

Supporting information

Inverse kinetic isotope effect of ammonia decomposition over Ru/CeO₂ using deuterated ammonia

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Experimental section

Catalyst Preparation

Cerium oxide ([CeO₂] Daiichi Kigenso Kagaku Kogyo, >99.0 %) were heated at 500 °C for 4 h in static air prior to use. After the heat treatment, wetness impregnation was performed. In a typical synthetic procedure, 500 mg of support materials was first placed in a glass beaker with a stir bar. After this step, 55 mg g of Ru₃(CO)₁₂ (Sigma Aldrich, 99 %) dissolved in 5 mL of tetrahydrofuran (Wako, 99.5 %) was added to the beaker and stirred at 400 rpm at room temperature. After 1 h of stirring, the beaker was heated at 80 °C until all tetrahydrofuran evaporated (typically 1 h). Next, the dried sample was moved to an alumina boat and placed in a tubular furnace. Ar (JFP, 99.9999 %) flowed at 50 mL min⁻¹ in the tubular furnace while the sample was heated to 350 °C for 5 h with a ramp rate of 3 °C min⁻¹. Samples were then cooled to room temperature, and air was slowly diffused into the furnace to avoid overoxidation. Samples were labeled as 5 wt% Ru/CeO₂. The catalysts were diluted and used by physical mixing of x times of the supports as appropriate to control the reaction rate. The TEM image of the catalyst was taken by JEOL, JEM-2010F.

Ammonia decomposition reaction

The samples were prepared by pelletizing, crushing, and sieving to a particle diameter of 250–500 μm prior to conducting activity measurements. The catalyst bed suspended by quartz wool was placed in a quartz tube with an internal diameter of 4 mm and heated with an electric furnace. The temperature of the cylindrical catalyst bed was measured using a thermocouple located outside the quartz tube at the catalyst bed. The four-way valve allows switching between a flow reactor and a recirculating batch reactor. The sample was pretreated under an H₂ (JFP, 99.99999 %) flow of 60 mL min⁻¹ for 2 h at 400°C and 0.1 MPa, before being set to the measurement temperature and stabilized under reaction conditions for at least 30 min using 10 mL min⁻¹ NH₃ (JFP, 99.9999 %) and 90 mL min⁻¹ Ar in the flow system.

In the Flow reaction, 0.5% NH₃ (diluted with argon) was introduced at flow rates of 25, 50, and 100 mL min⁻¹. After waiting 30 min for stabilization, NH₃ concentration was measured by the area of IR spectra using a Fourier-transform infrared spectrometer (Shimadzu, IRAffinity-1S). The area of the IR spectrum in the range of 3325 to 3342 cm⁻¹ was determined, and the concentration of NH₃ was calculated using the calibration curve.

In the recirculation batch reaction, the composition of H₂, N₂ (JFP, 99.99995 %), NH₃ and Ar was adjusted to achieve various partial pressures of H₂, N₂, NH₃ and Ar under total flow rate of 200

mL min⁻¹ to try to achieve gradient-less conditions inside the 81 mL closed circulation system. The quartz tube with the catalyst bed was connected to a gas cell, pump, and four way valve, as shown in Fig. 1. After waiting 30 min for stabilization, the four-way valve was switched to start the ammonia decomposition reaction as a recirculation batch reactor. NH₃ concentration was measured in the same way as for the flow reaction. The rates of each condition shown in Figs. 2-4 were obtained by the slope of the decrease in ammonia up to 10% conversion of the reaction and the lines (if any) show the fitting curves of the plot.

Derivation of equilibrium constants for D₂ chemisorption

The equilibrium constant can be expressed in the formalism of statistical mechanics as follows.

$$K = \frac{\prod_j q_p^{v_j}}{\prod_i q_r^{v_i}} \quad (1)$$

where q_r and q_p are the partition functions for reactants and products, and v_i and v_j the stoichiometric coefficients for reactant i and product j . In most cases, the largest part of the isotope effect results from a change in the ground-state vibrational frequency.

The isotope effect of the equilibrium constant for D/H chemisorption in Eq. (7) in the main text can be expressed as follows, assuming that the adsorbed atoms are not mobile and the degree of freedom is 3.¹

$$\frac{K_{7,D}}{K_{7,H}} = \left(\frac{m_{H_2}}{m_{D_2}} \right)^{5/2} \exp \left\{ \left[-2 \sum_{i=1}^3 (v_i^D - v_i^H) + (v_1^{D_2} - v_1^{H_2}) \right] h / (2kT) \right\} \quad (2)$$

where m_{H_2} and m_{D_2} are the masses of H₂ and D₂, v_i^H and v_i^D are the vibrational frequencies for adsorbed H and D atoms, and $v_1^{H_2}$ and $v_1^{D_2}$ are the vibrational frequencies for gaseous H₂ and D₂, and h is Planck's constant, k is Boltzmann's constant, and T is temperature.

Applying the values in Table S1, $\frac{K_{7,D}}{K_{7,H}}$ is below 1 between 180°C to 270°C. It has been claimed

that the ratio of equilibrium constants for D/H chemisorption is less than 1 on Pt², Ni³, and Ru¹.

Table S1. Vibrational Frequencies for Molecular and Atomically Adsorbed H₂ and D₂.⁴

Species	Mode	Frequency / cm ⁻¹
H ₂	$\nu(\text{H-H})$	4161
D ₂	$\nu(\text{D-D})$	2933
M-H	$\nu(\text{M-H})$	2250–1700
	$\delta(\text{M-H})^a$	800–600
M-D	$\nu(\text{M-D})$	1591–1202
	$\delta(\text{M-D})^a$	566–424

^a Doubly generate.

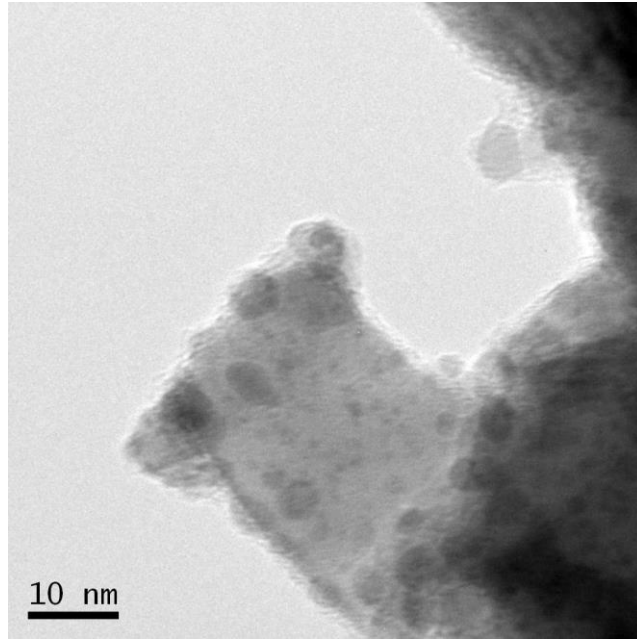


Figure S1. TEM image of 5wt% Ru/CeO₂.

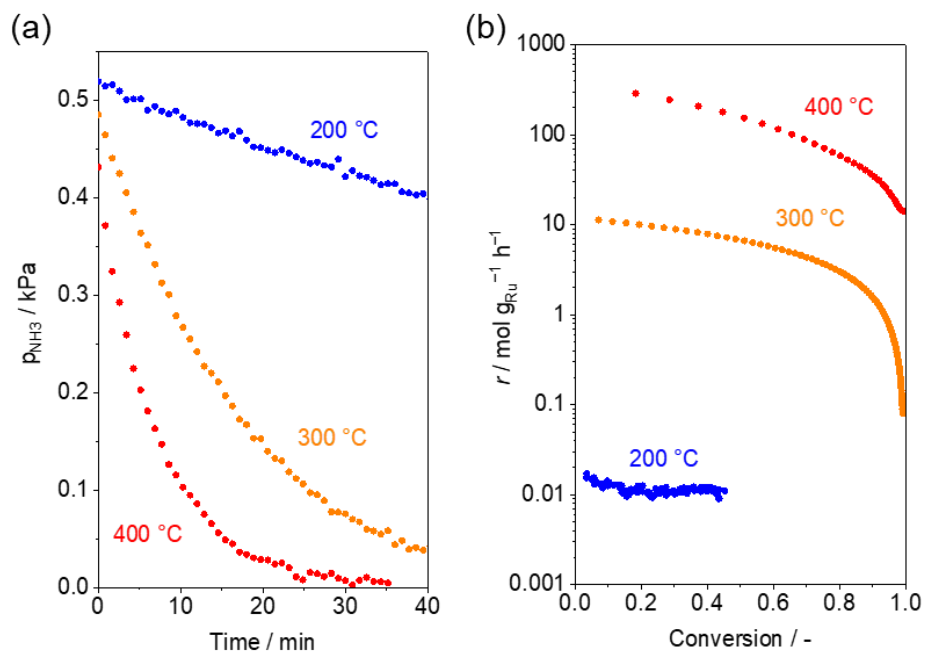


Figure S2. (a) Typical results of NH₃ decomposition in the recirculation batch system and (b) rate as a function of conversion plots. Catalyst: 0.1 mg of 5 wt% Ru/CeO₂ diluted with 9.9 mg of CeO₂ for 200 and 300 °C and 10× further dilution for 400 °C reaction within the pellets. Initial conditions: ~0.5 kPa NH₃ balanced with Ar, total 101 kPa. Absolute pressure of NH₃ was calculated from IR peak area. Pretreatment at 400 °C under H₂.

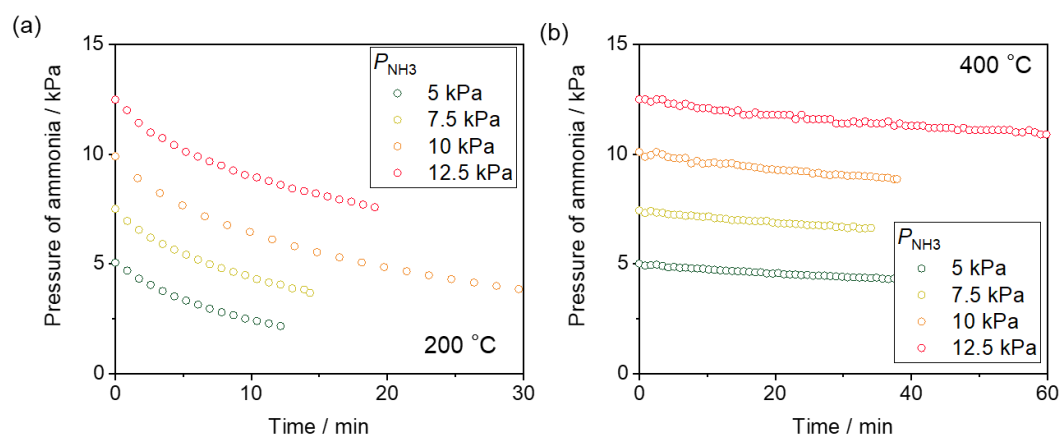


Figure S3. Time course measurement of NH₃ decomposition at various initial NH₃ pressures over supported Ru/CeO₂ at (a) 200°C (loaded Ru amount: 25 mg) and (b) 400°C (loaded Ru amount: 50 ng). The measurements were conducted in the recirculation batch reactor. The initial total pressure was balanced with Ar to 101 kPa.

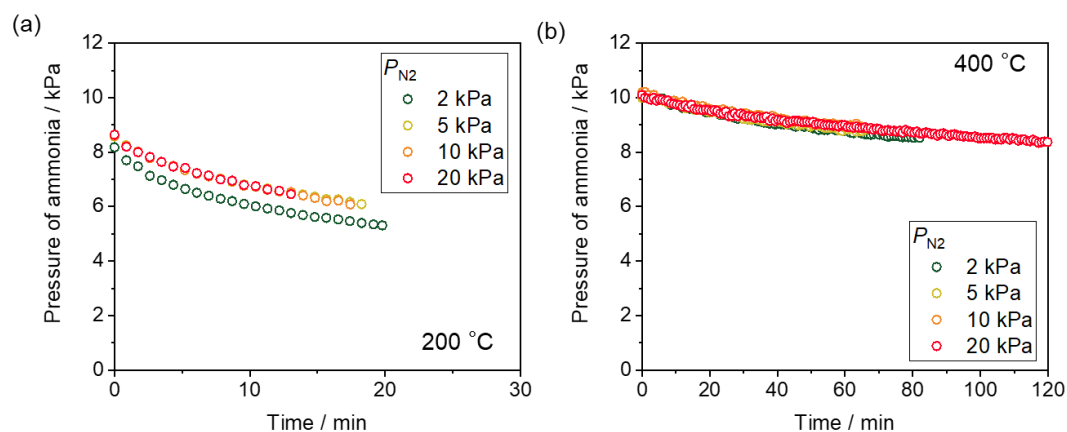


Figure S4. Time course measurement of NH_3 decomposition at various initial N_2 pressures over supported Ru/CeO_2 at (a) 200°C (loaded Ru amount: 25 mg) and (b) 400°C (loaded Ru amount: 50 ng). The measurements were conducted in the recirculation batch reactor. The initial pressure of NH_3 was ~ 10 kPa and total pressure was balanced with Ar to 101 kPa.

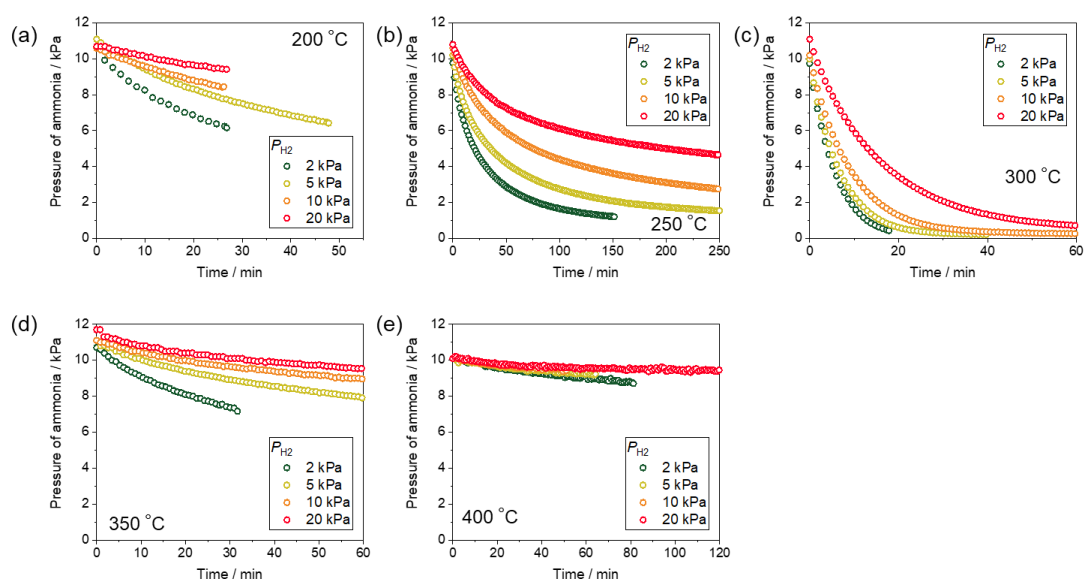


Figure S5. Time course measurement of NH_3 decomposition at various initial H_2 pressures over supported Ru/CeO_2 at (a) 200°C (loaded Ru amount: 0.5 mg), (b) 250°C (loaded Ru amount: 0.025 mg), (c) 300°C (loaded Ru amount: 5 μg), (d) 350°C, (loaded Ru amount: 0.25 μg) (e) 400°C (loaded Ru amount: 50 ng). The measurements were conducted in the recirculation batch reactor. The initial pressure of NH_3 was ~ 10 kPa and total pressure was balanced with Ar to 101 kPa.

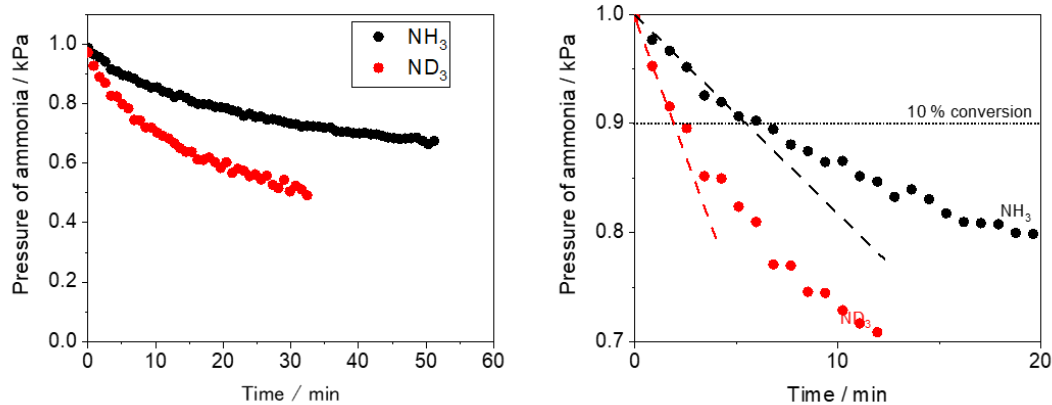


Figure S6. Time course measurement of NH_3 (black circle) and ND_3 (red line) decomposition at 200°C over supported Ru/CeO_2 (loaded Ru amount: 0.5 mg). The measurements were conducted in the recirculation batch reactor. The initial ratio of gas was $\text{Ar}:\text{NH}_3 = 100:1\text{ kPa}$ or $\text{Ar}:\text{ND}_3 = 100:1\text{ kPa}$. The reaction rate was calculated from the slope of the change in ammonia concentration until a conversion of 10% was reached as shown in the right panel.

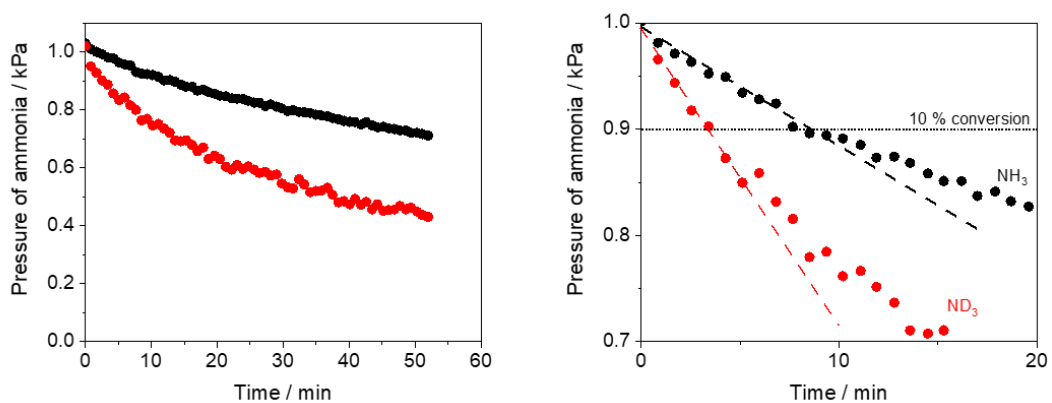


Figure S7. Time course measurement of NH_3 (black circle) and ND_3 (red line) decomposition at 250°C over supported Ru/CeO_2 (loaded Ru amount: 0.025 mg). The measurements were conducted in the recirculation batch reactor. The initial ratio of gas was $\text{Ar}:\text{NH}_3 = 100:1\text{ kPa}$ or $\text{Ar}:\text{ND}_3 = 100:1\text{ kPa}$. The reaction rate was calculated from the slope of the change in ammonia concentration until a conversion of 10% was reached as shown in the right panel.

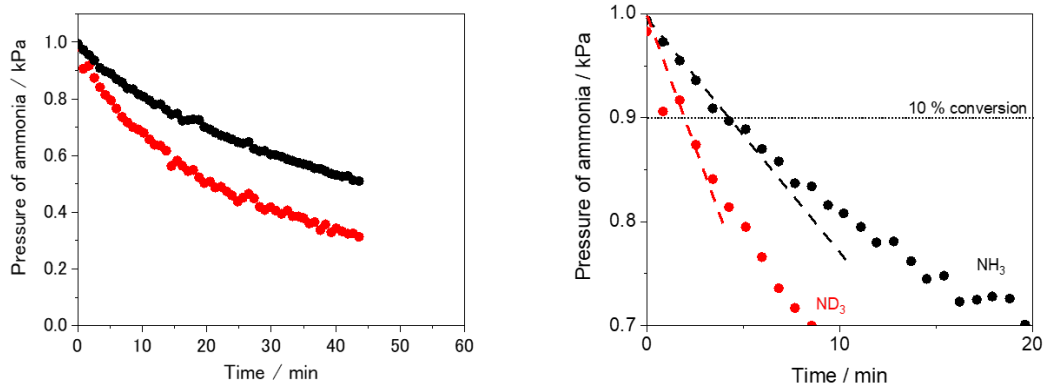


Figure S8. Time course measurement of NH₃ (black circle) and ND₃ (red line) decomposition at 300°C over supported Ru/CeO₂ (loaded Ru amount: 5 μg). The measurements were conducted in the recirculation batch reactor. The initial ratio of gas was Ar:NH₃ = 100:1 kPa or Ar/ND₃ = 100:1 kPa. The reaction rate was calculated from the slope of the change in ammonia concentration until a conversion of 10 % was reached as shown in the right panel.

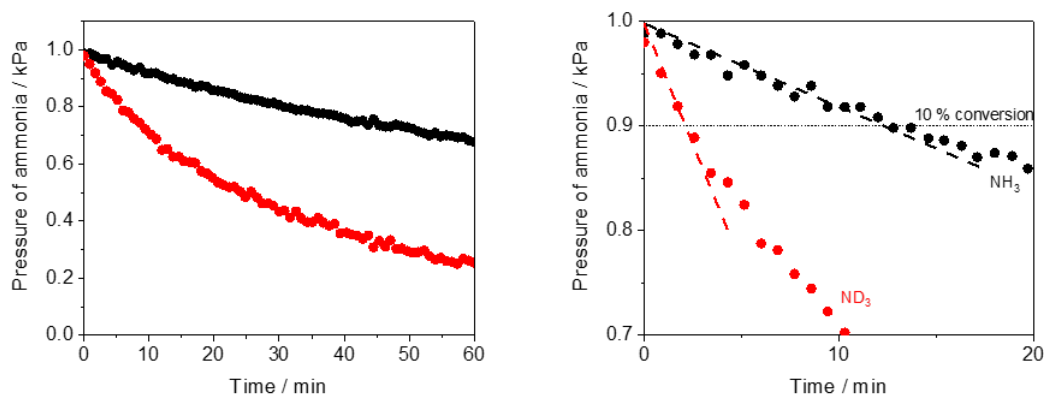


Figure S9. Time course measurement of NH₃ (black circle) and ND₃ (red line) decomposition at 350°C over supported Ru/CeO₂ (loaded Ru amount: 0.25 μg). The measurements were conducted in the recirculation batch reactor. The initial ratio of gas was Ar:NH₃ = 100:1 kPa or Ar/ND₃ = 100:1 kPa. The reaction rate was calculated from the slope of the change in ammonia concentration until a conversion of 10 % was reached as shown in the right panel.

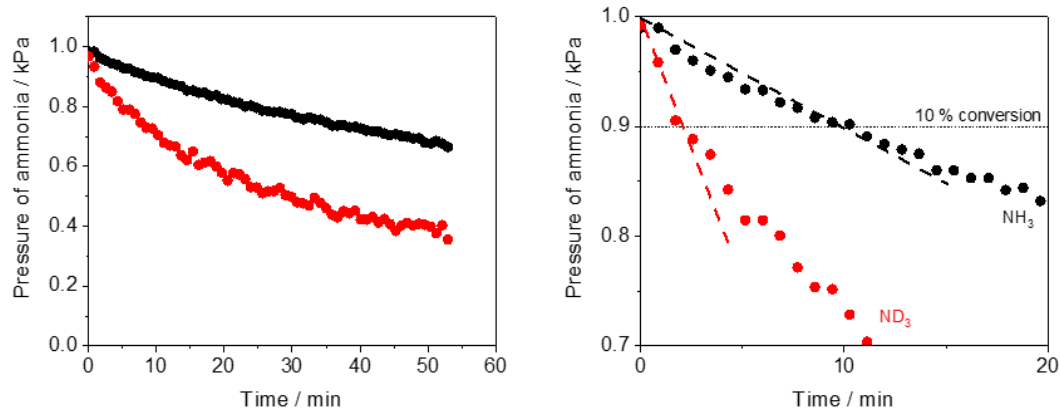


Figure S10. Time course measurement of NH₃ (black circle) and ND₃ (red line) decomposition at 400°C over supported Ru/CeO₂ (loaded Ru amount: 50 ng). The measurements were conducted in the recirculation batch reactor. The initial ratio of gas was Ar:NH₃ = 100:1 kPa or Ar/ND₃ = 100:1 kPa. The reaction rate was calculated from the slope of the change in ammonia concentration until a conversion of 10 % was reached as shown in the right panel.

References

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