Texture properties of 3Co/S1, 3Co/S1-250 h and 3Co/S1-250 h-C.

Catalysts	S_{BET}[a] (m^2/g)	S_{ext} (m^2/g)	V_{total}[b] (cm^3/g)	V_{micro} (cm^3/g)
3Co/S1	432	124	0.30	0.12
3Co/S1-250 h	260	58	0.20	0.08
3Co/S1-250 h-C	413	144	0.27	0.11

[a] Specific surface area calculated by the BET method;

[b] Total pore volume measured at $P/P_0 = 0.99$.

Table S5 Textural properties and Co content of 3Co/S1 catalysts before and after acid treatment.

Catalysts	Co content[a] (wt.%)	S_{BET}[b] (m^2/g)	S_{ext} (m^2/g)	V_{total}[c] (cm^3/g)	V_{micro} (cm^3/g)
S1	—	431	128	0.30	0.12
3Co/S1	3.3	432	124	0.30	0.12
3Co/S1-AW-1.7	2.7	373	170	0.27	0.11
3Co/S1-AW-2.5	1.9	354	199	0.29	0.08

[a] Co content was determined by XRF analysis;

[b] Specific surface area calculated by the BET method;

[c] Total pore volume measured at $P/P_0 = 0.99$.

Table S6 Quantitative XPS analysis of surface cobalt oxidation states in 3Co/S1 catalysts before and after acid treatment.

Catalysts	Co^{3+} (%)	Co^{2+} (%)
3Co/S1	43	57
3Co/S1-AW-1.7	40	60
3Co/S1-AW-2.5	33	67

Supplementary Figures

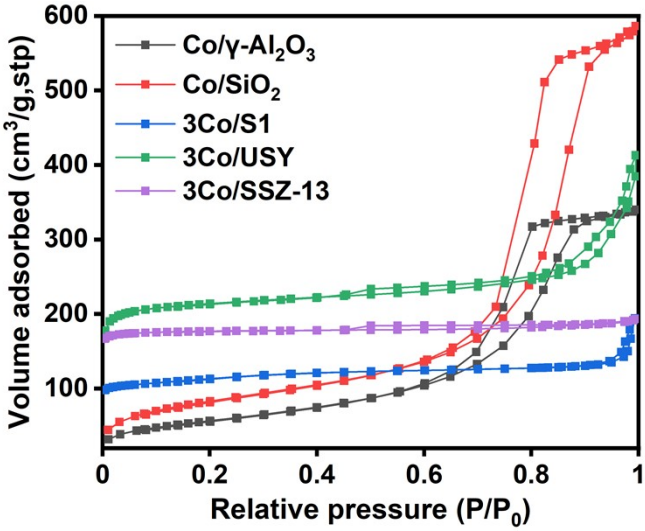

Fig. S1. N_2 adsorption and desorption isotherms of Co-based catalysts with different supports.

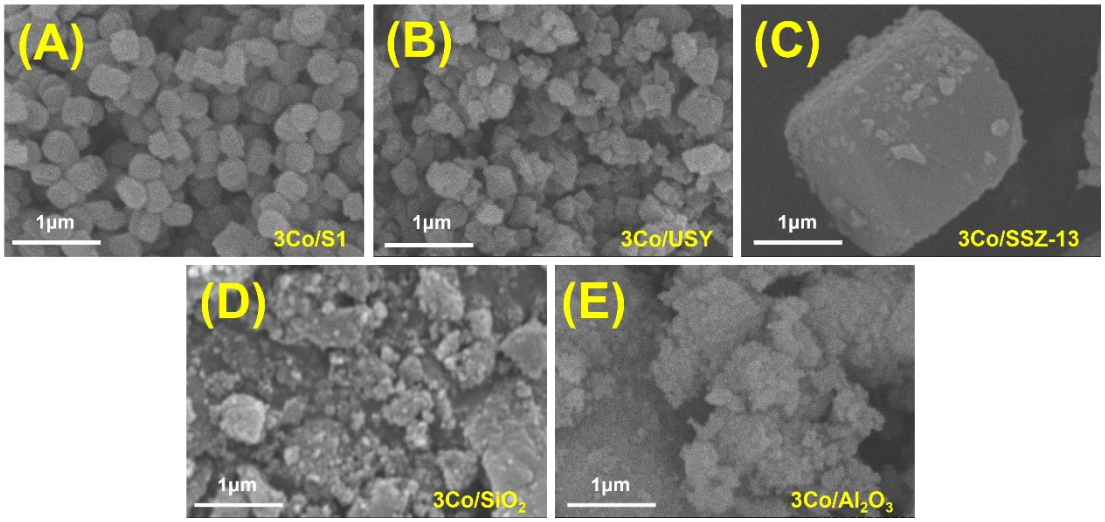

Fig. S2. SEM images of (A) 3Co/S1, (B) 3Co/USY, (C) 3Co/SSZ-13, (D) 3Co/SiO_2 and (E) 3Co/γ-Al_2O_3.

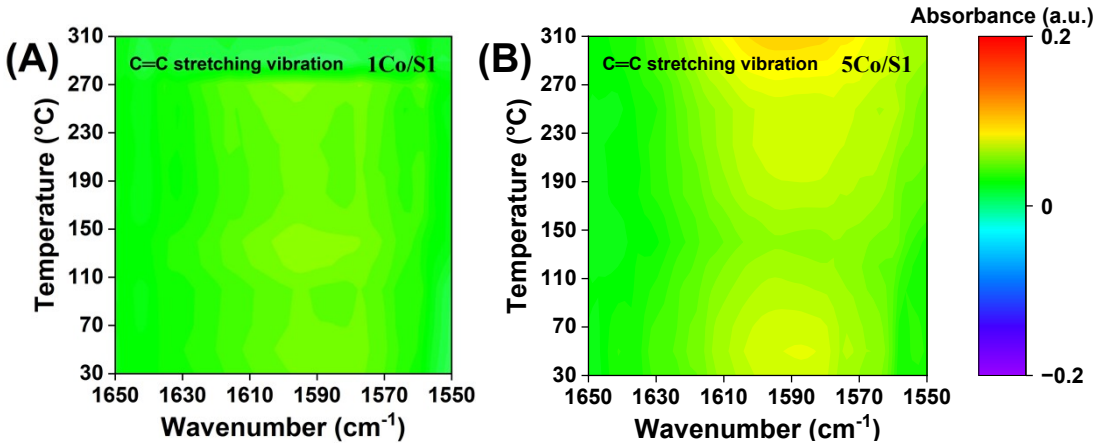

Fig. S3. FTIR spectra of adsorbed *n*-butanol on 1Co/S1 and 5Co/S1.

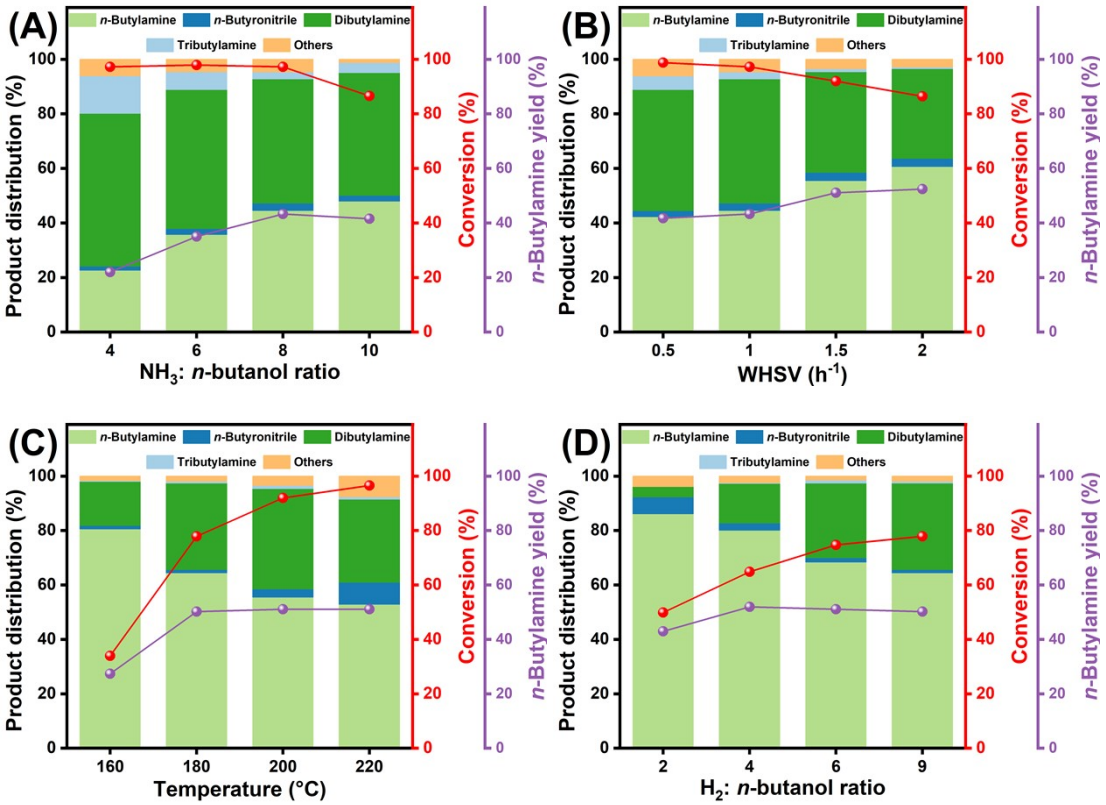

Fig. S4. *n*-Butanol conversion, product distribution, and *n*-butylamine yield over 3Co/S1 catalyst under varying reaction conditions.

Reaction conditions: (A) T = 200 °C, WHSV = 1 h^{-1}, molar ratio H_2: *n*-butanol = 9; (B) T = 200 °C, molar ratio H_2: NH_3: *n*-butanol = 9:8:1; (C) molar ratio H_2: NH_3: *n*-butanol = 9:8:1, WHSV = 1.5 h^{-1}; (D) T = 180 °C, molar ratio NH_3: *n*-butanol = 8:1, WHSV = 1.5 h^{-1}.

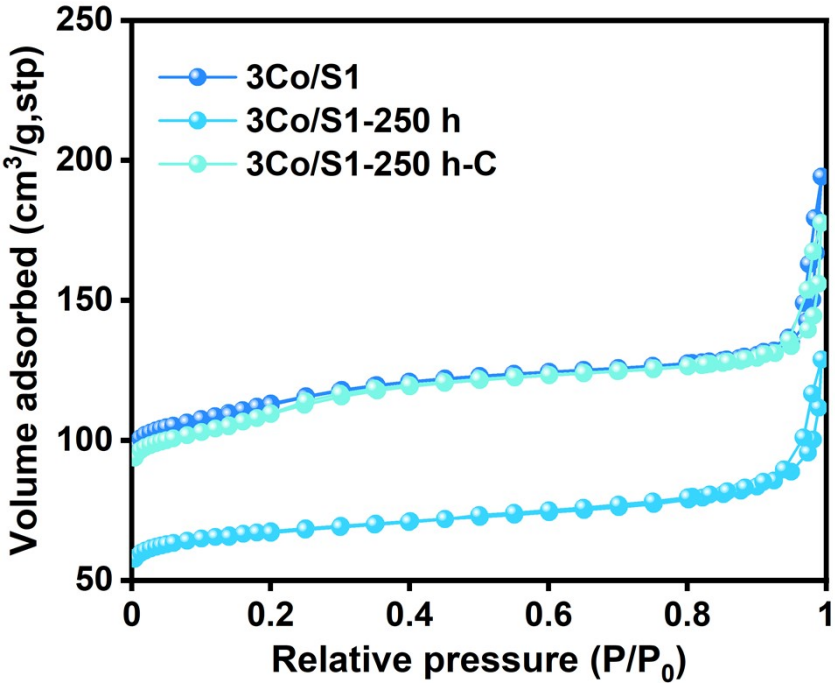

Fig. S5. N_2 adsorption and desorption isotherms of 3Co/S1, 3Co/S1-250 h and 3Co/S1-250 h-C.

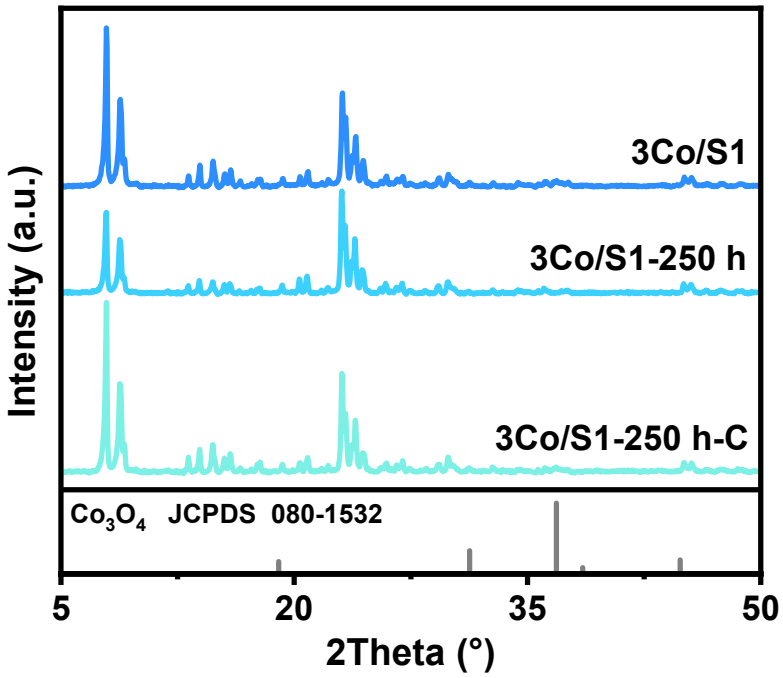

Fig. S6. XRD patterns of 3Co/S1, 3Co/S1-250 h and 3Co/S1-250 h-C.

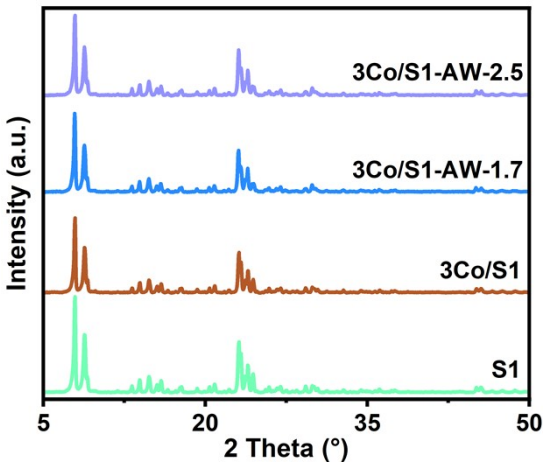

Fig. S7. XRD patterns of 3Co/S1 catalysts before and after acid treatment and support S1.

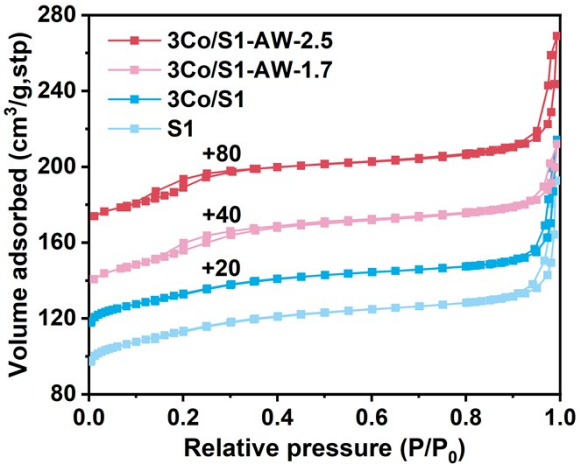

Fig. S8. N_2 adsorption and desorption isotherms of 3Co/S1 catalysts before and after acid treatment and support S1.

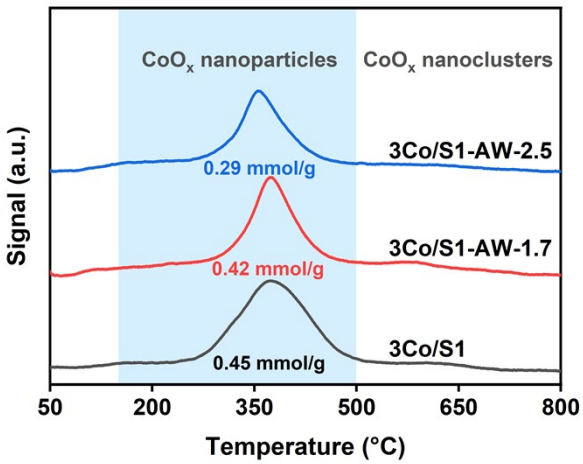

Fig. S9. H_2-TPR profiles of 3Co/S1 catalysts before and after acid treatment.

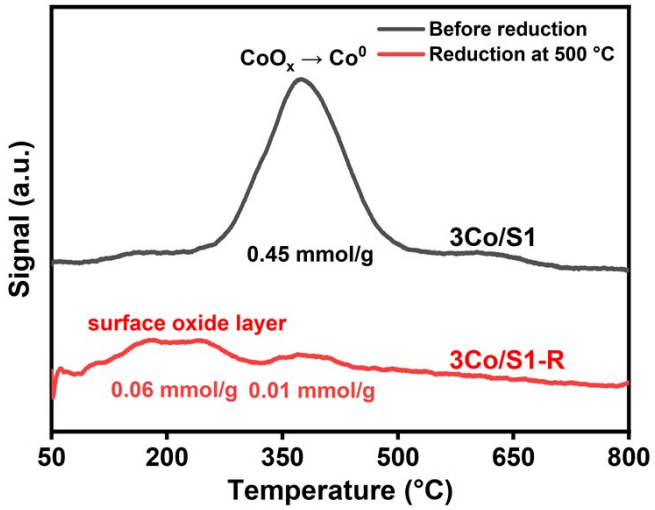

Fig. S10. H_2-TPR profiles of 3Co/S1 catalyst before and after reduction. Reduction condition: 500 °C in the fix bed for 2 h with 50 ml/min of H_2.

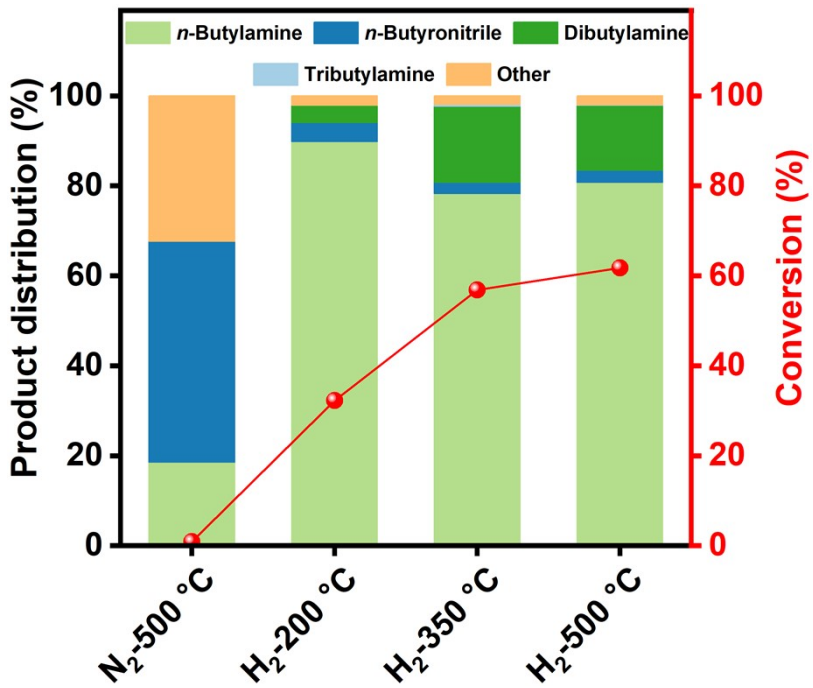

Fig. S11. Effect of reduction temperature on *n*-butanol conversion and product distribution over 3Co/S1 catalyst.
Reaction conditions: $T_{reaction}$ = 180 °C; molar ratio H_2: NH_3: *n*-butanol = 4:8:1; WHSV = 1.5 h^{-1}.