Supporting Information

Multifaceted Role of Mobile Bismuth Promoter in Alcohol Amination over Cobalt Catalysts

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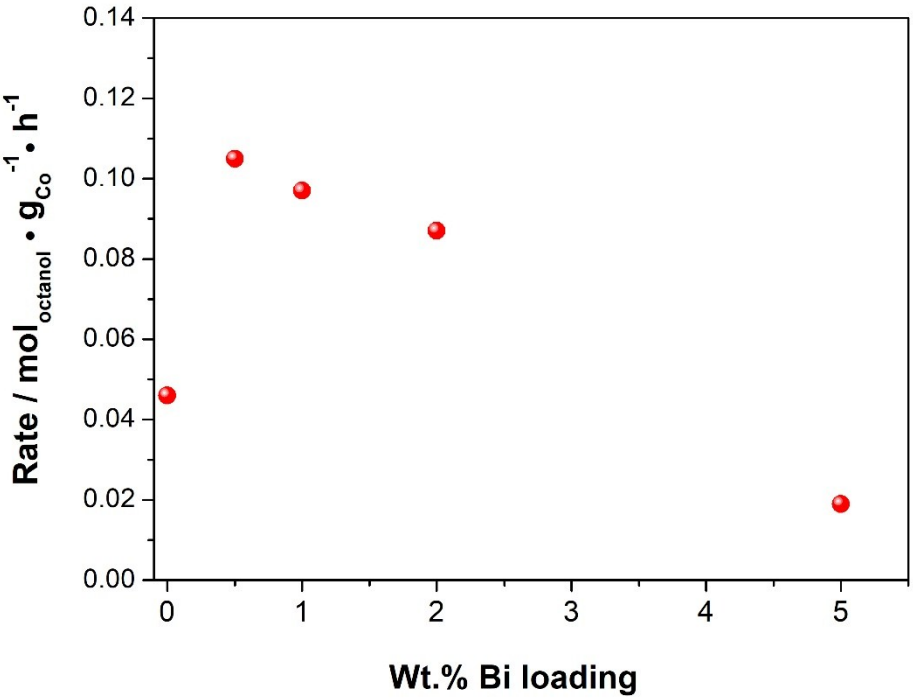

Figure S1 Catalytic reaction rate for liquid phase amination of 1-octanol over cobalt catalysts with different Bi loading content (1-octanol, 0.84 g; molar ratio of 1-octanol/NH_3/H_2 = 1/4.5/0.85; P_{H2} = 3 bar; catalyst amount, 100 mg; reaction temperature, 180 ^oC; time, 0-48 h; no solvent used).

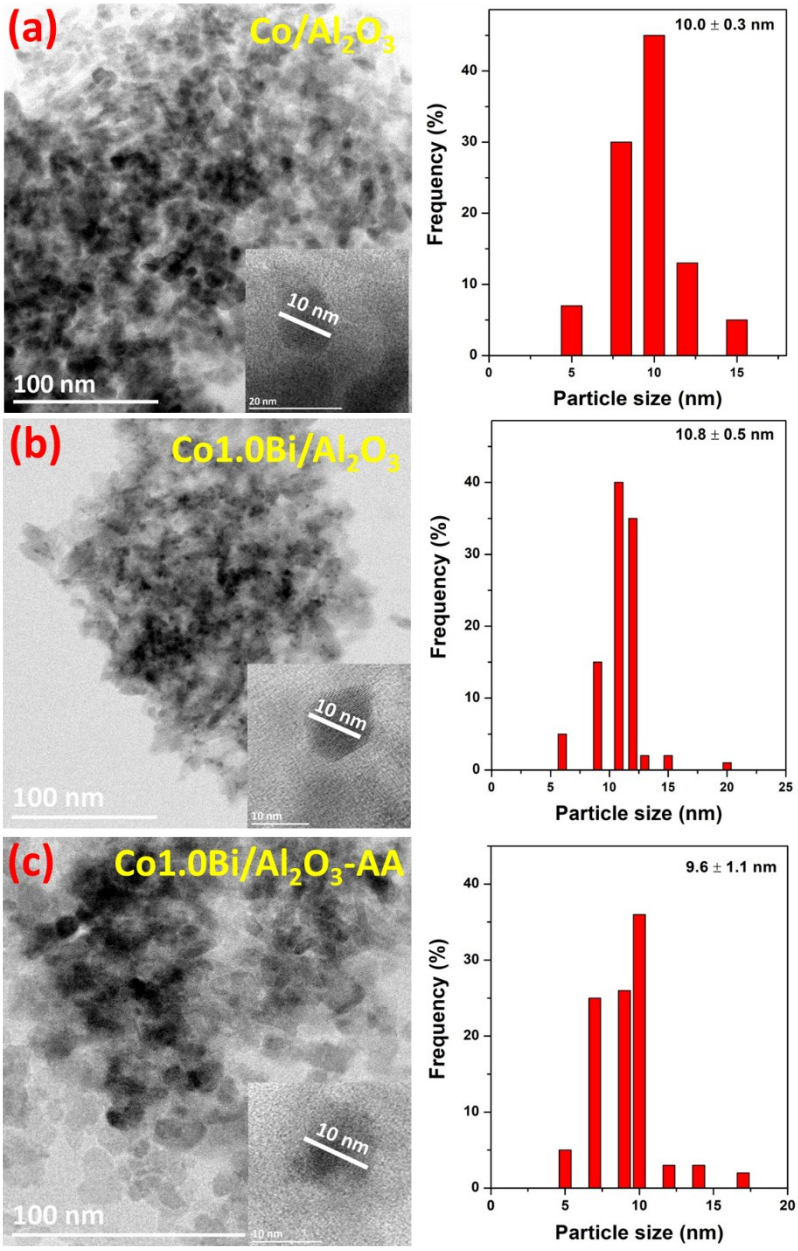

Figure S2 STEM images and histograms of Co particle size distribution of catalysts (a) Co/Al_2O_3, (b) $Co1.0Bi/Al_2O_3$, and (c) $Co1.0Bi/Al_2O_3$-AA.

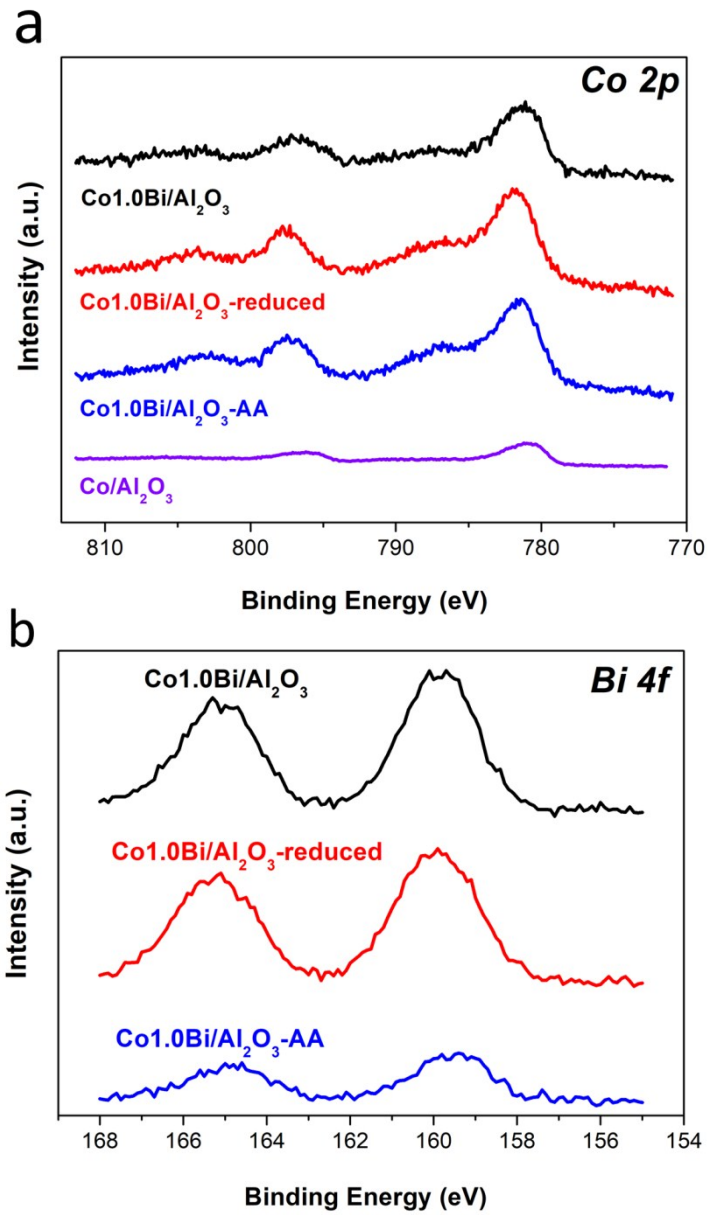

Figure S3 XPS spectra of (a) Co 2p and (b) Bi 4f for Co1.0Bi/Al_2O_3 catalyst in the case of calcination, reduction and after amination.

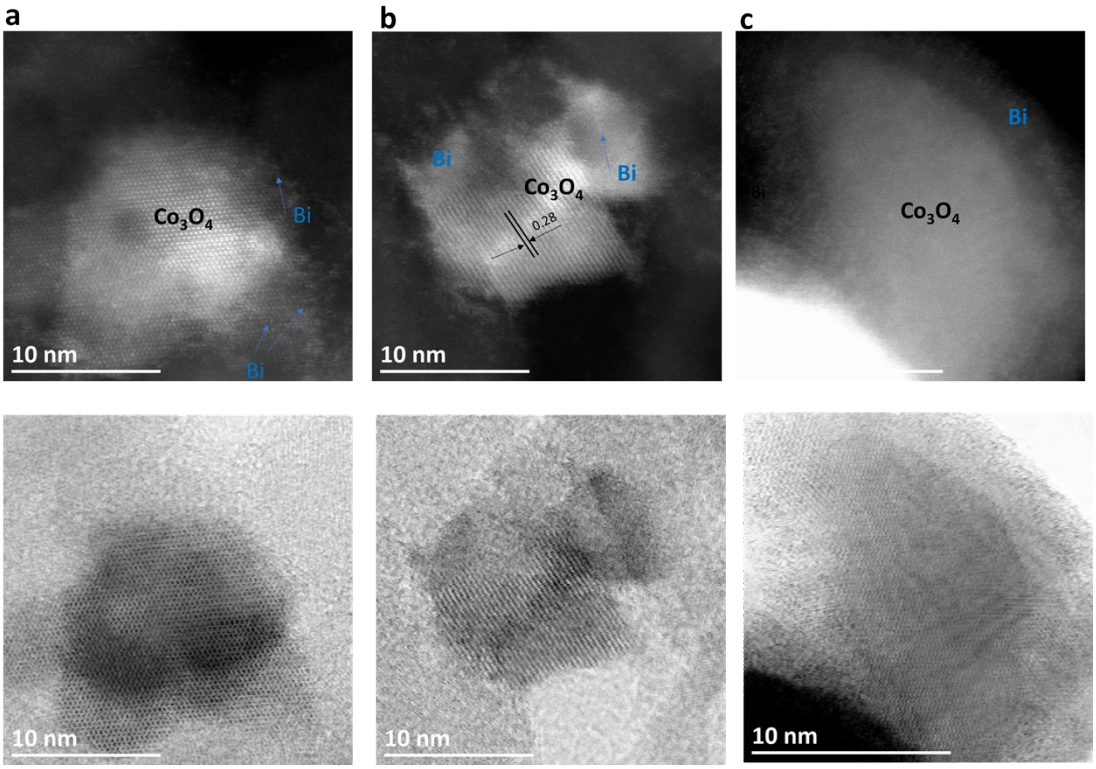

Figure S4 HR STEM images of catalyst Co1.0Bi/Al_2O_3 after preparation (a), reduction (b) and amination reaction (c).

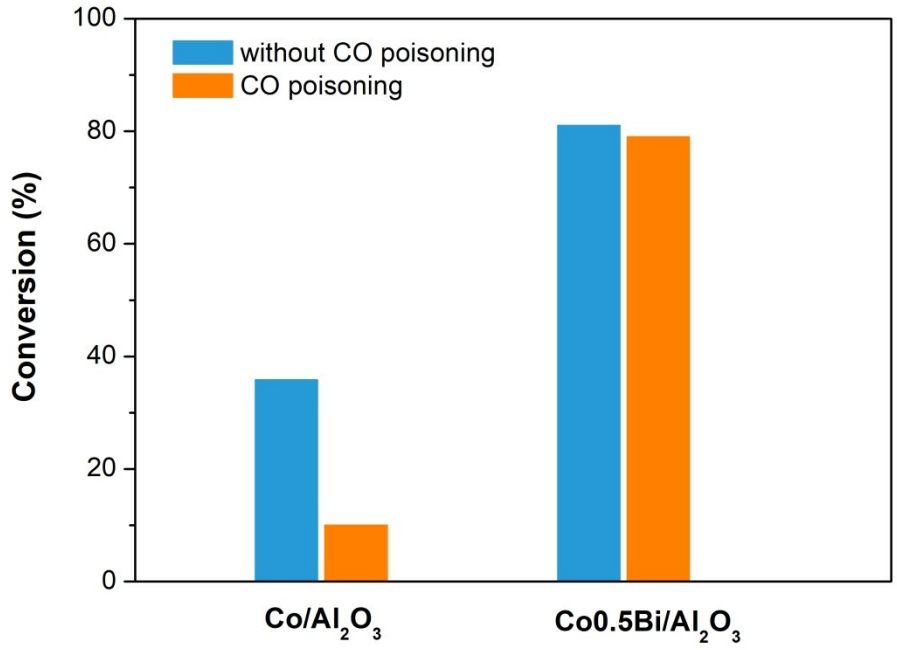

Figure S5 Catalytic amination of 1-octanol over Co/Al_2O_3 and $Co0.5Bi/Al_2O_3$ catalysts with and without CO poisoning. (1-octanol, 0.84 g; molar ratio of 1-octanol/NH_3/H_2 = 1/4.5/0.85; P_{H2} = 3 bar; catalyst amount, 100 mg; reaction temperature, 180 ^oC; time, 0-48 h; no solvent used).

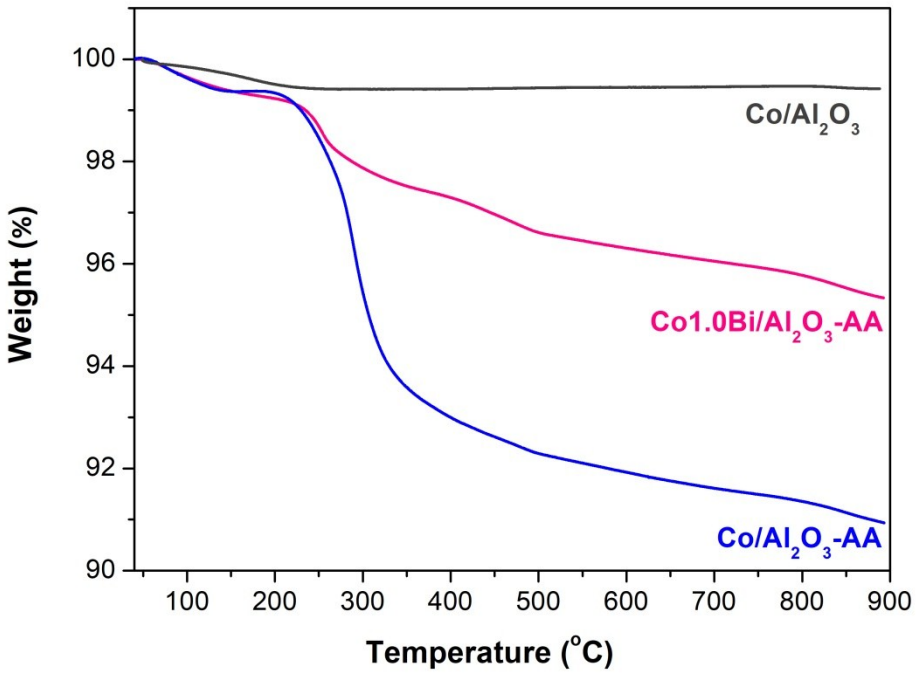

Figure S6 TGA profiles of fresh Co/Al_2O_3 and used catalysts Co/Al_2O_3-AA and $Co1.0Bi/Al_2O_3$-AA.

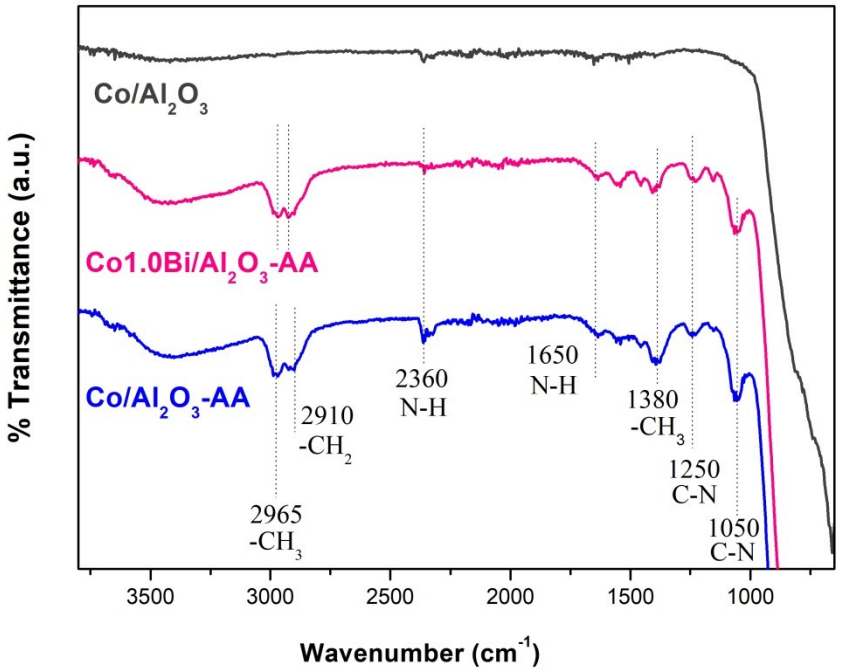

Figure S7 Ex situ FTIR spectroscopy of fresh Co/Al_2O_3 and used catalysts Co/Al_2O_3-AA and $Co1.0Bi/Al_2O_3$-AA.

Table S1. ICP analysis of the catalyst Co1.0Bi/Al_2O_3 before and after catalytic cycles

Catalysts	**Theoretical Bi loading (wt.%)**	**ICP measured Bi loading (wt.%)**
Co1.0Bi/Al_2O_3	1	0.96
Co1.0Bi/Al_2O_3-after cycles	1	0.94

Table S2. TOF values for 1-octanol amination and 1-octylamine self-coupling reactions for supported fresh and Bi promoted cobalt catalysts

Catalyst	Conversion for 1-octanol amination (%)	Yield for 1-octylamine coupling (%)	TOF for 1-octanol amination (h^{-1}) [a]	TOF for octylamine coupling (h^{-1}) [a]	Ratio of TOF (octylamine coupling)/TOF (octanol amination)
Co/Al_2O_3	5	7	207.5	364.5	1.76
$Co0.5Bi/Al_2O_3$	7	4	213.9	290.4	1.36
$Co1.0Bi/Al_2O_3$	7	2.5	210.6	217.1	1.03
$Co2.0Bi/Al_2O_3$	6	1.5	209.1	196.1	0.94
$Co5.0Bi/Al_2O_3$	4	0.6	211.3	148.4	0.70
Bi/Al_2O_3	-	-	-	-	-

[a] The TOF value is defined as $mol_{reactant} \cdot mol_{Co_{surf}}^{-1} \cdot h^{-1}$ at low conversion (< 10%).