Supporting Information

Structural Requirements for Chemoselective Ammonolysis of Ethylene Glycol to Ethanolamine over Supported Cobalt Catalysts

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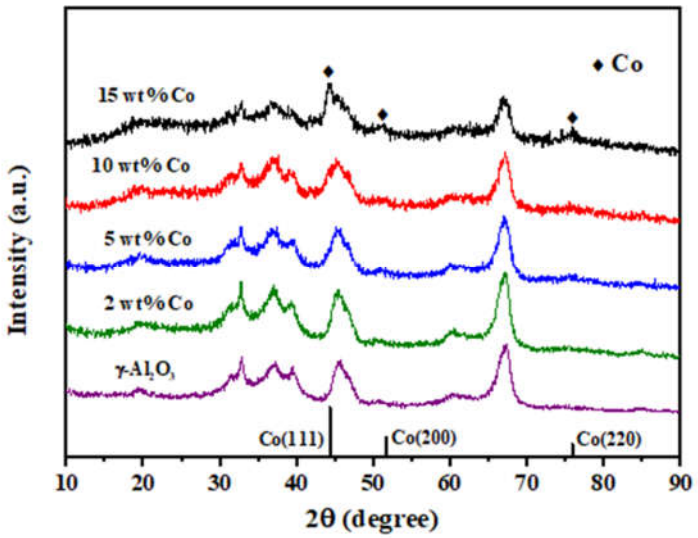

Fig. S1. Powder XRD patterns for Co/γ-Al_2O_3 samples (Co 2 wt%-15 wt%) and the γ-Al_2O_3 support with metallic Co (JCPDS 15-0806) as reference.

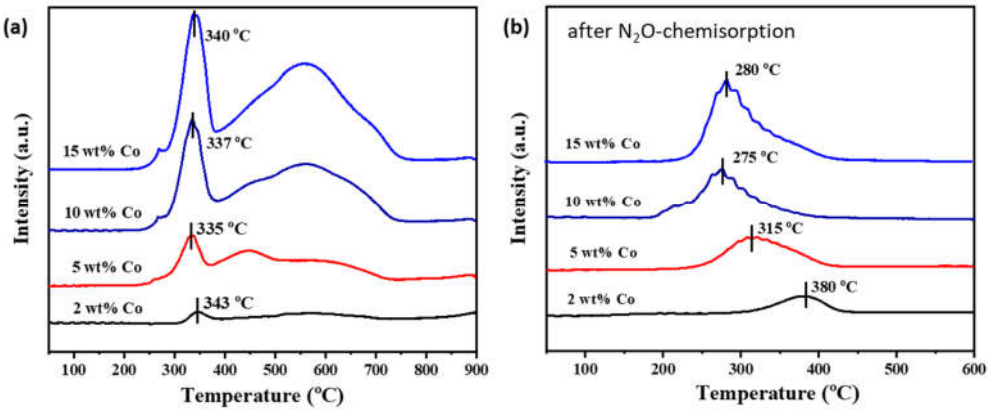

Fig. S2. H_2-TPR profiles for (a) the oxide persursors of the Co/γ-Al_2O_3 catalysts (Co 2 wt%-15 wt%) and (b) the Co/γ-Al_2O_3 catalysts after treated in flowing 5% N_2O/N_2 at 323 K for 1 h.

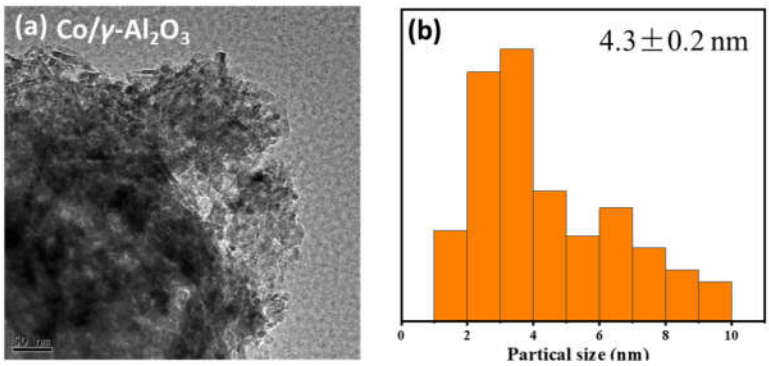

Fig. S3. TEM image for (a) 5 wt% Co/γ-Al_2O_3 with (b) the corresponding statistic size distribution of the Co nanoparticles.

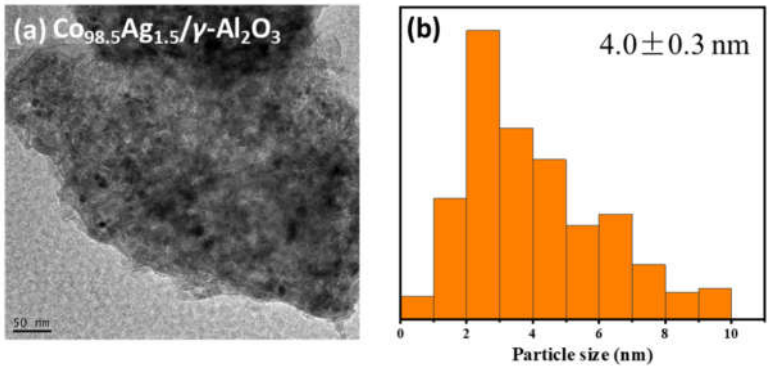

Fig. S4. TEM image for (a) $Co_{98.5}Ag_{1.5}/\gamma$-Al_2O_3 with (b) the corresponding statistic size distribution of the Co nanoparticles.

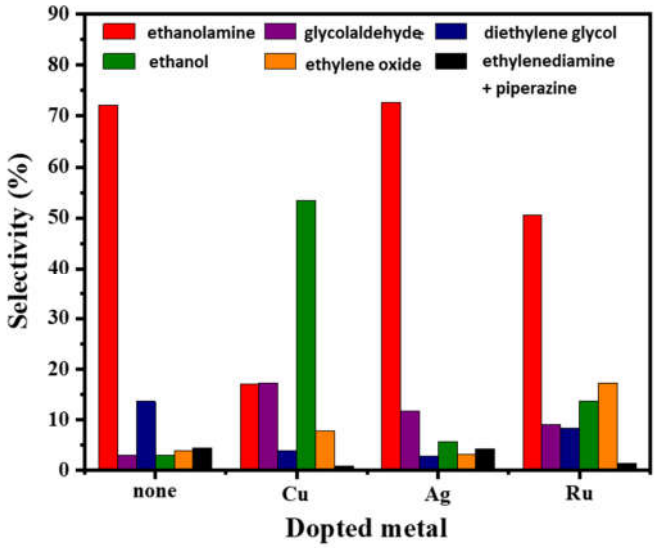

Fig. S5. Detailed product disturibution of the ammonolysis of ethylene glycol on $Co_{98.5}M_{1.5}/\gamma\text{-}Al_2O_3$ (M = Cu, Ag, and Ru; 5 wt% Co) catalysts at ~20% conversion (453 K, 0.6 MPa NH_3, 3.0 MPa H_2, 0.067 mol/L ethylene glycol in tetrahydrofuran solution, 2 h).

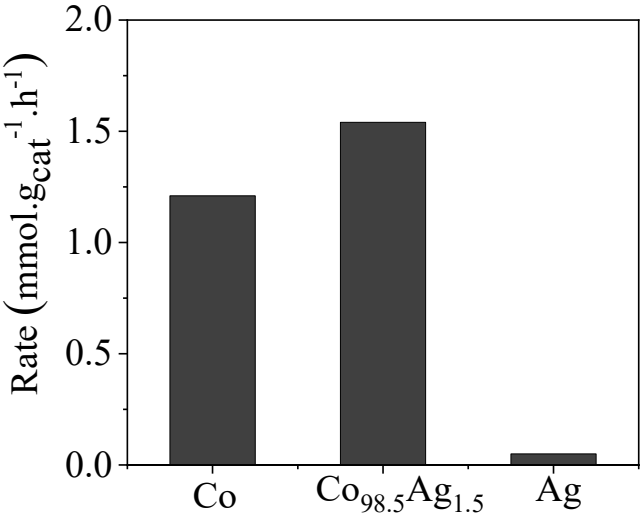

Fig. S6. Activity comparison among 5 wt% $Co/\gamma\text{-}Al_2O_3$, 5 wt% $Co_{98.5}Ag_{1.5}/\gamma\text{-}Al_2O_3$, and 5 wt% $Ag/\gamma\text{-}Al_2O_3$ in catalytic ammonolysis of ethylene glycol (453 K, 0.6 MPa NH_3, 3.0 MPa H_2, 0.067 mol/L ethylene glycol in tetrahydrofuran solution, 2 h).

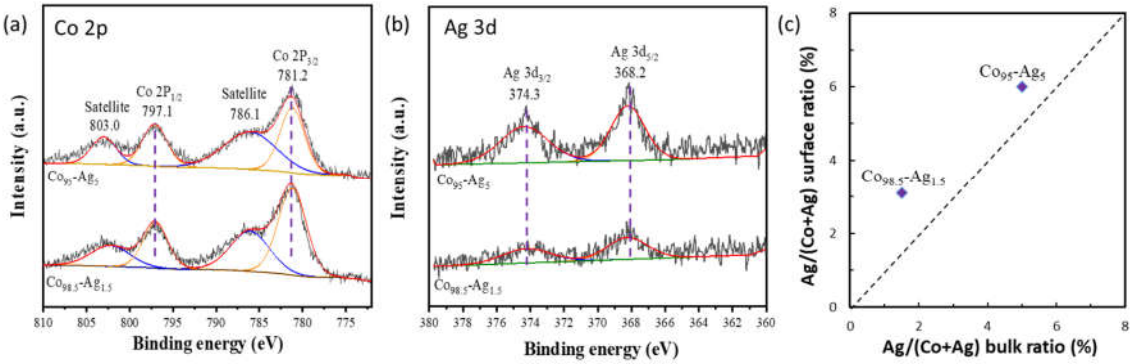

Fig. R7. (a) Co 2p and (b) Ag 3d XPS spectra for the $Co_{98.5}Ag_{1.5}/\gamma$-Al_2O_3 and $Co_{95}Ag_5/\gamma$-Al_2O_3 catalysts and (c) the corresponding Ag/(Co+Ag) surface ratios determined from these spectra.

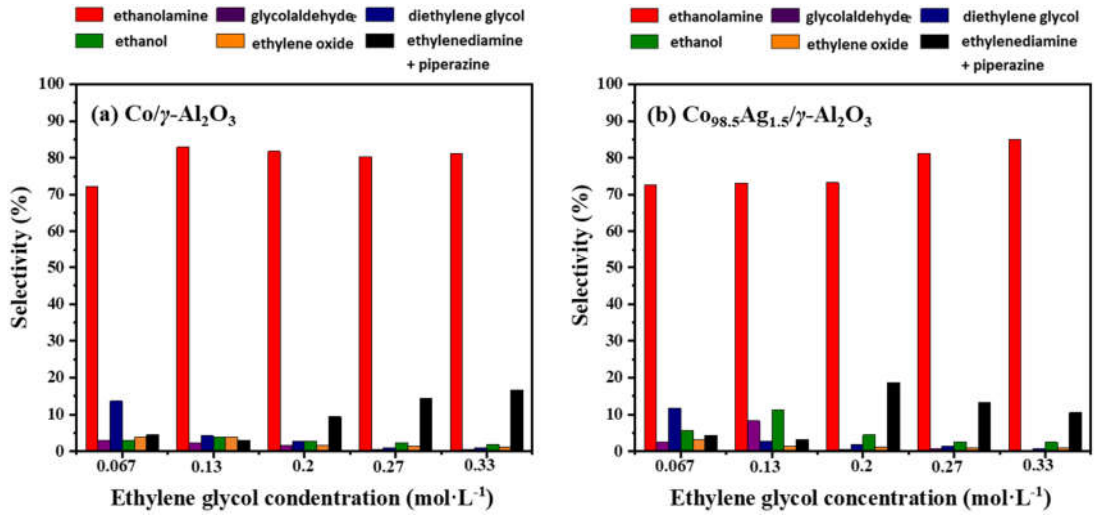

Fig. S8. Selectivities of ethylene glycol concentration on (a) Co/γ-Al_2O_3 and (b) $Co_{98.5}Ag_{1.5}/\gamma$-Al_2O_3 catalysts (Co 5 wt%) as a function of ethylene glycol concentration (453 K, 0.6 MPa NH_3, 3.0 MPa H_2, 2 h, ~20% ethylene glycol conversion obtained by varying the catalyst amount or reaction time).

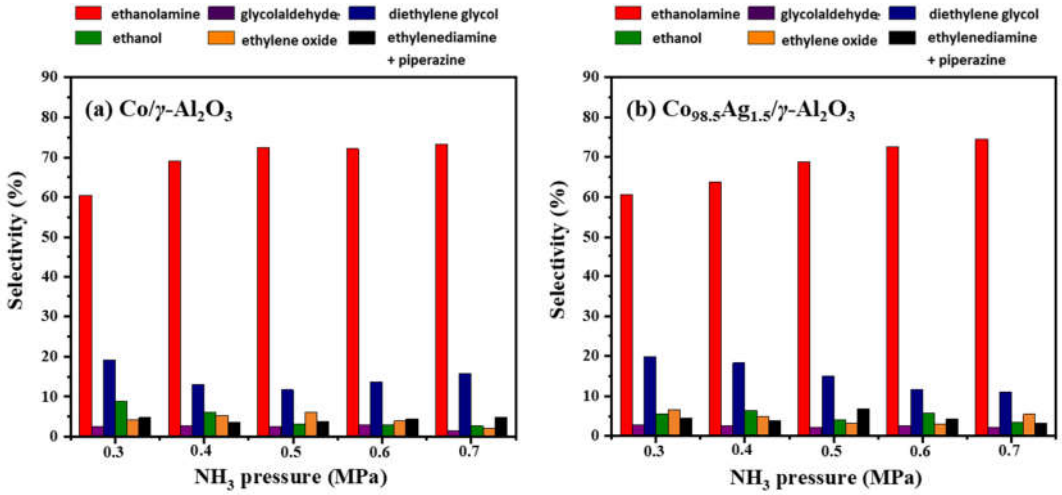

Fig. S9. Selectivities of ethylene glycol concentration on (a) Co/γ-Al_2O_3 and (b) $Co_{98.5}Ag_{1.5}$/γ-Al_2O_3 catalysts (Co 5 wt%) as a function of NH_3 pressure (453 K, 3.0 MPa H_2, 0.067 mol/L ethylene glycol in tetrahydrofuran solution, 2 h, ~20% ethylene glycol conversion obtained by varying the catalyst amount or reaction time).

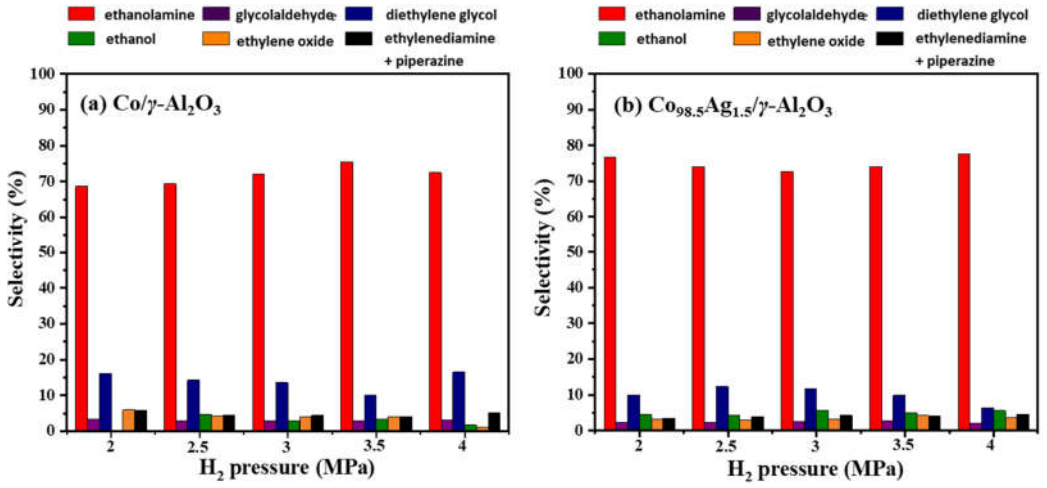

Fig. S10. Selectivities of ethylene glycol concentration on (a) Co/γ-Al_2O_3 and (b) $Co_{98.5}Ag_{1.5}$/γ-Al_2O_3 catalysts (Co 5 wt%) as a function of H_2 pressure (453 K, 0.6 MPa NH_3, 0.067 mol/L ethylene glycol in tetrahydrofuran solution, 2 h, ~20% ethylene glycol conversion obtained by varying the catalyst amount or reaction time).

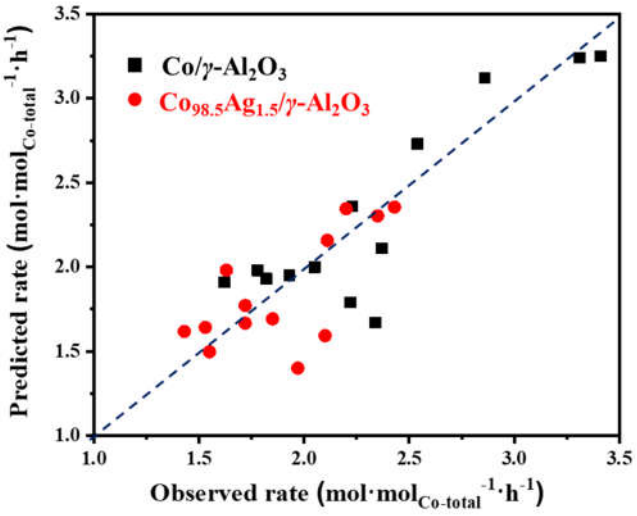

Fig. S11. A parity plot for the measured and predicted rates of ethylene glycol amination (Equation 2) on the Co/γ-Al_2O_3 and $Co_{98.5}Ag_{1.5}$/γ-Al_2O_3 catalysts.

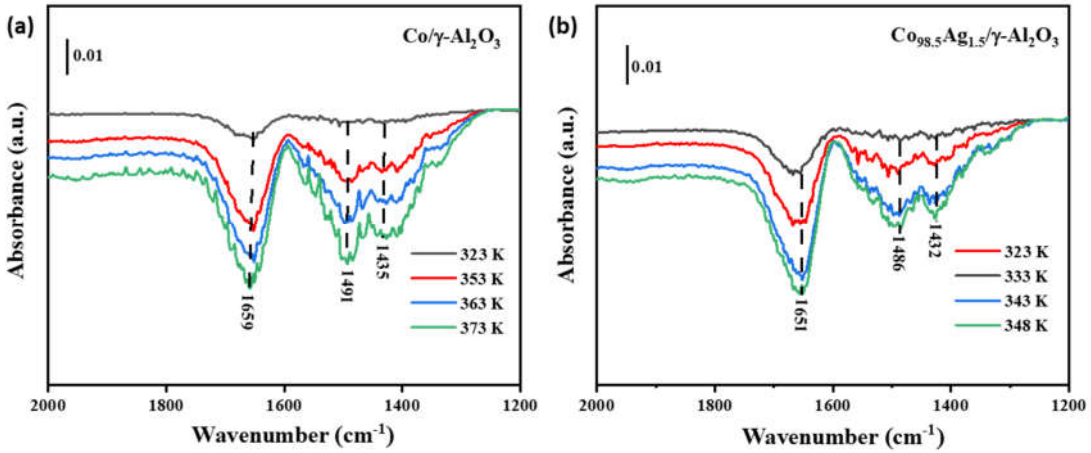

Fig. S12. Infrared spectra of NH_3 desorption as a function of temperature for (a) Co/γ-Al_2O_3 and (b) $Co_{98.5}Ag_{1.5}$/γ-Al_2O_3 (using the respective spectra collected at ambient temperature as the background).

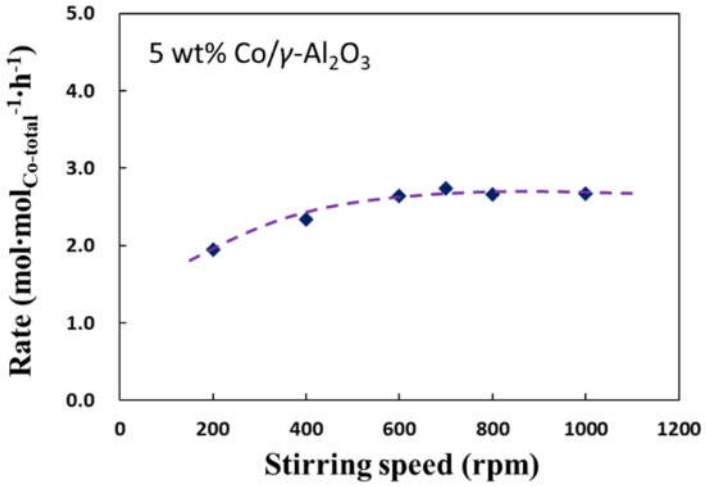

Fig. S13. Effect of stirring speed on the rate of ethylene glycol ammonolysis over 5 wt% Co/γ-Al_2O_3 (453 K, 0.6 MPa NH_3, 3.0 MPa H_2, 0.067 mol/L ethylene glycol in tetrahydrofuran solution, 2 h).

As shown in Figure S13, the rate of ethylene glycol ammonolysis on 5 wt% Co/γ-Al_2O_3 increased with the stirring speed until the speed was above 600 rpm, which reflects the threshold value to overcome the interphase diffusion limitation at the examined reaction condition. Our kinetic measurements were all conducted at a high speed of 800 rpm, ensuring that the interphase diffusion limitation was avoided in this study.

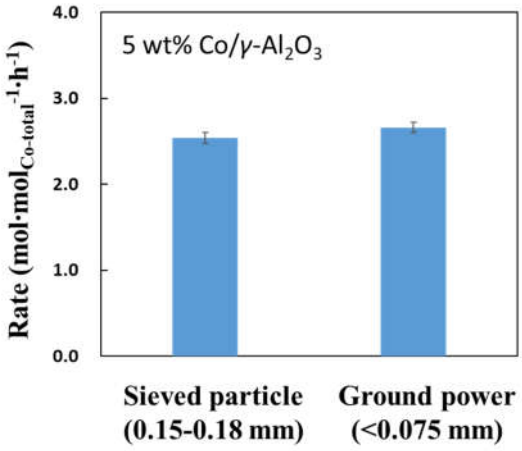

Fig. S14. Effect of particle size on the rate of ethylene glycol ammonolysis over 5 wt% Co/γ-Al_2O_3 (453 K, 0.6 MPa NH_3, 3.0 MPa H_2, 0.067 mol/L ethylene glycol in tetrahydrofuran solution, 2 h).

As shown in Figure S14, the rate of ethylene glycol ammonolysis obtained on two different particle-sized Co/γ-Al_2O_3 samples (0.15-0.18 vs. < 0.075 mm) were nearly identical (2.54 vs. 2.66 mol·$mol_{Co\text{-}total}^{-1}$·$h^{-1}$), indicating the intra-particle diffusion limitation can also be excluded.