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Strong Metal−Support Interactions of Co-Based Catalysts Facilitated by Dopamine for High Efficient Ammonia Synthesis: *In Situ* XPS and XAFS Spectroscopy Coupled with TPD Study

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Experimental

Synthesis of Co/CeO_2 precursor

Nitrate salts of cobalt and cerium were simultaneously dissolved in deionized water. The content of Co was 20 wt.% against CeO_2. Aqueous ammonia was dropped slowly into the mixture with vigorous stirring. The resultant slurry was stirred for 0.5 h and washed several times with deionized water, then aged at 40 °C for 4 h and dried at 120 °C for 24 h to give the Co/CeO_2 precursor.

Synthesis of Co/CeO_2@dopamine

The as-prepared Co/CeO_2 precursor (0.5 g) was stirred in dopamine-containing (1 mg/mL) tris-buffer solution (100 mL, 10 mM; pH 8.5) for 24 h. The suspension was filtered out and washed with deionized water and ethanol for several times, and then dried at 40 °C under vacuum for 12 h. The obtained powder is herein labeled as Co/CeO_2@dopamine.

Synthesis of Co/CeO_2-D-T (T denotes the temperature for heat treatment in N_2)

The as-generated Co/CeO_2@dopamine was treated in N_2 at different temperatures (400, 500 and 600 °C) for 4 h, and then calcined in 10%O_2/Ar at 500 °C for 6 h (for carbon removal) to obtain the Co/CeO_2@-D-T samples. For the purpose of performance comparison, a sample labeled herein as Co/CeO_2 was obtained by having Co/CeO_2@dopamine subject to heat treatment at 500 °C for 6 h.

1.2 Evaluation of catalytic activity.

Before the evaluation of catalytic activity for ammonia synthesis, the samples (0.30 g, diluted with quartz powder in a 1:10 volumetric ratio) were reduced in a 10%H_2/Ar mixture at 450 °C for 2 h. Under the condition of 1 MPa (N_2:H_2 = 1:3) at a GHSV of 70,000 h^{-1}, the outlet ammonia concentrations were analyzed based on a known amount of diluted H_2SO_4 solution (0.02 mol L^{-1}), as well as measured by ion chromatography (Thermo Scientific, DIONEX, ICS-600). Finally, the ammonia synthesis rates were calculated based on the outlet ammonia concentrations.

1.3 Characterization.

Powder X-ray diffraction (XRD) was performed on a Panalytical X'Pert Pro diffractometer using Co-K_α radiation. N_2 physisorption measurements were carried out at 77 K on an ASAP 2020 apparatus. High-resolution transmission electron microscopy (HR-TEM) measurement was performed on a JEM-2010 microscope. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was carried out using an Ultima 2 spectrometer. Temperature-programmed desorption was carried out by mass spectrometry using an Autochem 2920 instrument. After being reduced in hydrogen at 400 °C for 2 h, flushed in Ar, and cooled down to 50 °C, the catalyst (100 mg) was exposed to hydrogen or nitrogen at 50 °C for 1 h. The sample was flushed with Ar for 1 h, then heated up to 900 °C at a rate of 10 °C min^{-1}. The desorption of hydrogen or nitrogen was monitored by having the mass signals of m/z = 2 (H_2) and 28 (N_2) recorded. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Physical Electronics Quantum 2000 (provided with a path-heated gas cell) spectrometer equipped with monochromatic Al-K_α source (K_α = 1,486.6 eV) and a charge neutralizer. During *in situ* XPS experiments processes, Co/CeO_2@dopamine was firstly pretreated with N_2 at 400, 500 or 600 °C for 4 h to acquire Co/CeO_2@dopamine-400, Co/CeO_2@dopamine-500 and Co/CeO_2@dopamine-600, and then all of them were treated with 10%O_2/Ar at 500 °C for 6 h (for carbon removal) to obtain the Co/CeO_2@-400, Co/CeO_2-500 and Co/CeO_2-600 samples, respectively. To be noted, Co/CeO_2 was obtained via directly treating Co/CeO_2 precursor with 10%O_2/Ar at 500 °C for 6 h. Finally, they were transformed to UHV chamber to perform XPS in high vacuum.

Raman spectra of samples were collected under ambient condition on a Renishaw spectrometer using a laser beam of λ = 532 nm for excitation. X-ray absorption fine structure (XAFS) measurements were performed at the 1W2B beam line of Beijing Synchrotron Radiation Facility. The Co K-edge spectra of samples in fluorescence mode were recorded at room temperature. A Si (111) double-crystal monochromator was used to reduce the harmonic content of the monochrome beam.

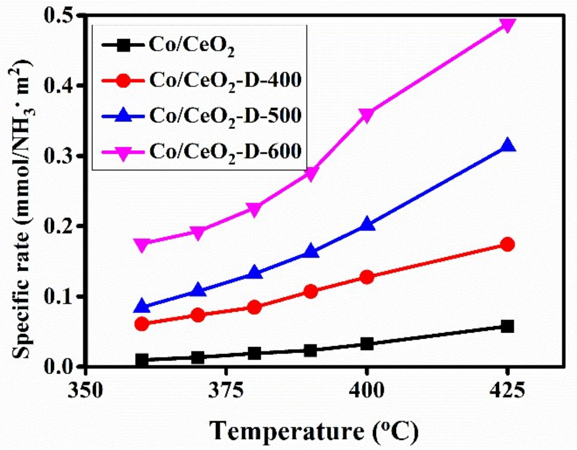

Figure S1 Ammonia synthesis reaction rates normalized with respect to BET surface area.

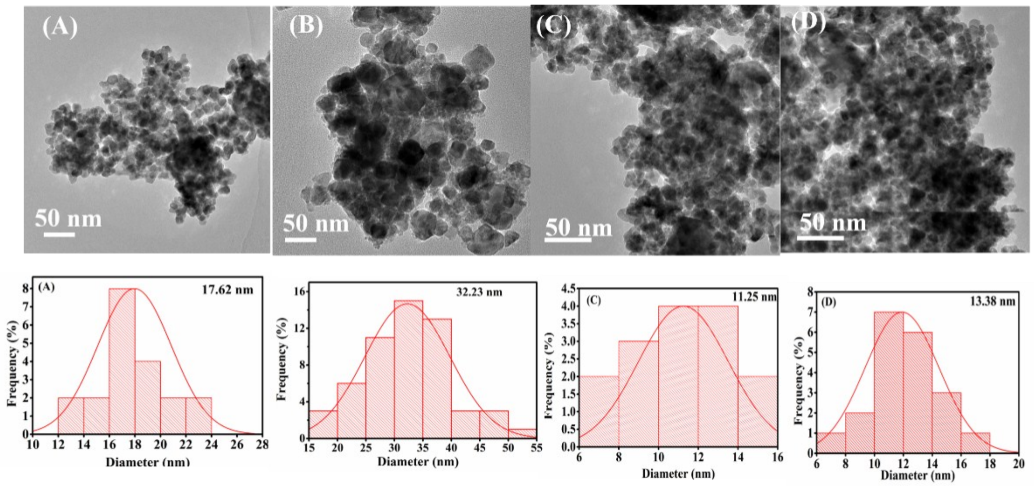

Figure S2 TEM images of fresh Co/CeO_2 (A) and Co/CeO_2-D-500 (C), used Co/CeO_2 (B) and Co/CeO_2-D-500 (D); Particle distribution of Co nanoparticles over fresh Co/CeO_2 (A) and Co/CeO_2-D-500 (C), used Co/CeO_2 (B) and Co/CeO_2-D-500 (D).

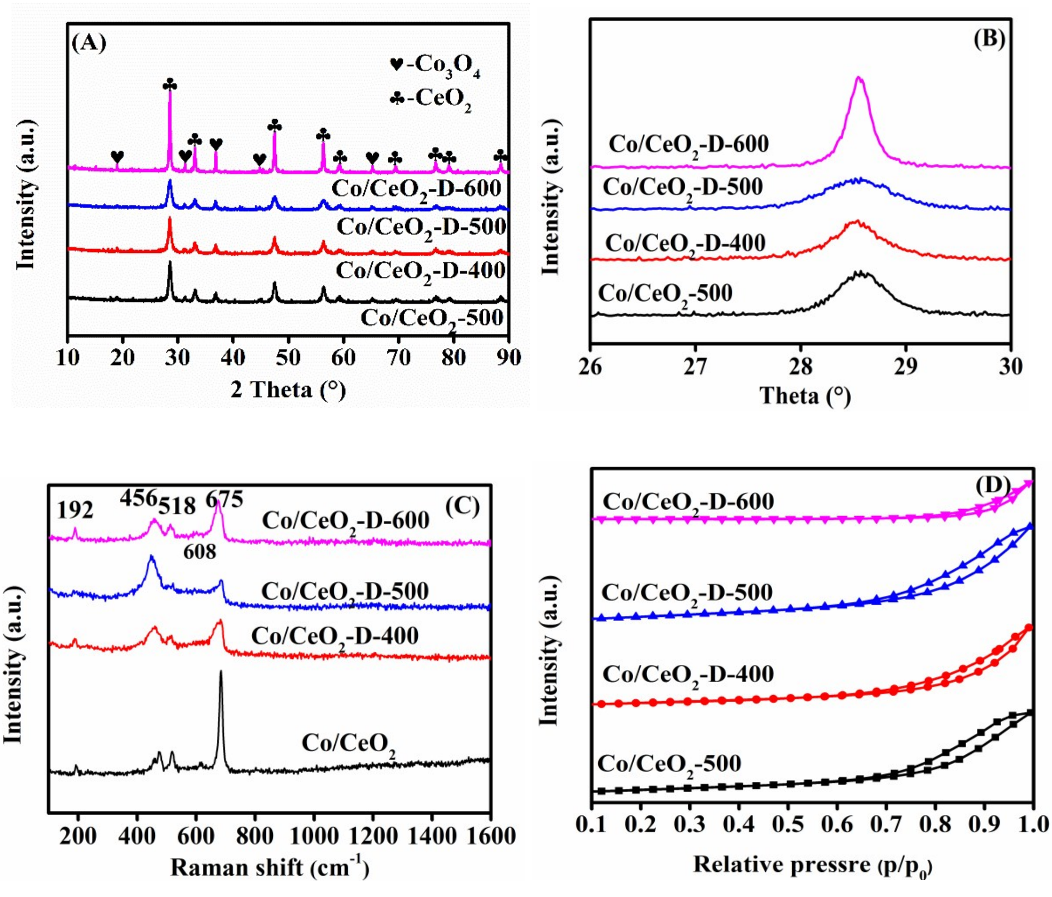

Figure S3 (A) XRD patterns, (B) the magnified XRD patterns of CeO_2 (111); (C) Raman spectra and (D) N_2 adsorption-desorption profiles of as-prepared catalysts.

The bands at 192 and 675 cm^{-1} are characteristics of tetrahedral (CoO_4) and octahedral (CoO_6) sites, corresponding to the $F_{2g}{}^1$ symmetry and $O_h{}^7$ spectroscopic symmetry, respectively. In comparison with Co/CeO_2, the Raman peaks located at 456, 518 and 675 cm^{-1} in Co/CeO_2-D-400, Co/CeO_2-D-500 and Co/CeO_2-D-600 are red shifted and broadened, plausibly a result of interaction between cobalt and cerium species in various extents.

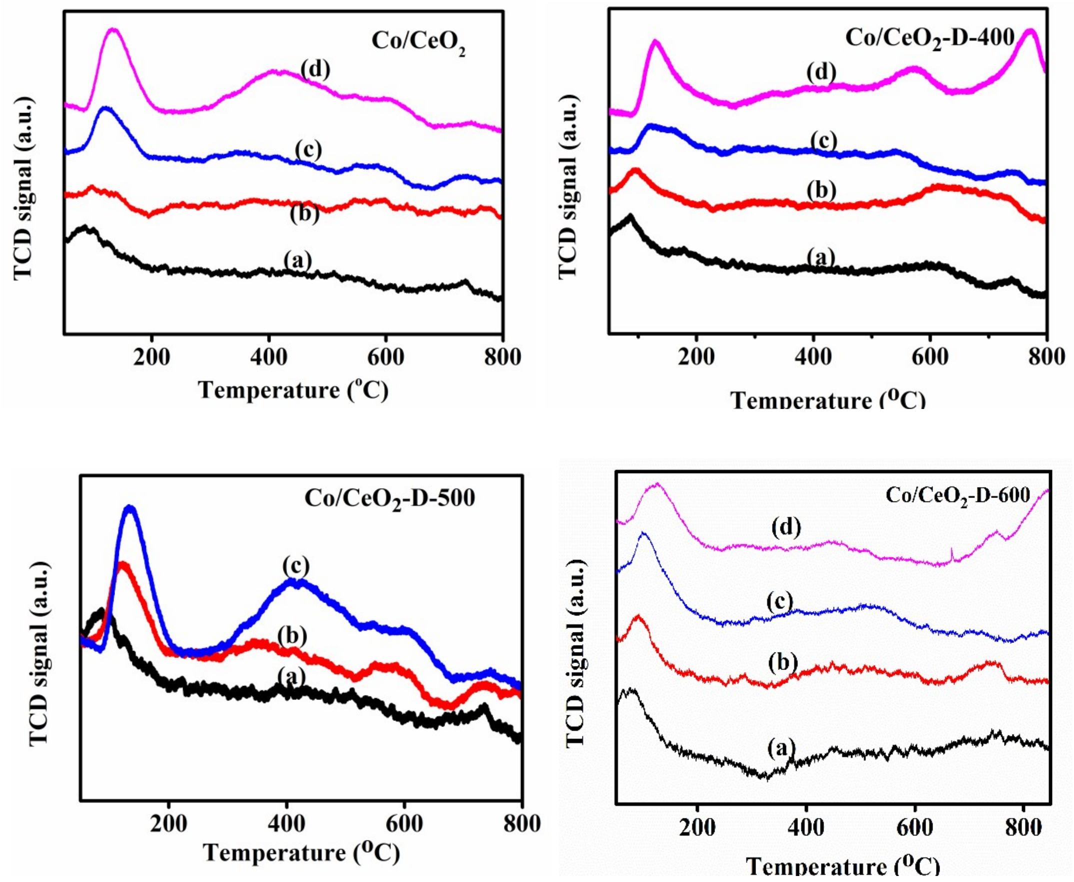

Figure S4 N_2-TPD profiles of as-prepared catalysts with different heating rates: (a) 5 °C/min, (b) 10 °C/min, (c) 20 °C/min and (d) 30 °C/min.

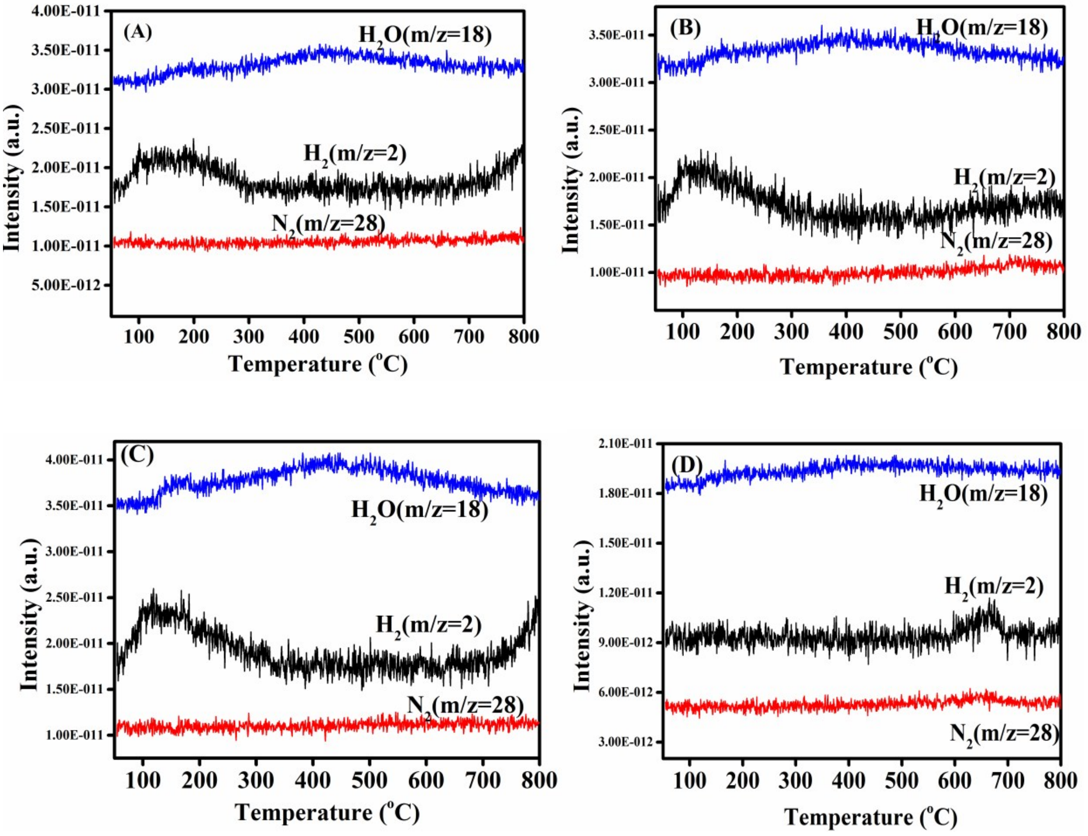

Figure S5 N_2+H_2-TPD-MS profiles of (A) Co/CeO_2, (B) Co/CeO_2-D-400, (C) Co/CeO_2-D-500 and (D) Co/CeO_2-D-600.

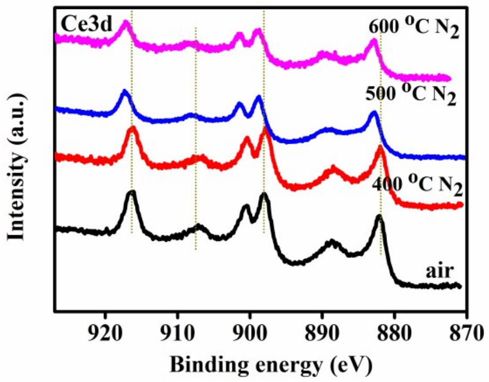

Figure S6 Ce3d spectra acquired during *in situ* XPS analysis of Co/CeO_2@dopamine treated at different temperatures (more details see the XPS experiments section).

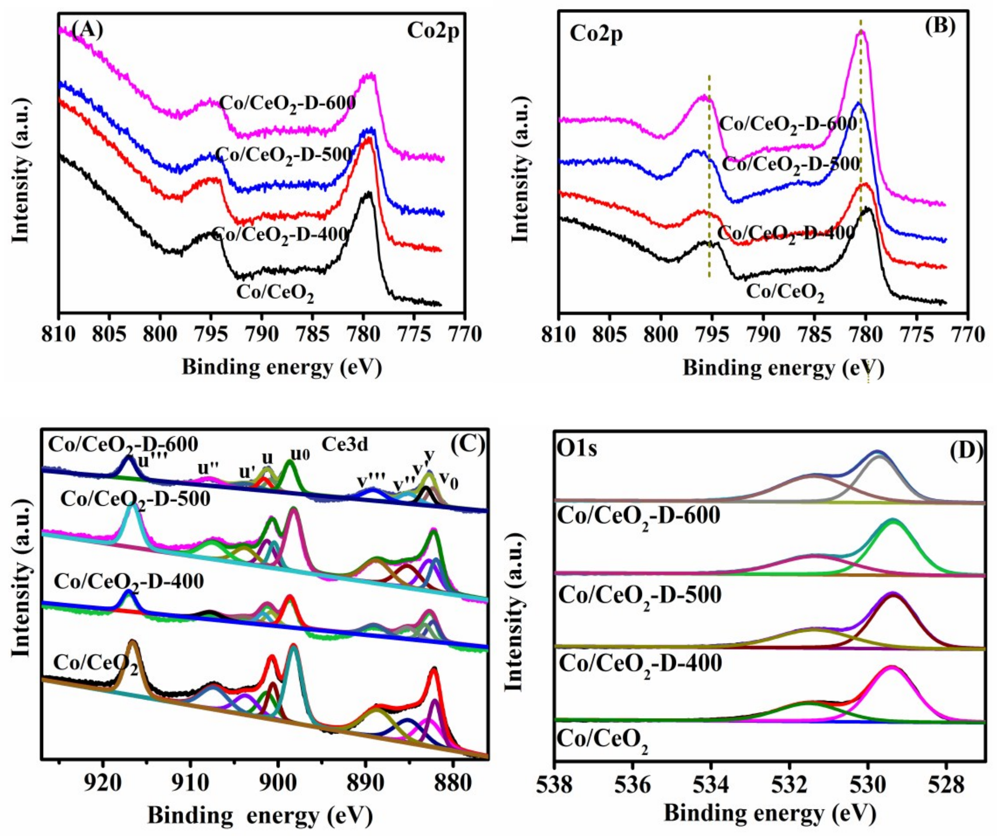

Figure S7 Co2p spectra of (A) as-prepared catalysts and (B) catalysts *in situ* treated with 10%H_2/Ar at 450 °C for 2 h; (C) Ce3d and (D) O1s spectra of as-prepared catalysts *in situ* treated with 10%H_2/Ar at 450 °C for 2 h.

For the Ce3d spectra (Figure S6C), the peaks labeled U′, U_0, V′ and V_0 are indicative of surface Ce^{3+} species with $3d^{10}4f^1$ initial electronic configuration, while the peaks labeled U, U″, U‴, V, V″ and V‴ are indicative of surface Ce^{4+} species with $3d^{10}4f^0$ electronic configuration. The Ce^{3+}/Ce ratio was calculated and the results are given in Table S3. To clarify the type of oxygen species that could be involved in the redox or associative mechanisms, we have the O1s spectra of catalysts compiled in Figure S6D. The peak at 529.3–529.7 eV can be assigned to lattice oxygen (O_{latt}), while the one at 531.3–531.5 eV to surface adsorbed oxygen species (O_{ads}) generated in the adsorption of gaseous O_2 onto oxygen vacancies. The $O_{ads}/(O_{ads} + O_{latt})$ ratio of the as-prepared catalysts are in the order of Co/CeO$_2$-D-600 (50%) > Co/CeO$_2$-D-500 (38%) ~ Co/CeO$_2$-D-400 (37%) > Co/CeO$_2$ (31%), indicating that the oxygen vacancies may not take part in the ammonia synthesis process.

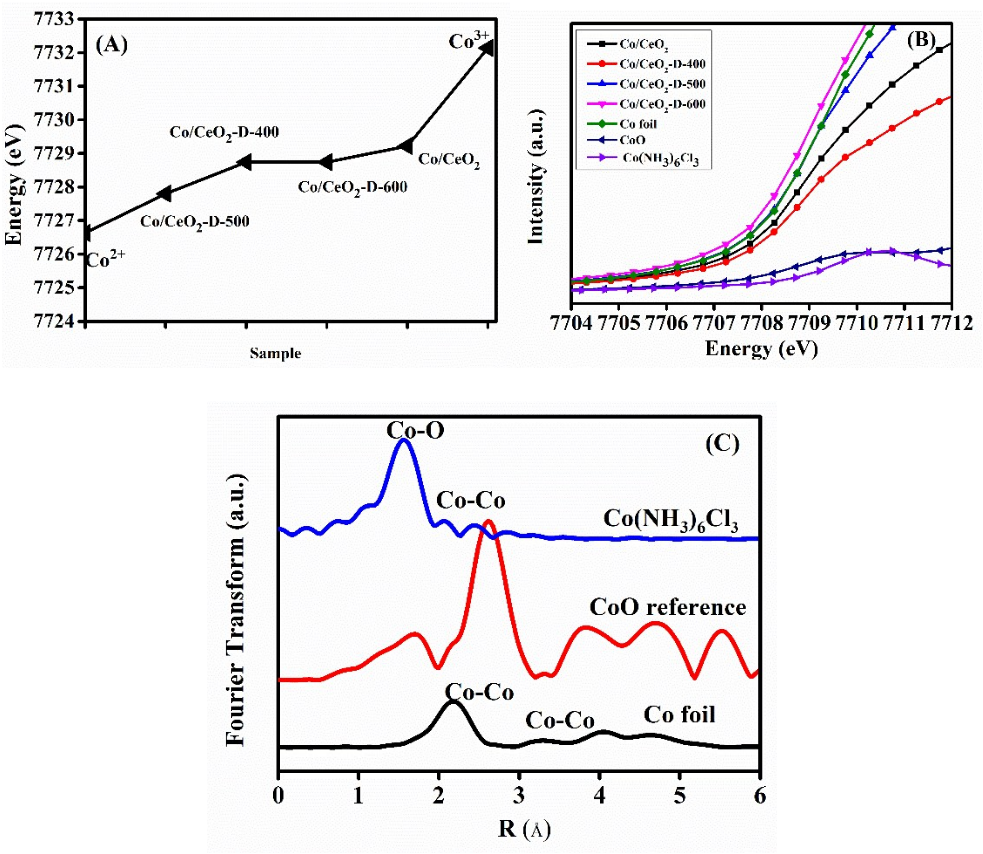

Figure S8 (A) Energy position of main Co K-edge absorption over the samples, (B) pre-edge of XANES spectra at the Co K-edge of catalysts, and (C) Co K-edge EXAFS spectra of reference samples.

The pre-edge of Co K-edge recorded over the reduced catalysts are shown in Figure S7C. The pre-edge peaks disappear after the catalysts were reduced in H_2 at 450 °C for 2 h, a result of Co_3O_4 transformation to Co nanoclusters. The electronic structure of Co species over the as-prepared catalysts is further proved by the spectra of extended X-ray absorption fine structure (EXAFS) analysis.

Table S1 Crystalline size, textural properties, Co content and reaction activation energy (E_a) of as-prepared catalysts.

Sample	Crystalline size of CeO_2 (nm)	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)	Co content (%)	E_a (kJ/mol)
Co/CeO_2	15.01	66	0.081	5.36	18.4	107
Co/CeO_2-D-400	14.73	65	0.143	14.9	18.2	77
Co/CeO_2-D-500	10.39	61	0.099	6.06	18.8	72
Co/CeO_2-D-600	33.91	20	0.093	15.04	18.9	81

Table S2 N_2-TPD data and E_d of N_2 desorption energies over Co/CeO_2-D-500 and Co/CeO_2 catalysts.

Sample	β (°C/min)				E_d (kJ/mol)
	T_1 (5) (°C)	T_1 (10) (°C)	T_1 (20) (°C)	T_1 (30) (°C)	
Co/CeO_2	81	97	123	138	39.1
Co/CeO_2-D-400	84	97	120	132	35.5
Co/CeO_2-D-500	88	113	138	-	27.4
Co/CeO_2-D-600	80	95	110	124	41.2

Table S3 Surface element concentration, binding energy, $Ce^{3+}/(Ce^{3+}+Ce^{4+})$ and $O_{ads}/(O_{ads}+O_{latt})$ ratio

Sample	Surface element concentration (%)	Binding energy (eV)	$Ce^{3+}/(Ce^{3+}+Ce^{4+})$ (%)	$O_{ads}/(O_{ads}+O_{latt})$ (%)
	Co	$Co2p_{3/2}$		
Co/CeO_2	14.13	779.87	33.1	31
Co/CeO_2-D-400	14.16	780.08	35.5	37
Co/CeO_2-D-500	14.96	780.59	35.6	38
Co/CeO_2-D-600	18.06	780.40	32.0	50

Mass Transfer Calculation for ammonia synthesis over the Co/CeO$_2$-D-500 catalyst

Mears Criterion for External Diffusion (Fogler, p841; Mears, 1971)

If $\frac{-r_A'\rho_b R n}{k_c C_{Ab}}$ < 0.15, then external mass transfer effects can be neglected.

$-r_A'$ = reaction rate of nitrogen, kmol/(kg·cat·s)

n = reaction order with respect to nitrogen gas.

R = catalyst particle radius, m

ρ_b = bulk density of catalyst bed, kg/m^3

C_{Ab} = bulk gas concentration of nitrogen, kmol/m^3

k_c = mass transfer coefficient, m/s

$\frac{-r_A' \rho_b R n}{k_c C_{Ab}}$ =[6 x 10^{-7} kmol-N_2/(kg·cat·s)] [910 kg/m^3][2.5 x 10^{-4} m][1]/(1.7m/s)]*[0.04 kmol/m^3])**=2.0x10^{-7} <0.15 {Mears for External Diffusion}**

Weisz-Prater Criterion for Internal Diffusion (Fogler, p839)

If $C_{WP} = \frac{-r'_{A(obs)} \rho_c R^2}{D_e C_{As}} < 1$, then internal mass transfer effects can be neglected.

$-r'_{A(obs)}$ = reaction rate of nitrogen, kmol/(kg·cat·s)

ρ_c is solid catalyst density, kg/m^3

R = catalyst particle radius, m

ρ_b = bulk density of catalyst bed, kg/m^3

C_{Ab} = bulk gas concentration of nitrogen, kmol/m^3

D_e = effective gas-phase diffusivity, m^2/s **[Fogler, p815]**

C_{As} = gas concentration of A at catalyst surface, kmol-A/m^3

$C_{WP} = \frac{-r'_{A(obs)} \rho_c R^2}{D_e C_{As}}$ =[6 x 10^{-7} kmol-N_2/(kg·cat · s] [2.8*10^3 kg-cat/m^3] *[2.5 x 10^{-4} m]^2/(3.3 x 10^{-6} m^2/s)]* [0.04kmol-N_2/m^3]) = **7.95x 10^{-4} < 1**

{Weisz-Prater Criterion for Internal Diffusion}