

Electronic Supplementary Information

Improved H₂ Utilization by Pd doping in Cobalt Catalysts for Reductive Amination of Polypropylene Glycol

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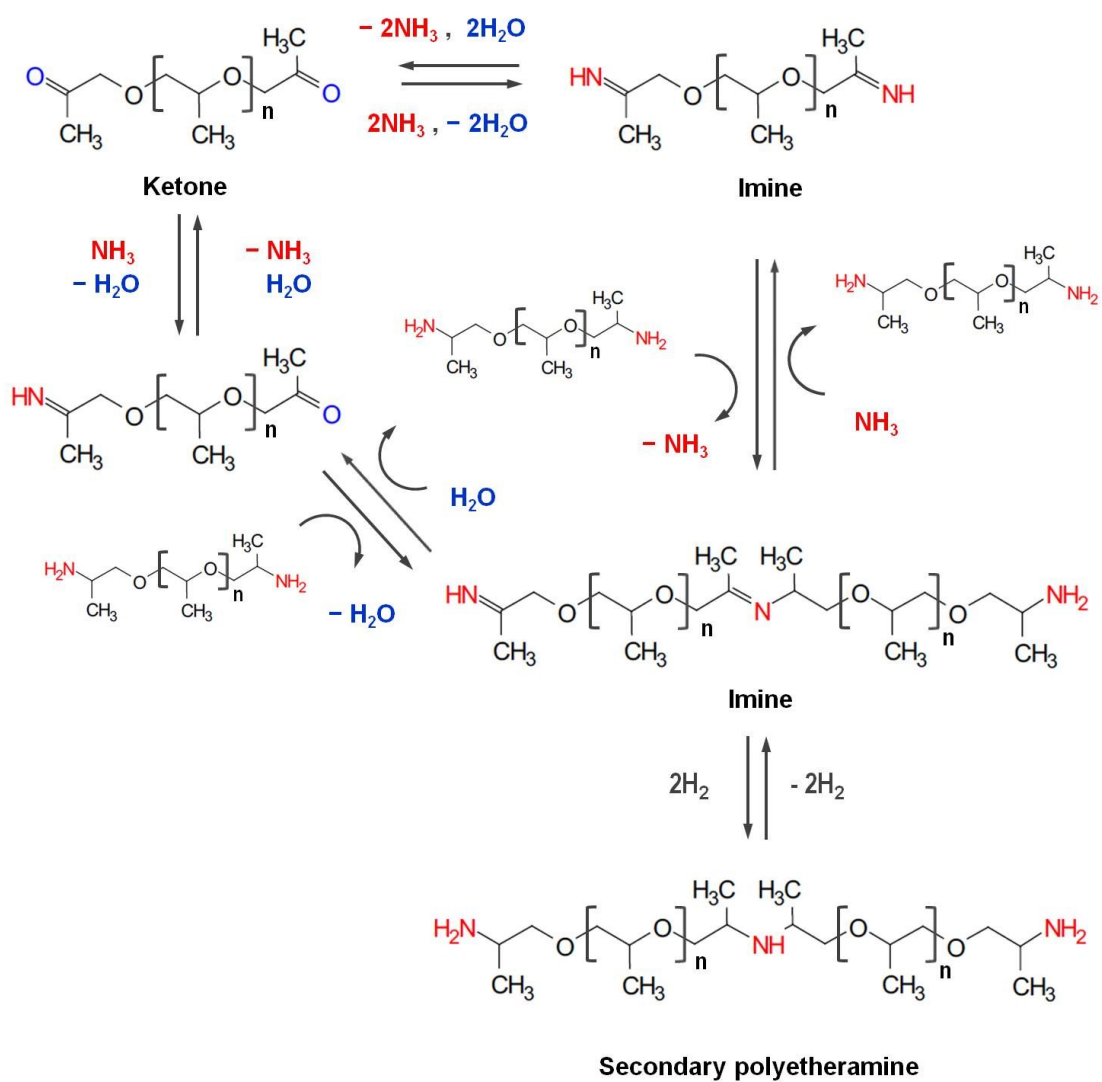
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Scheme S1. Reaction mechanism for the formation of secondary polyetheramine.

Table S1. Catalyst properties of Co-based catalysts including different Pd amounts.

Catalysts	Contents of Co/Y/Pd ^{a)} (wt%)			$S_{\text{BET}}^{\text{b)}$ (m ² /g)	$D_{\text{Co}}^{\text{c)}$ (nm)
	Co	Y	Pd		
Co-Y ₂ O ₃ -Pd(0)/MS	34.89	0.527	-	2.15x10 ²	8.2
Co-Y ₂ O ₃ -Pd(0.02)/MS	35.66	0.542	0.018	2.36x10 ²	15.9
Co-Y ₂ O ₃ -Pd(0.03)/MS	35.04	0.532	0.028	2.59x10 ²	16.8
Co-Y ₂ O ₃ -Pd(0.06)/MS	35.42	0.537	0.059	2.49x10 ²	13.9
Co-Y ₂ O ₃ -Pd(0.1)/MS	35.32	0.535	0.105	2.32x10 ²	14.0
Co-Y ₂ O ₃ -Pd(0)	70.17	1.155	-	2.95x10	19.9
Co-Y ₂ O ₃ -Pd(0.02)	68.18	1.113	0.017	2.91x10	19.0
Co-Y ₂ O ₃ -Pd(0.04)	69.30	1.134	0.038	3.10x10	17.9
Co-Y ₂ O ₃ -Pd(0.05)	69.48	1.140	0.054	2.74x10	18.6

^{a)} Determined by ICP-OES analysis for the fresh catalysts. ^{b)} BET surface area for fresh catalysts. ^{c)} The Co crystal size of the fresh catalysts was estimated by XRD patterns.

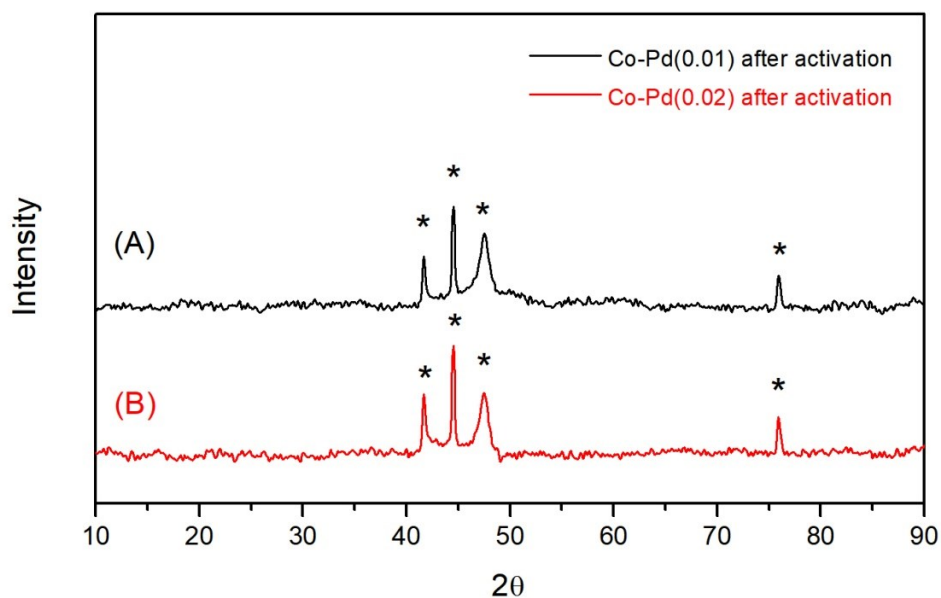


Fig. S1. XRD for pre-activated Co-Pd(0.01) at $P(\text{H}_2)=50$ bar (A) and XRD for pre-activated Co-Pd(0.02) at $P(\text{H}_2)=50$ bar (B). (*): Co^0 .

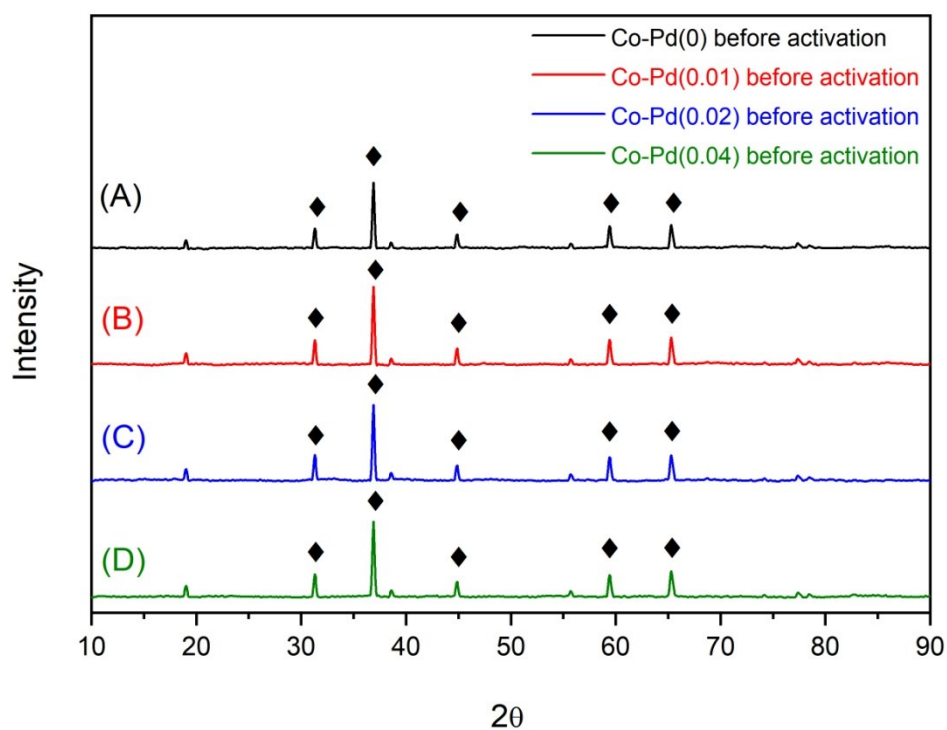


Fig. S2. XRD for Co-Pd(0) before catalyst activation (A), XRD for Co-Pd(0.01) before catalyst activation (B), XRD for Co-Pd(0.02) before catalyst activation (C), and XRD for Co-Pd(0.04) before catalyst activation (D). (◆): Co_3O_4 .

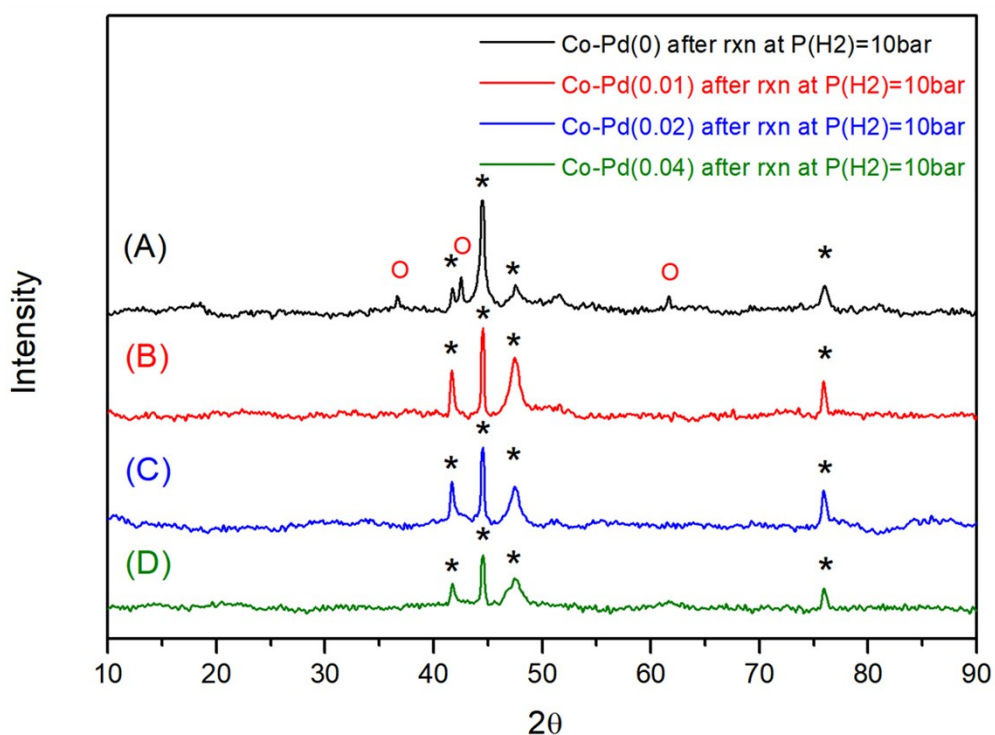


Fig. S3. XRD for spent Co-Pd(0) at $P(H_2)=10$ bar (A), XRD for spent Co-Pd(0.01) at $P(H_2)=10$ bar (B), XRD for spent Co-Pd(0.02) at $P(H_2)=10$ bar (C) and XRD for spent Co-Pd(0.04) at $P(H_2)=10$ bar (D). (*): Co^0 , (O): CoO , (◆): Co_3O_4 .

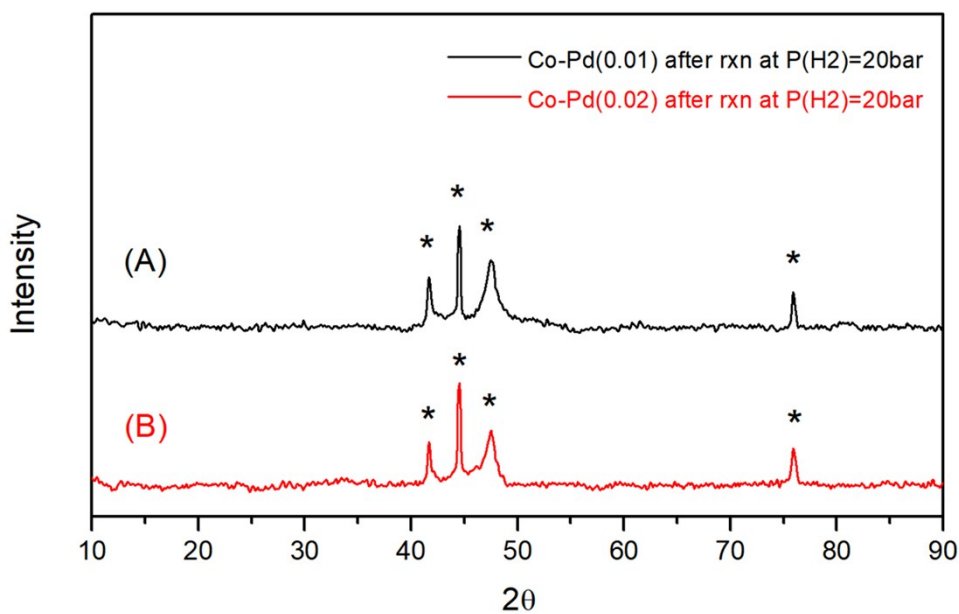


Fig. S4. XRD for spent Co-Pd(0.01) at $P(H_2)=20$ bar (A) and XRD for spent Co-Pd(0.02) at $P(H_2)=20$ bar (B). (*): Co^0 , (O): CoO , (◆): Co_3O_4 .

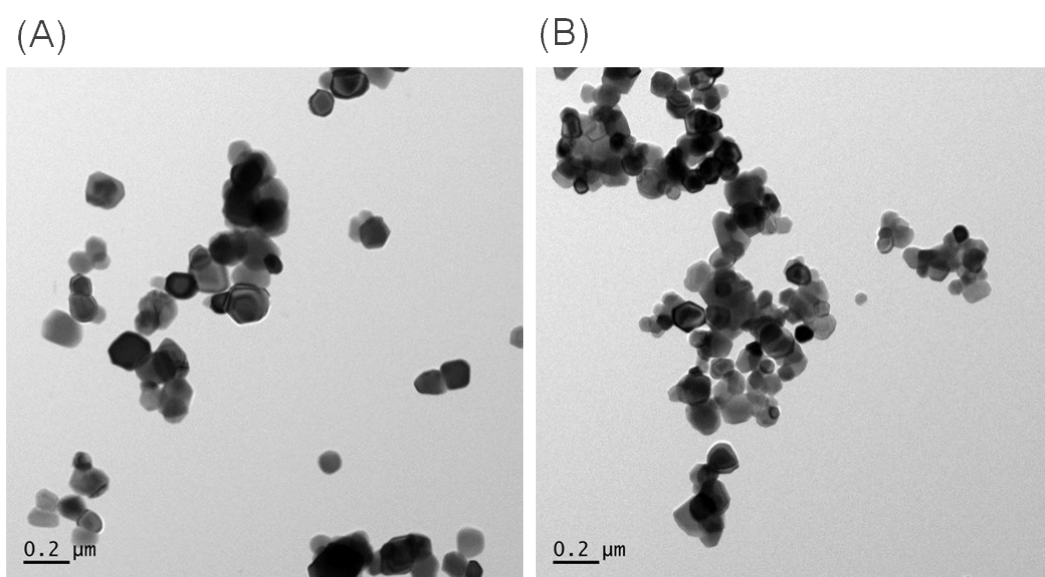


Fig. S5. TEM images for Co-Pd(0) before catalyst activation (A), for Co-Pd(0.04) before catalyst activation (B).

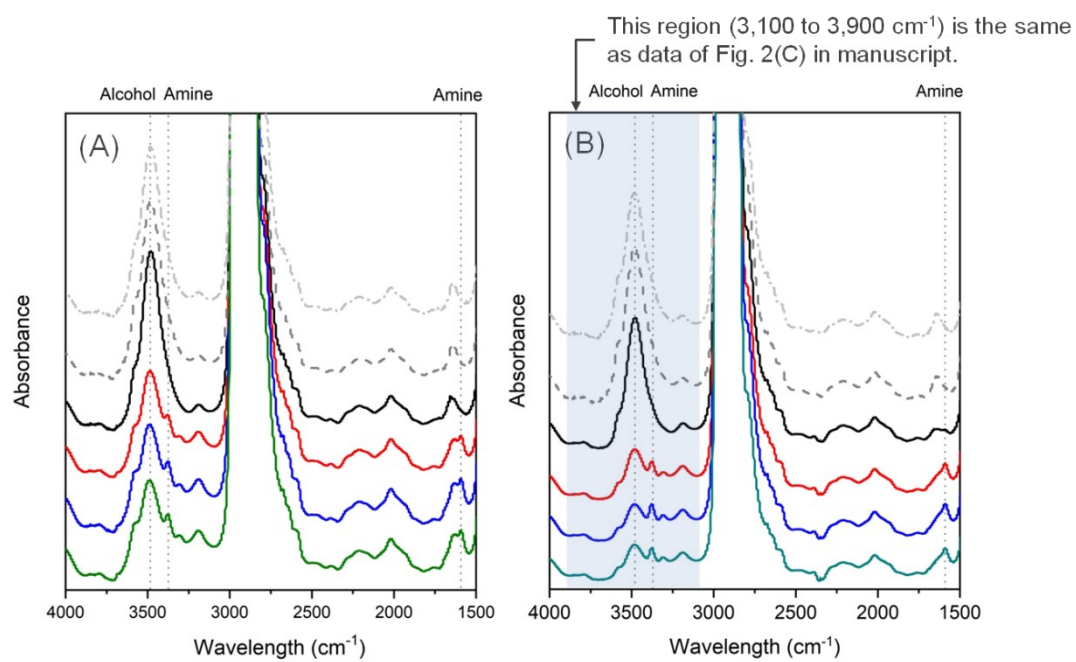


Fig. S6. IR results for PEA product at $P(H_2)=10$ bar by Co-Pd catalysts (A), at $P(H_2)=20$ bar by Co-Pd catalysts.

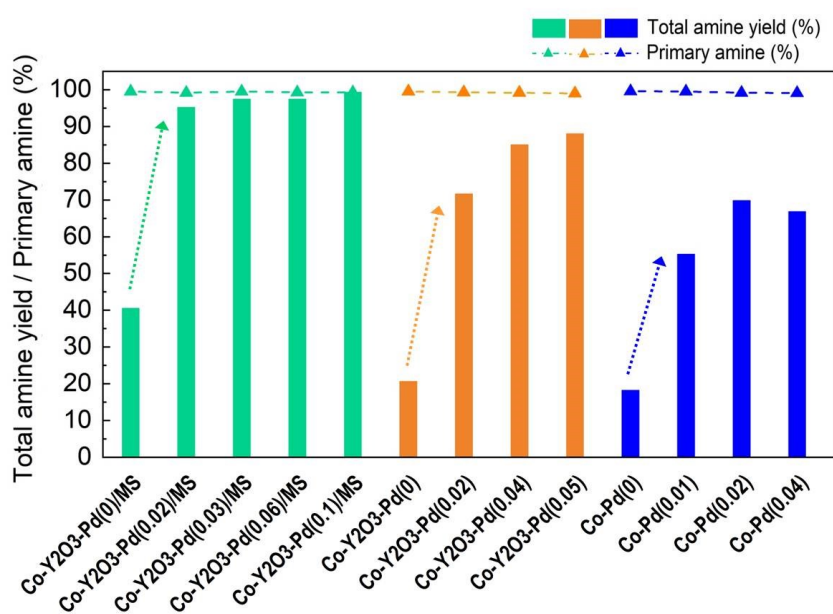


Fig. S7. Catalytic performance of Co based catalysts such as Co-Y₂O₃-Pd/MS, Co-Y₂O₃-Pd and Co-Pd with varying Pd amounts under P(H₂)=40 bar. Reaction conditions are NH₃/PPG-2000=40, PPG-2000: 70g, reaction temperature: 220°C, P(H₂)=40 bar and catalyst weight: 3.5 g for Co-Y₂O₃-Pd/MS, 2.0 g for Co-Y₂O₃-Pd and Co-Pd.

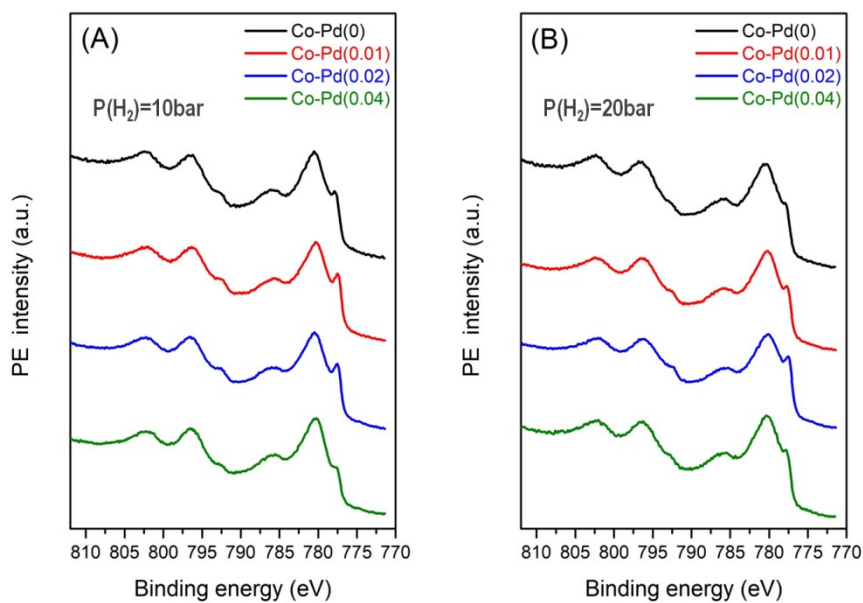


Fig. S8. Co 2p XPS for catalysts after reaction at $P(\text{H}_2)=10\text{ bar}$ (A), at $P(\text{H}_2)=20\text{ bar}$ (B). Co 2p peaks in each sample were normalized to compare quantitatively as a way of dividing Co 2p peak intensity with relative ratio of Co 2p area (771 eV to 812 eV) in each sample.

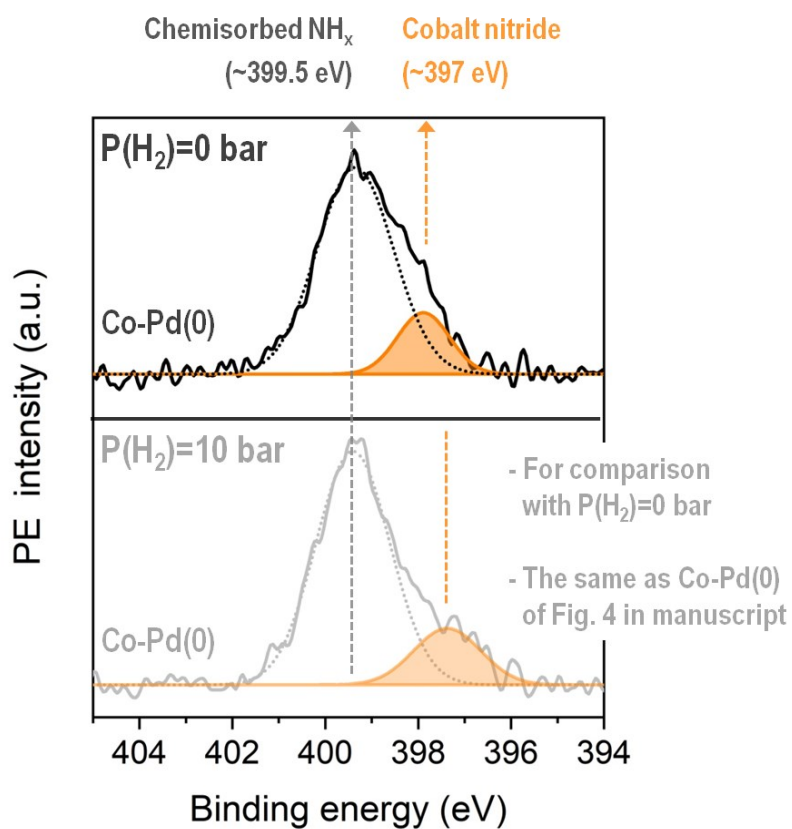


Fig. S9. N 1s XPS for spent Co-Pd(0) after reaction at P(H_2)=0 bar.

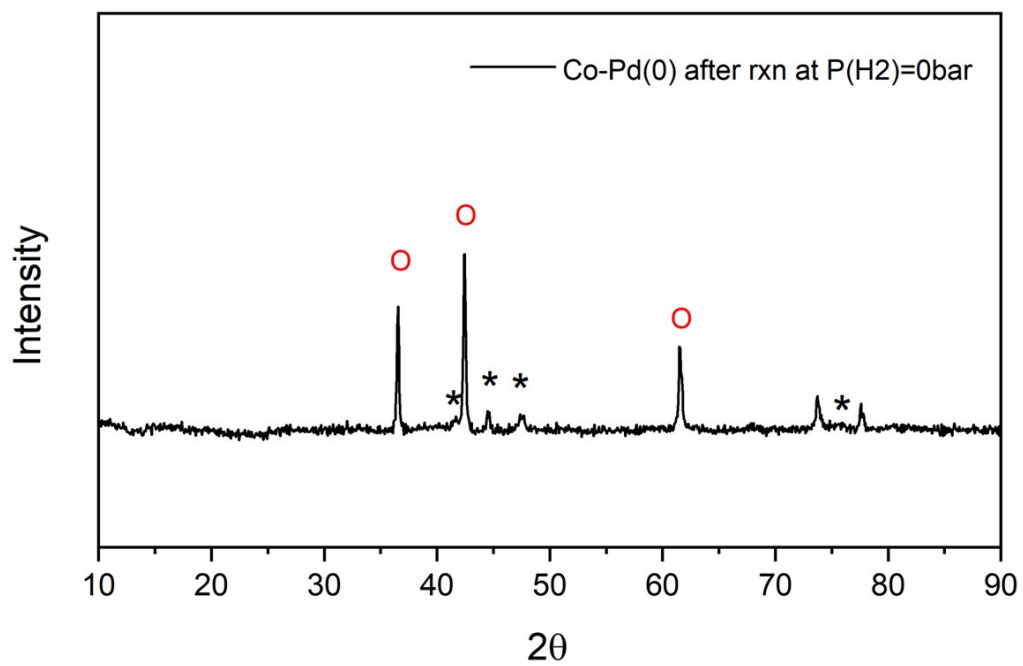


Fig. S10. XRD for spent Co-Pd(0) at P(H₂)=0 bar. (*): Co⁰, (○): CoO.

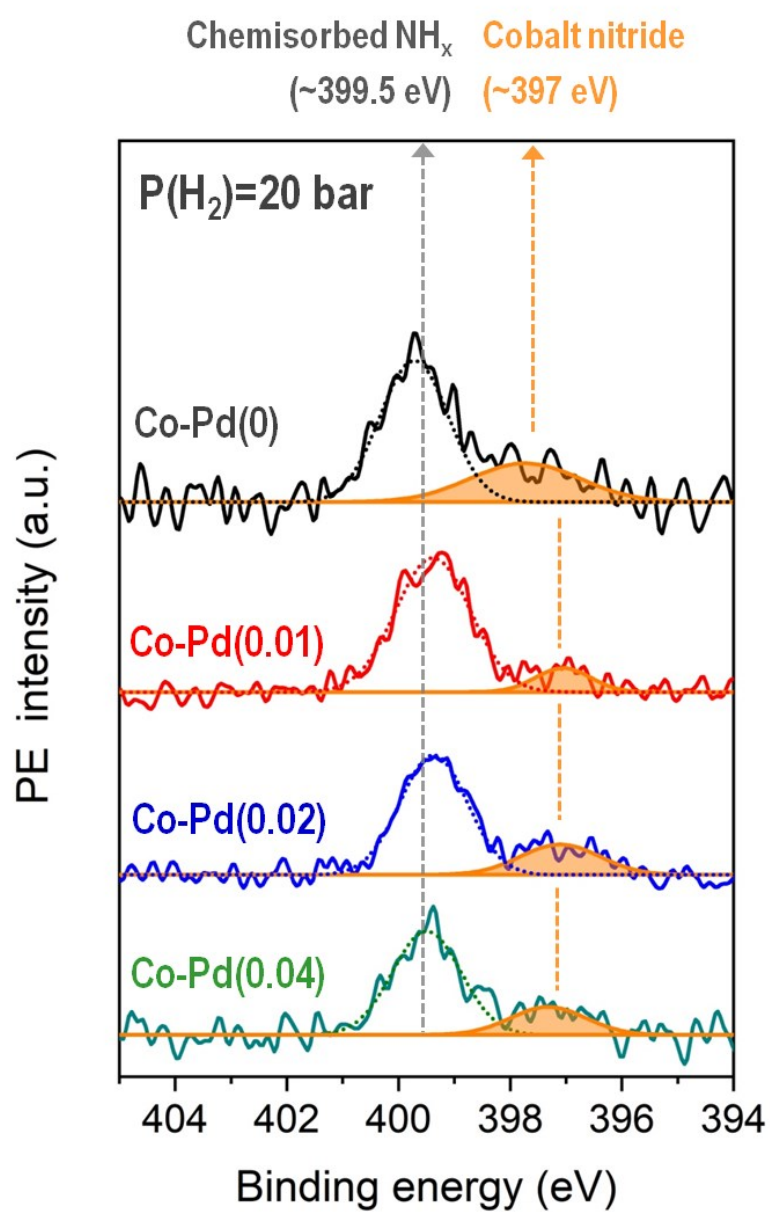


Fig. S11. N 1s XPS for spent catalysts after reaction at $\text{P}(\text{H}_2)=20$ bar.

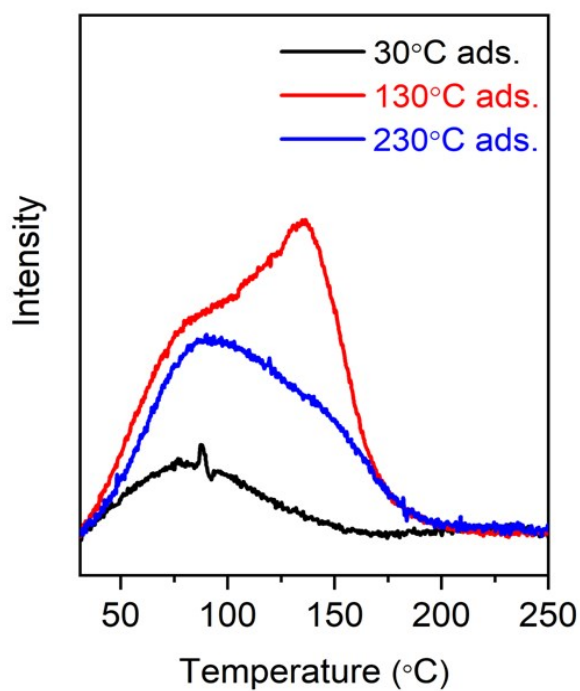


Fig. S12. H₂-TPD for Co-Pd(0) catalyst depending on H₂ adsorption temperature. Pretreatment conditions: After catalyst reduction in 5.0 % H₂/Ar by 460 °C, temperature was maintained at 460 °C for 15 min in Ar for removing both free H₂ and adsorbed H₂. In addition, H₂ was adsorbed at each temperature for 2 h and then the catalysts were cooled to room temperature. Measurement conditions: Ramping rate 10 °C/min, Ar 30 sccm.

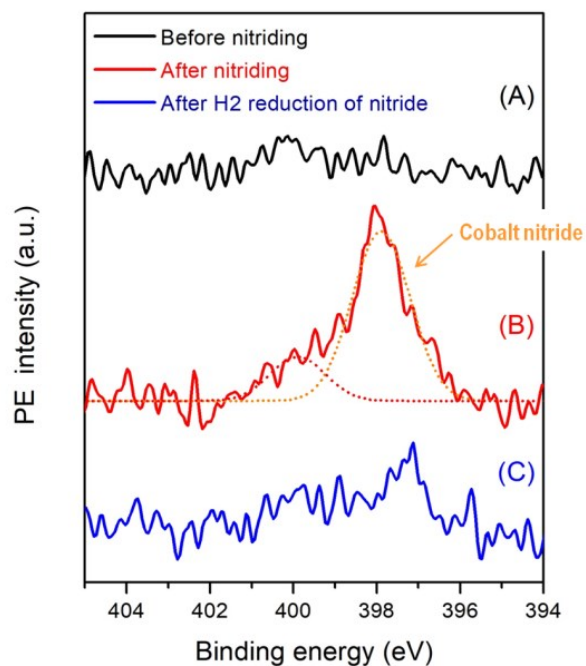


Fig. S13. N 1s XPS for Co-Pd(0) after catalyst activation by 5.0 % H₂/Ar by 460 °C (Before nitriding) (A), XPS N1s for Co-Pd(0) after introducing 5.0 % NH₃/He into activated catalyst at 230 °C for 0.5 h (After nitriding) (B), and XPS N1s for Co-Pd(0) after introducing H₂ into Co₃N containing catalyst until temperature reaches to 220 °C (After H₂ reduction of nitride) (C).

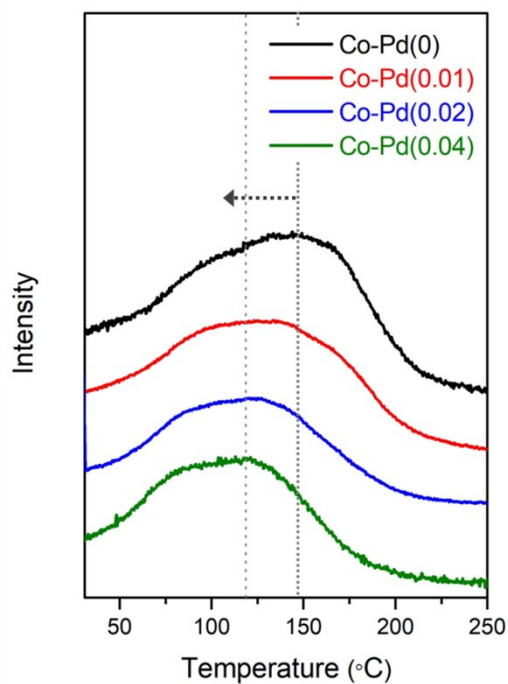


Fig. S14. H₂-TPD for Co-Pd catalysts with the step for the formation of cobalt nitride. Pretreatment conditions: After catalyst reduction in 5.0 % H₂/Ar by 460 °C, temperature was maintained at 460 °C for 15min in Ar for removing both free H₂ and adsorbed H₂. And 5.0 % NH₃/He was introduced at 230 °C for 0.5 h to form cobalt nitride. Catalysts were cooled to the room temperature. H₂ was introduced to reduce cobalt nitride until temperature reached to 220 °C, followed by maintaining at 220 °C to remove both free H₂ and adsorbed H₂. Then H₂ was adsorbed at 130 °C for 2 h and catalysts were cooled to the room temperature. Measurement conditions: Ramping rate 10 °C/min, Ar 30 sccm.

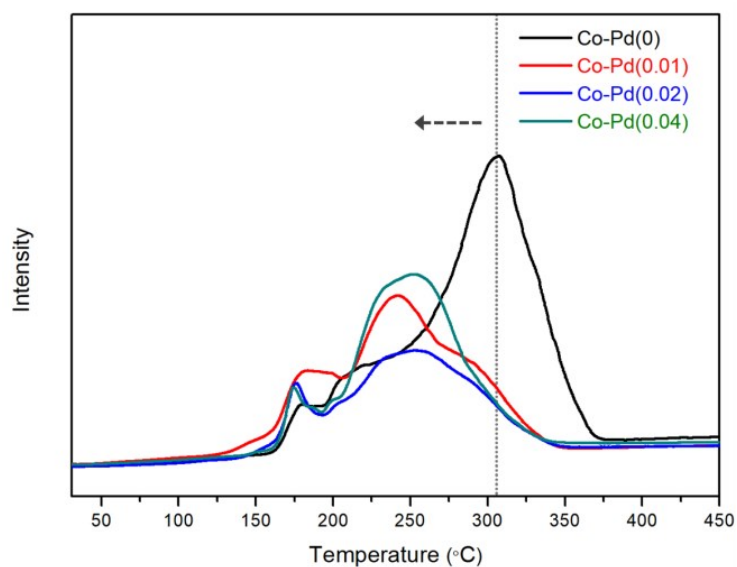


Fig. S15. H_2 temperature programmed adsorption of the Co-Pd catalysts containing cobalt nitride. Pretreatment conditions: After catalyst reduction in 5.0 % H_2 /Ar by 460 °C and temperature was maintained at 460 °C for 15 min in Ar for removing both free H_2 and adsorbed H_2 . 5.0 % NH_3 /He was introduced at 230 °C for 0.5 h to form cobalt nitride. Catalysts were cooled to the room temperature. Measurement conditions: Ramping rate 10 °C/min, 5.0 % H_2 /Ar 30 sccm.