

Supporting Information

Effect of pretreatment on ceria-supported cobalt catalyst for ammonia synthesis

Bingyu Lin*, Yanchao Qi, Kemei Wei, Jianxin Lin

1. The main species detected

When CeO₂ or Co catalysts prepared from Ce(NO₃)₂ and Co(NO₃)₃ was reduced in hydrogen, different species such as H_xO (x=0, 1, 2), NO₂, NO, NH₃ (x=0, 1, 2, 3) would be produced. The amount of some species such as hydrogen or oxygen may also change. Consequently, the signal measured at an m/z value may be mixed with two contributions. One is due to the direct ionization of a specie, and the other is due to the dissociative ionization of larger species in the ionization chamber. Table S1 gives some m/z values in mass spectra and their corresponding species during the heating treatment process of CeO₂ or Co catalysts.

Table S1 Different m/z values detected by means of mass spectrometer and their corresponding

species	
m/z	species
2	H ₂
15	NH
16	NH ₂ , O
17	NH ₃ , HO
18	H ₂ O
30	NO, N ₂ H ₂
32	O ₂ , N ₂ H ₄
46	NO ₂

Fig. S1 showed the mass signal for blank tube with 5 vol% NH₃/He pulse chemisorption at 50 °C and the ratios of relative signal intensity at 50 and 430 °C. These signals measured for m/z =15, 16 and 17 results all were from the dissociative ionization of ammonia. The ratios of

NH/NH₃ and NH₂/NH₃ ranged from 0.34-0.50 and 7.4-10.1, respectively. The ratios of O/H₂O and HO/H₂O, which obtained by heating of silica gel pre-adsorbed water in Ar gas, were in the range of 0.11-0.12 and 0.16-0.17, respectively (Fig. S2).

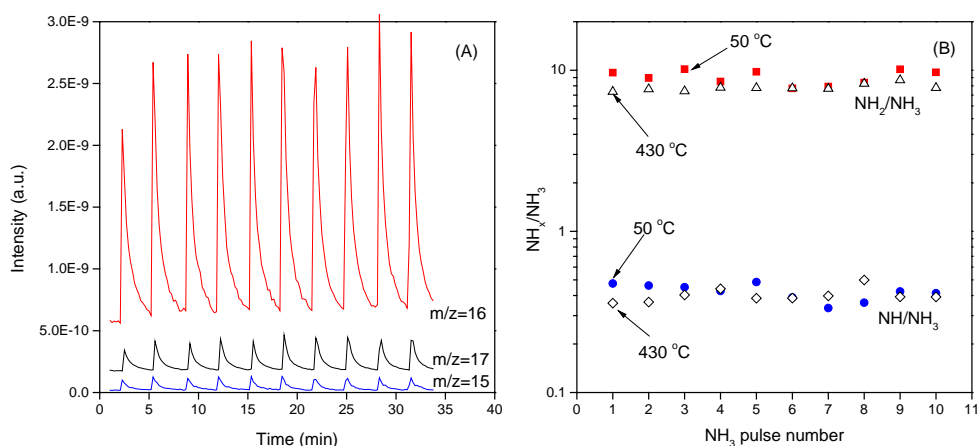


Fig. S1 (A) 5 vol% NH₃/He pulse chemisorption results at 50 °C measured by mass spectrometer and (B) The ratios of relative mass signal intensity: NH/NH₃ and NH₂/NH₃ versus NH₃ pulse number.

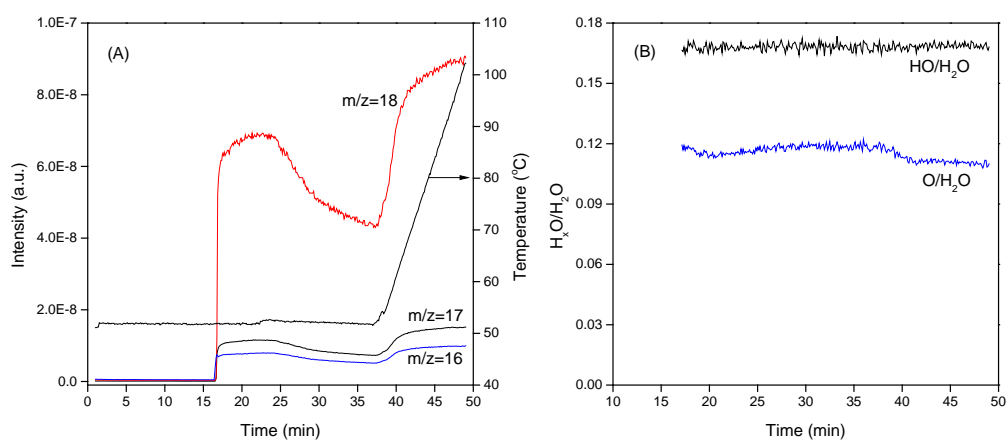


Fig. S2 (A) Temperature programmed desorption results for silica gel pre-adsorbed water and (B) The ratios of relative signal intensity measured by mass spectrometer: O/H₂O and HO/H₂O as a function of the heating time.

Obviously, different species with same m/z values would be distinguished by comparing the shape and the intensity ratio of the mass spectra with different m/z values.

2. Surface area and pore size distributions

Table S2 BET surface area, micropore surface area and pore size of CeO₂ and Co catalysts

Sample	S _{BET} (m ² /g)	Micropore surface area (m ² /g)	Pore size (nm)
CeO ₂	121.2	16.4	8.7
Co/CeO ₂	111.6	15.8	8.9
Co/CeO ₂ -H	87.3	13.3	10.6
Co/CeO ₂ -O	56.0	10.1	14.3

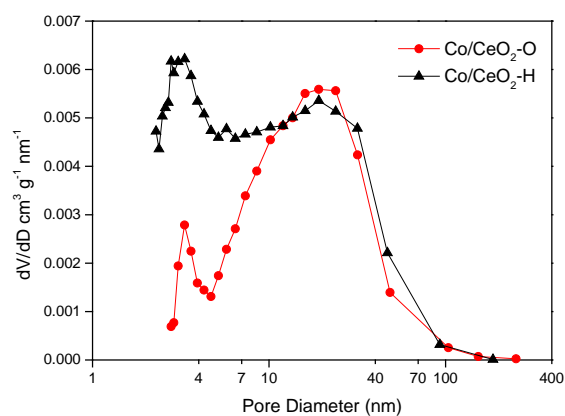


Fig. S3 pore size distributions of Co catalysts.

3. Pulse chemisorption measurement with pure hydrogen

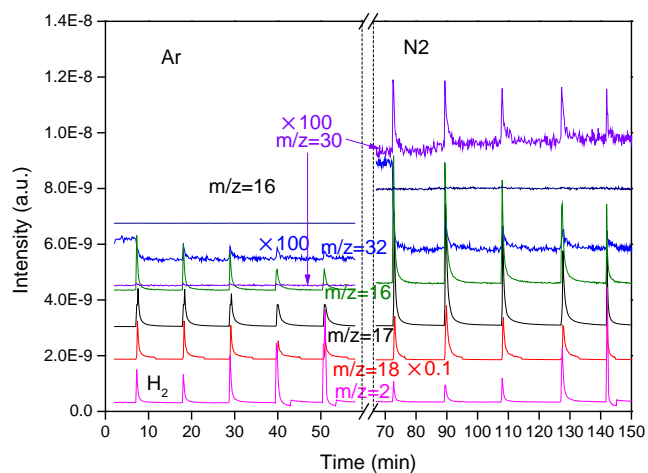


Fig. S4 Hydrogen pulse chemisorption results for Co/CeO₂-H.

4. N₂-TPD profiles of Co/CeO₂-H

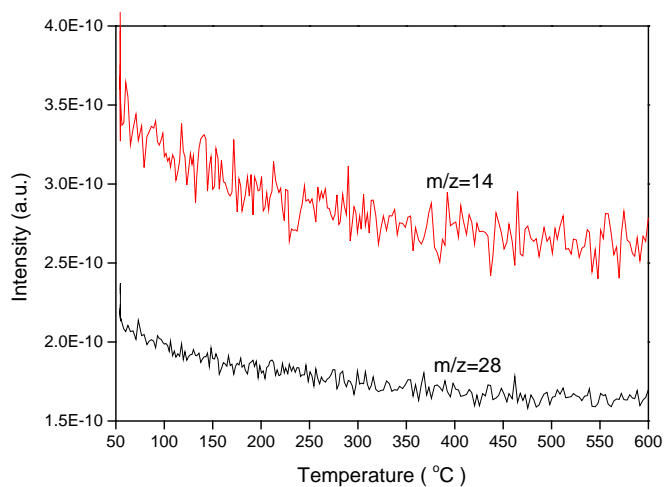


Fig. S5 Nitrogen temperature programmed desorption results of Co/CeO₂-H.

5. Elimination of Heat- and Mass-Transfer Artifacts in ammonia synthesis test

The exothermic nature of ammonia synthesis can cause temperature and concentration gradients that corrupt the kinetic origins and chemical significance of rates. These artifacts can be eliminated by decreasing the size of catalyst or by volumetric dilution within the catalyst bed [1]. Co/CeO₂-H with different pellet sizes (0.30-0.56 mm and 0.56-0.80 mm) and different dilution ratios (quartz sand : catalyst 15:1-60:1) were used to measure the ammonia synthesis rates. The space velocities changed from 0.8 to 2.6 cm³ g_{cat}⁻¹ h⁻¹) at 430 °C. The results are shown in Fig. S6. Neither pellet size and the nor dilution ratio affected the measured ammonia synthesis rates. The catalyst showed high ammonia synthesis rate with space velocity at above 1.8 m³ g_{cat}⁻¹ h⁻¹, and the rate did not increase by further increasing space velocity. These results confirmed the absence of transport artifacts during the activity measurement process.

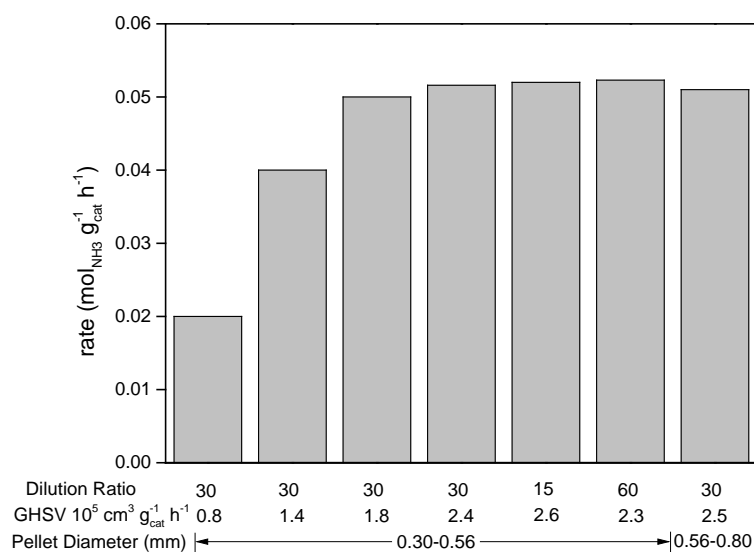


Fig. S6 Ammonia synthesis rates for Co/CeO₂-H (pellet diameters, 0.30-0.56 mm and 0.56-0.80 mm; quartz sand:catalyst 15:1-60:1) at 430 °C (0.8-2.6 cm₃ g_{cat}⁻¹ h⁻¹ space velocities).

6. Pulse chemisorption

Co/CeO₂-H was reduced in hydrogen at 500 °C for 6 h, then flushed in Ar and cooled down to 430 °C. A single pulse of known volume (0.3541 mL) of hydrogen and nitrogen was introduced into Co/CeO₂-H with Ar as carrier gas, the pulse sequence used was H₂→N₂→H₂. Fig. S7 shows the MS signal response for pulse scheme H₂→N₂→H₂. For H₂ pulse 1, only the H₂ peak can be observed. During N₂ pulse 2, the MS signal showed the peaks of nitrogen and hydrogen suggesting the addition of nitrogen led to hydrogen desorbed from the catalyst. The concurrence of nitrogen and hydrogen peaks can also be found in the MS signal obtained from the subsequent H₂ pulse 3. This result further confirmed hydrogen and nitrogen competitively adsorb on same active sites for Co catalysts.

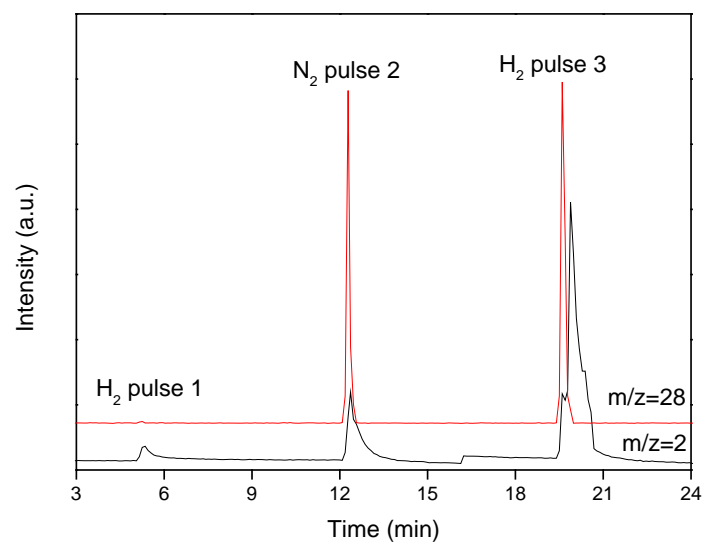


Fig. S7 MS signal response for pulse scheme H₂→N₂→H₂ for Co/CeO₂-H

Reference:

- [1] R. M. Koros and E. J. Nowak, Chem. Eng. Sci., 1967, 22, 470.