ESI (Supporting Information)

Low-temperature NH_3 decomposition assisted by surface protonics

Yukino Ofuchi[#a], Kenta Mitarai[#b], Sae Doi[#a], Koki Saegusa[a], Mio Hayashi[a], Hiroshi Sampei[a], Takuma Higo[a], Jeong Gil Seo*[c] and Yasushi Sekine*[a]

a. Department of Applied Chemistry, Waseda University, 3-4-1, Okubo, Shinjuku, Tokyo, 169-8555, Japan, E-mail: ysekine@waseda.jp

b. Research & Development Center, Yanmar Holdings, 2481, Umegahara, Maibara, Shiga, 521-8511, Japan

c. Department of Chemical Engineering, Hanyang University, 222 Wangsimri-ro, Seongdong-gu, Seoul 04763, Republic of Korea. E-mail: jgseo@hanyang.ac.kr

*Corresponding authors

Catalyst preparation

CeO_2 (JRC-CEO-1) was used as a catalyst support. Active metal (Ru, Fe, Ni, Co; 8.2 mol%) was loaded over the CeO_2 using an impregnation method. These catalysts have equimolar metal sites. (i.e. 5.0wt%Ru/CeO_2, 2.8wt%Fe/CeO_2, 3.0wt%Co/CeO_2, 3.0wt%Ni/CeO_2). In kinetic consideration such as partial pressure change tests and temperature dependence, 0.85 mol% (=0.5wt%) Ru/CeO_2 was used to reduce ammonia conversion below 10%. Tris(acetylacetonate)ruthenium(III) ($Ru(acac)_3$, Tanaka Holdings Co., Ltd.), $Fe(NO_3)_3{\cdot}9H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, and $Ni(NO_3)_2{\cdot}6H_2O$ (Kanto Chemical Co. Inc.) were used as metal precursors. After CeO_2 powder and each precursor were dissolved in distilled water (Fe, Co, Ni) or acetone (Ru), the slurry was stirred at room temperature for 2 h. The obtained slurry was evaporated at 300°C (Fe, Co, Ni) or 100°C (Ru) and dried at 120°C. The obtained powder was calcined at 450°C for 2 h (Fe, Co, Ni) or reduced at 450°C for 2 h(Ru) in the stream of Ar:H_2=1:1 at 100 SCCM. The synthesized catalyst was molded into 355–500 μm particles.

Current changing test

The effect of changing the current value on the activity was investigated using 8.2 mol%Ru/CeO_2. The current value was varied from 1 to 20 mA. The current density was increased from 0.035-0.71 mA mm^{-2}. The catalyst weight was 100 mg and the gas flow rate was 50 SCCM. Before the test the same pretreatment as for the activity test was performed. The catalyst bed temperature was adjusted to be approximately 125°C regardless of the change in current value.

Partial pressure changing test

The change in reaction order during applying an electric field or in thermo-catalysis was confirmed by partial pressure change tests. 5%NH_3/Ar, 5%H_2/Ar, N_2, and Ar gases were used, respectively, and the partial pressure was changed so that the total gas flow rate was 100 SCCM. We used 0.85 mol%Ru/CeO_2 catalyst and before the test the same pretreatment as for the activity test was performed.
H_2 dependence: 5%H_2/Ar=10, 20, 30, 40, 50 SCCM, balance: 5%NH_3/Ar
NH_3 dependence: 5%NH_3/Ar=50, 60, 80, 100 SCCM, balance: Ar
N_2 dependence: 100%N_2=7, 13, 20, 30 SCCM, balance: 5%NH_3/Ar

ND_3 isotope exchange test

In this test 0.85 mol%Ru/CeO_2 was used and the catalyst weight was 200 mg. The inlet gas was 5%NH_3/Ar or 5%ND_3/Ar and the flow rate was 50 SCCM. The ammonia conversion was calculated from the amount of nitrogen produced.

AC impedance measurements

The comparison of conductivity of the CeO_2(JRC-CEO-1) under Ar, 5%H_2/Ar and 5%NH_3/Ar was investigated. CeO_2 was ball-milled (300 rpm, 30 min) and then about 1 g of CeO_2 was pressed into pellets under the condition of 60 kN for 2 h. The pellets were calcined at 800℃, 2 h, 5°C min^{-1} and sputterd with about 100 nm of Pt to form an electrode. The relative density of the samples was about 60%. In the measurements, the samples were pretreated in an Ar atmosphere at 500°C until a steady-state condition was reached, and then the gas flow rate was set to 30 SCCM at 200°C. The frequency of the measurement was 106-120 Hz. The measurement frequency was 10^6-10^{-3} Hz and the voltage amplitude was 1.5 V rms. Fitting was performed with an RQ parallel circuit.

GHSV change test

The activity test was performed by altering the SV (space velocity). As the catalyst, 300 mg of 8.2 mol% Ru/CeO_2 was used, and the catalyst layer height was 0.66 cm. The imposed current was 6.0 mA, and the response voltage was about 0.32 kV for all tests. The catalyst bed temperature was adjusted to be about 125°C regardless of the change in SV.

Low-temperature adsorbed species trap test

To examine the proton content, the catalyst adsorbed species during the reaction were trapped at low temperatures, and then the temperature was increased, and the desorption peak was observed. First, the ammonia decomposition reaction was conducted until steady state using 0.3 g of 8.2 mol% Ru/CeO_2. The reaction gas was 50 SCCM 5%NH_3/Ar. The temperature was set at 373 K with EF and 573 K without EF. For Q-MASS sensitivity, the H_2/N_2 ratio at steady state of the reaction was set to 3. Then, 5% NH_3/Ar was switched to Ar and quenched to about 250 K. After the gas in the flow path was replaced by Ar, the temperature was gradually increased and the exit gas was observed by Q-MASS.

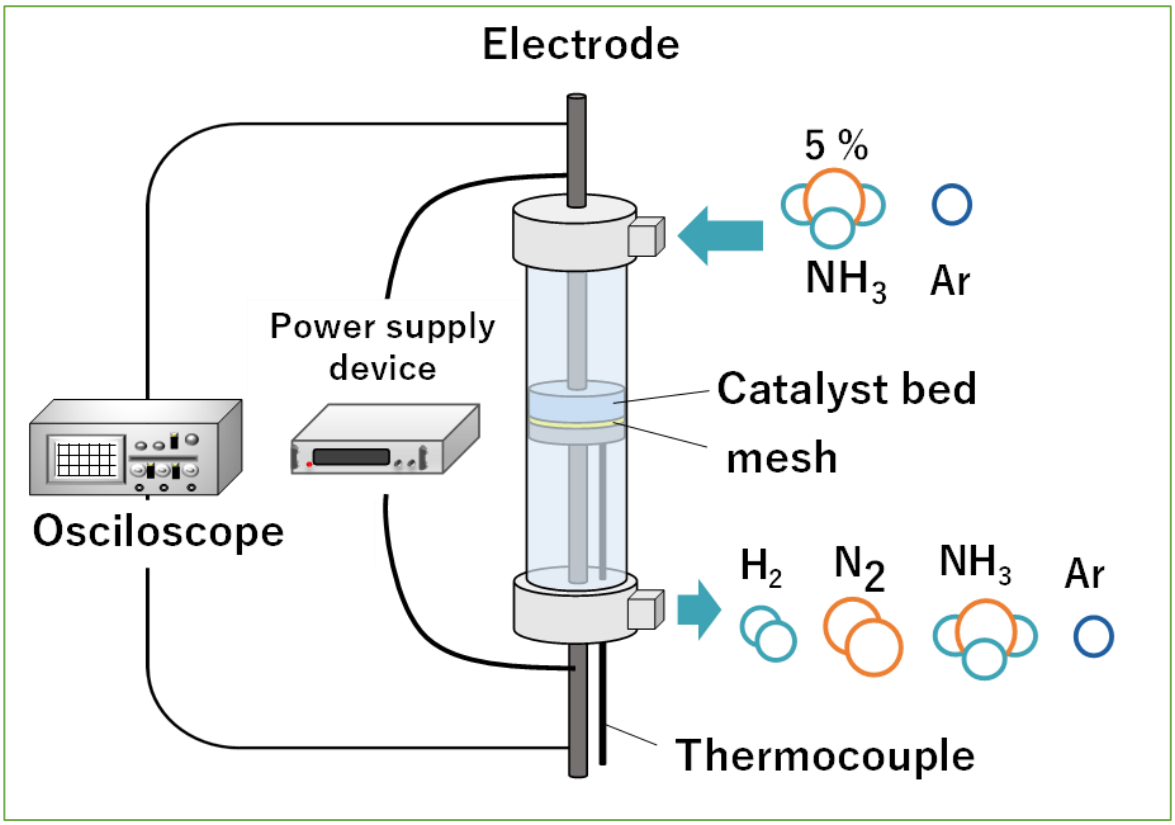

Fig. S1 Schematic image of a reactor for the activity test in the electric field.

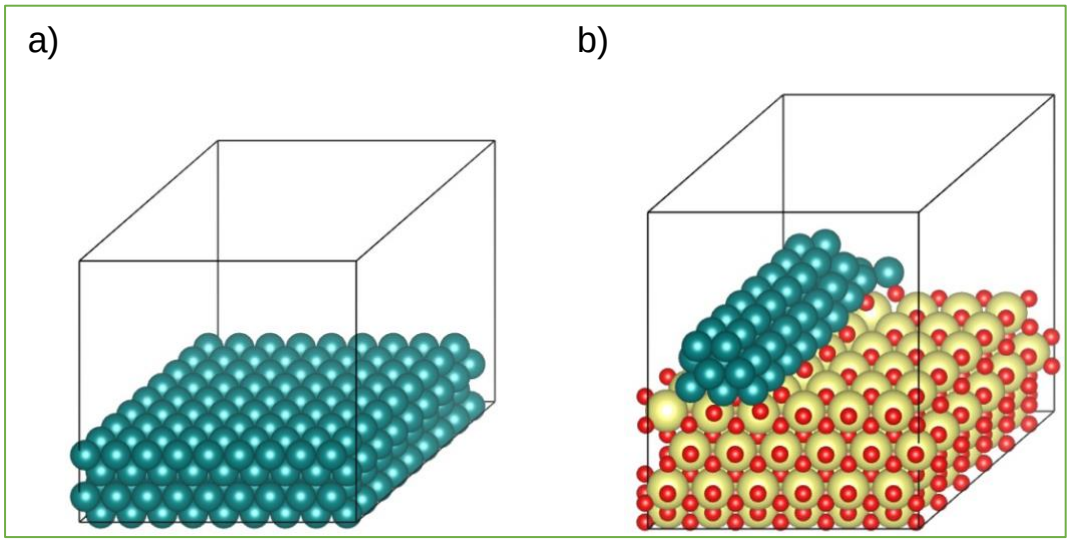

Fig. S2 Calculation model of (a) Ru surface and (b) Ru-CeO_2 interface. Ru, Ce, and O atoms are shown in green, yellow, and red, respectively.

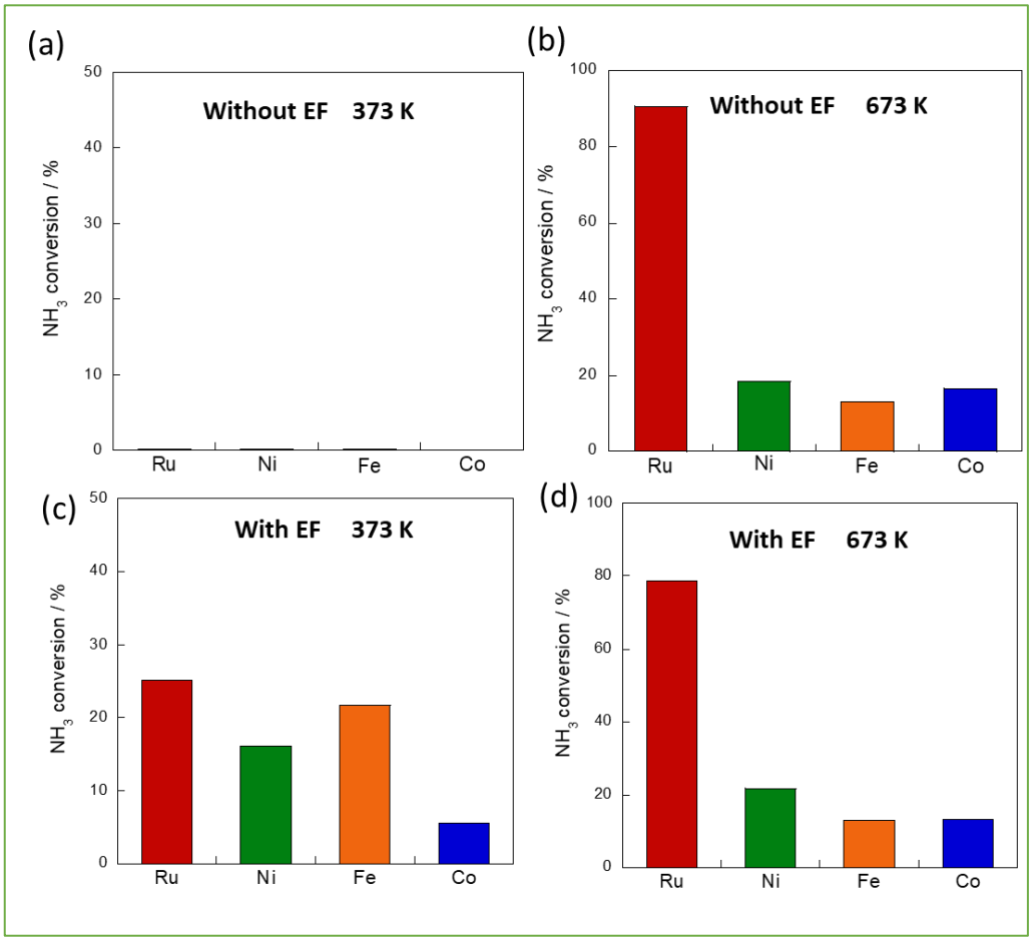

Fig. S3 Temperature dependence of NH_3 decomposition on catalysts with equimolar (i.e. 8.2 mol%) metal sites with and without an electric field. 5%NH_3/Ar = 50 SCCM, 100 mg cat, 0.1 MPa, 0 or 6.0 mA; (a) without EF at 373 K, (b) without EF at 673 K, (c) with EF at 373 K, and (d) with EF at 673 K.

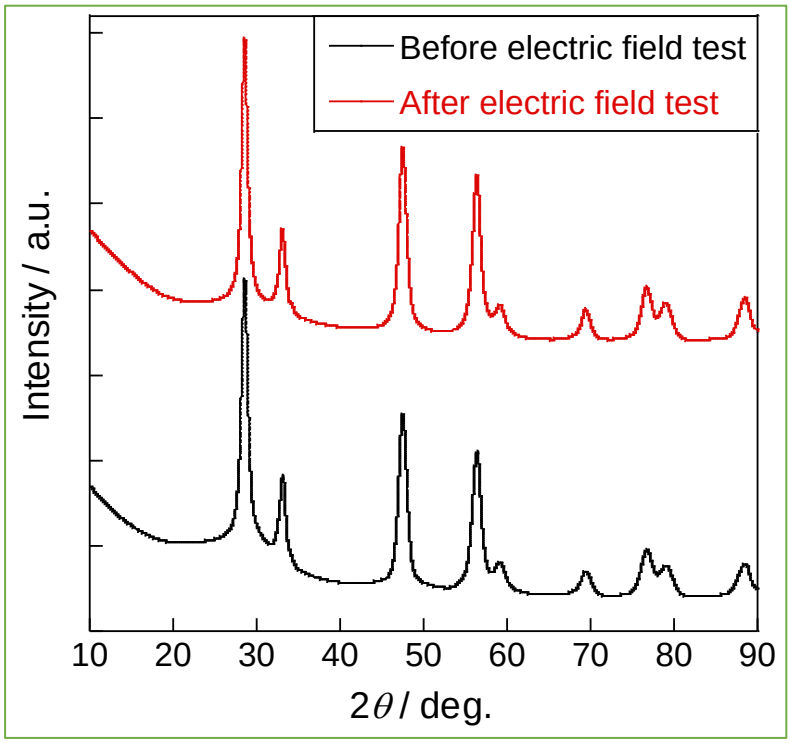

Fig. S4 XRD measurement before and after electric field tests over 8.2 mol% Ru/CeO_2. 5%NH_3/Ar = 50 SCCM, 100 mg cat, 0.1 MPa, 6.0 mA.

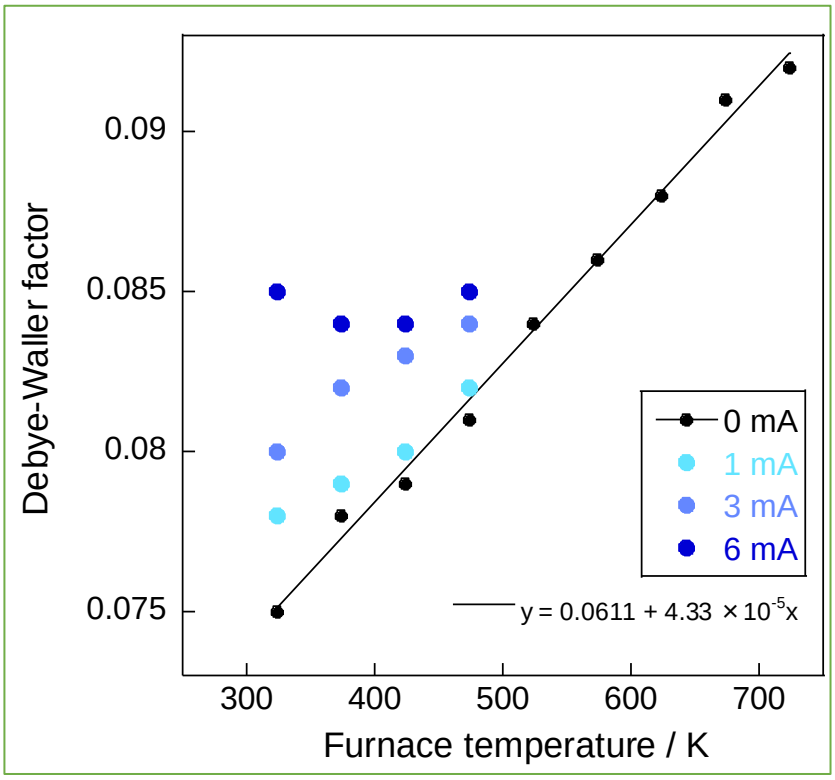

Fig. S5 Debye-Waller factor obtained from *in situ* XAFS measurements over 8.2 mol%Ru/CeO_2.

5%NH_3/Ar = 50 SCCM, 160 mg cat, 0.1 MPa, 0, 1, 3, 6.0 mA.

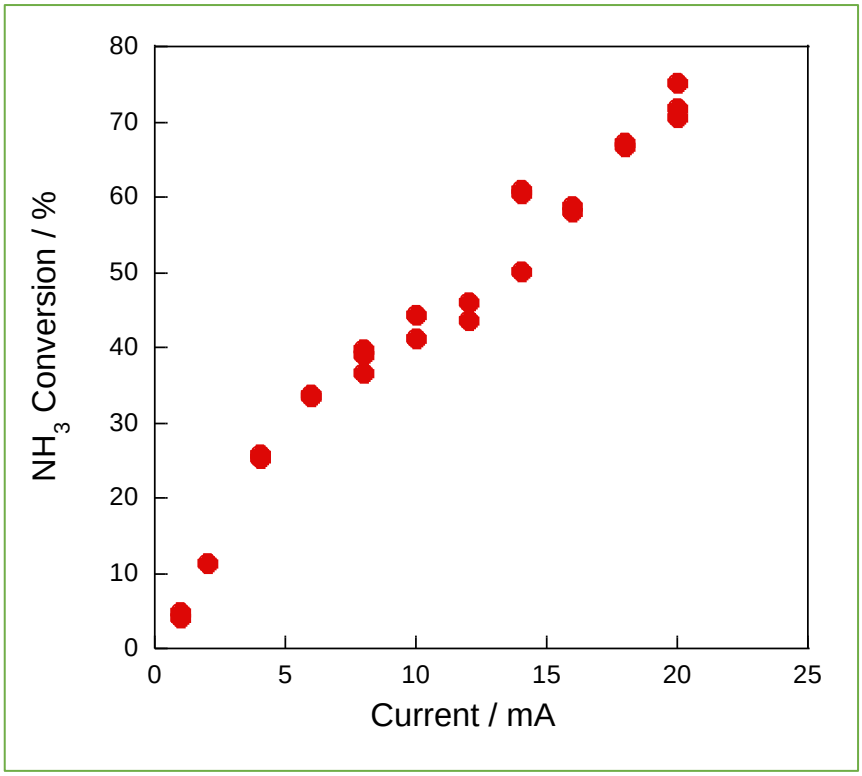

Fig. S6 The current dependence of NH_3 decomposition rate over 8.2 mol%Ru/CeO_2; 5%NH_3/Ar = 50 SCCM, 300 mg cat, 0.1 MPa, 398 K.

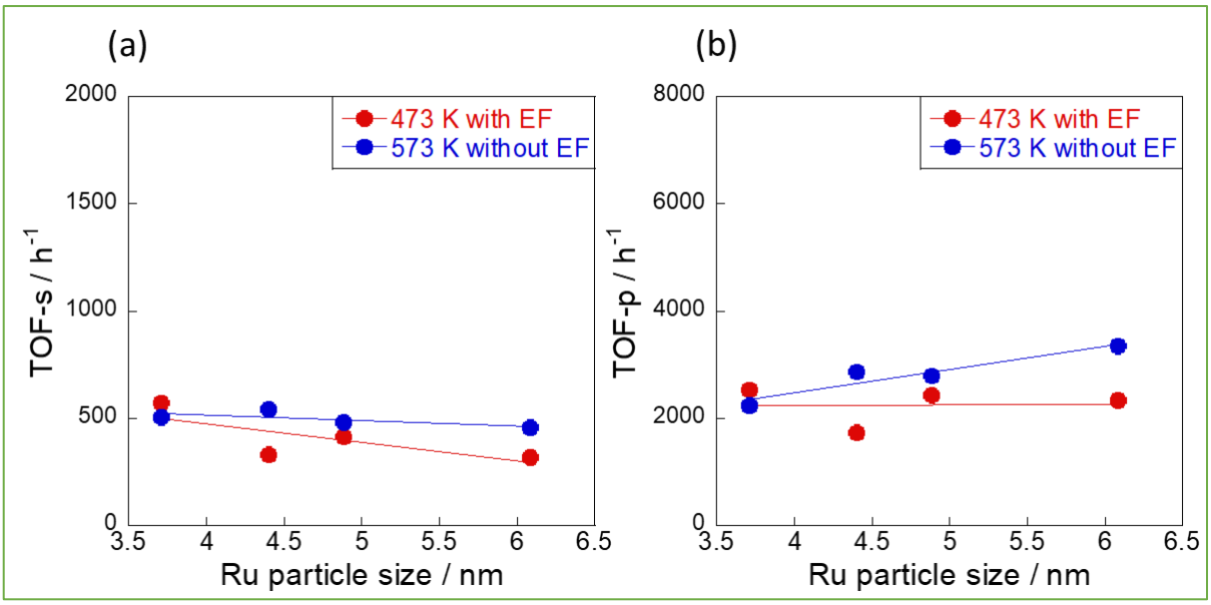

Fig. S7 Amount of H_2 molecules produced per number of Ru atoms (a) present on the surface (TOF-s) and (b) at the Ru-CeO_2 interface (TOF-p) over 0.85, 5.0, and 8.2 mol% Ru/CeO_2; 5%NH_3/Ar = 50 SCCM, 100 mg cat, 0.1 MPa, 0 or 6 mA.

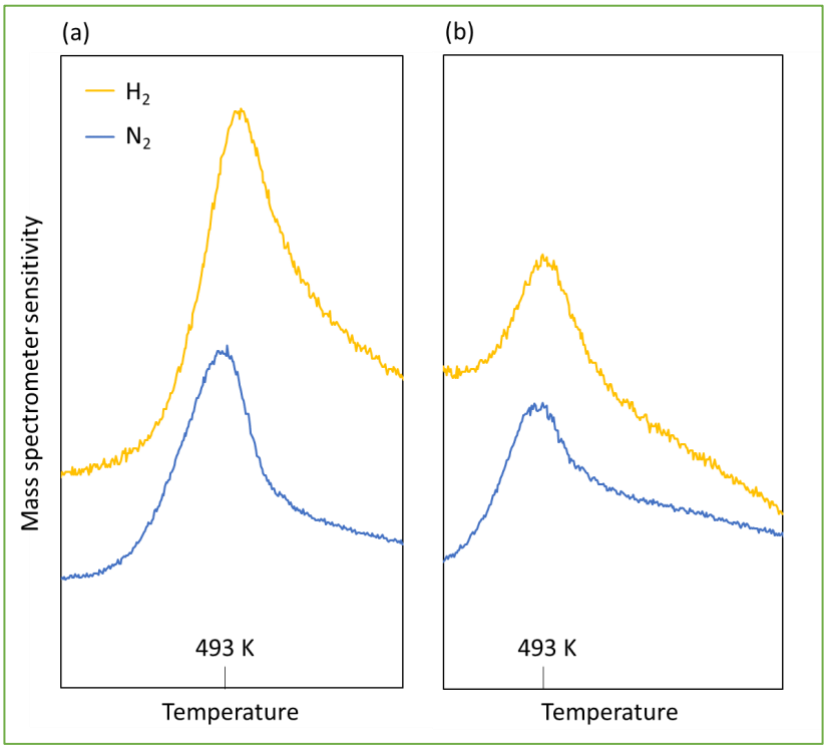

Fig. S8 Desorption peak of hydrogen and nitrogen adsorbed on 8.2 mol% Ru/CeO_2 during the ammonia decomposition reaction; (a) with EF at 373 K, (b) without EF at 573 K.

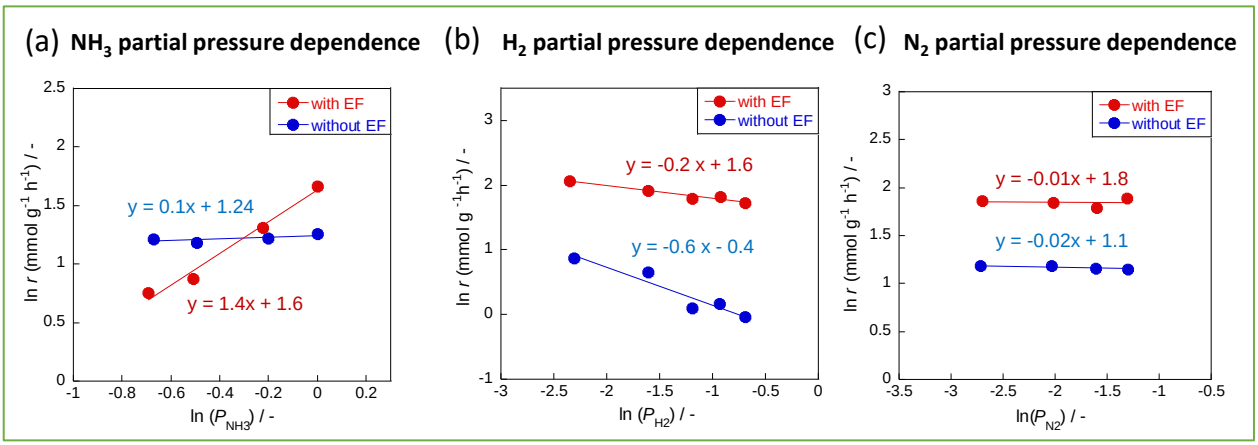

Fig. S9 The effect of partial pressure on the reaction rate; (a) for the partial pressure of NH_3, (b) for the partial pressure of H_2, (c) for the partial pressure of N_2.

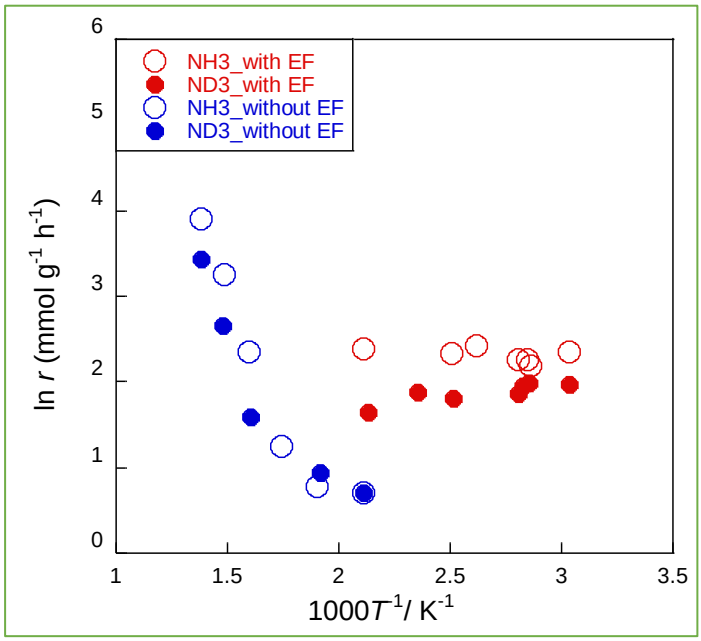

Fig. S10 NH_3 and ND_3 decomposition reactions over 0.85 mol%Ru/CeO_2 catalyst.

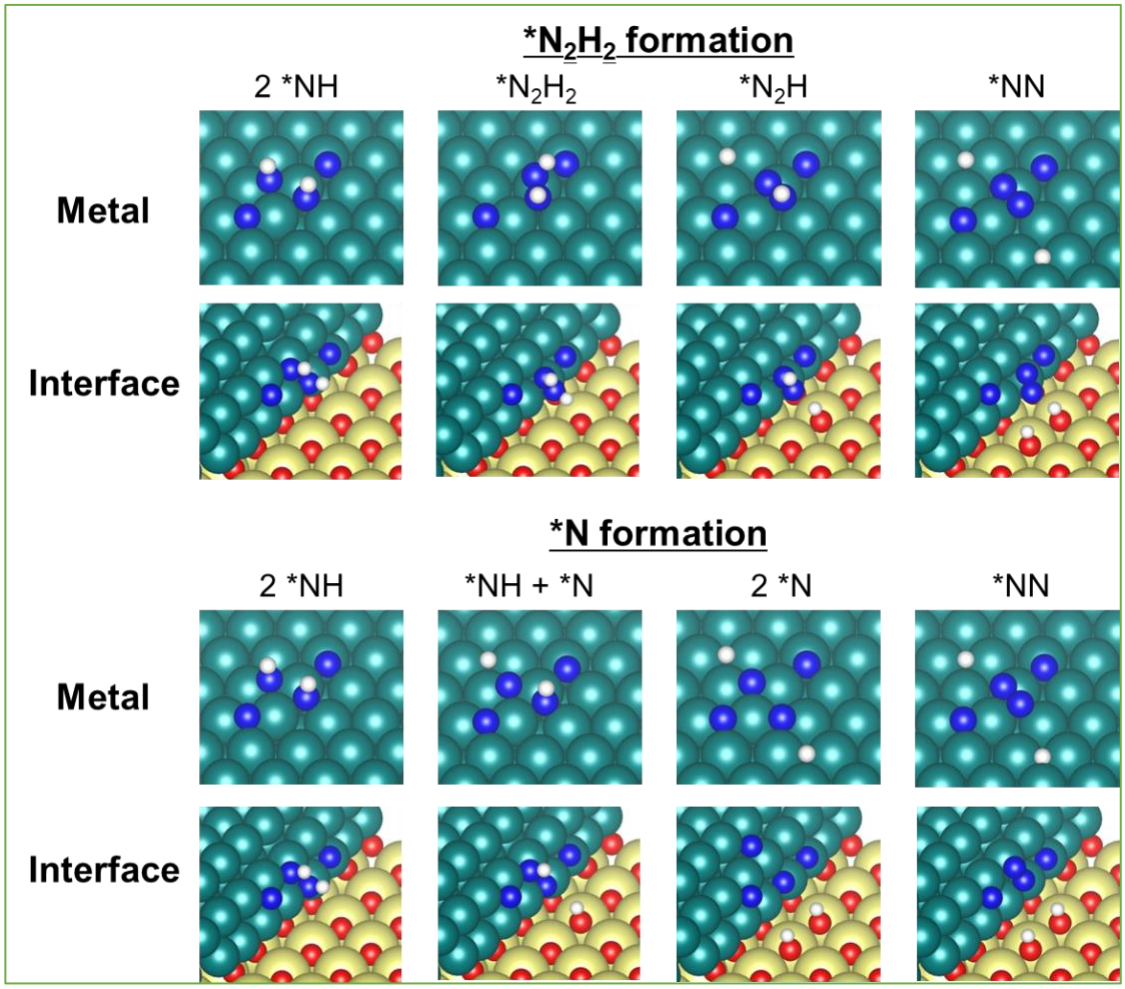

Fig. S11 Calculation model of each elementary step on N-terminate model.

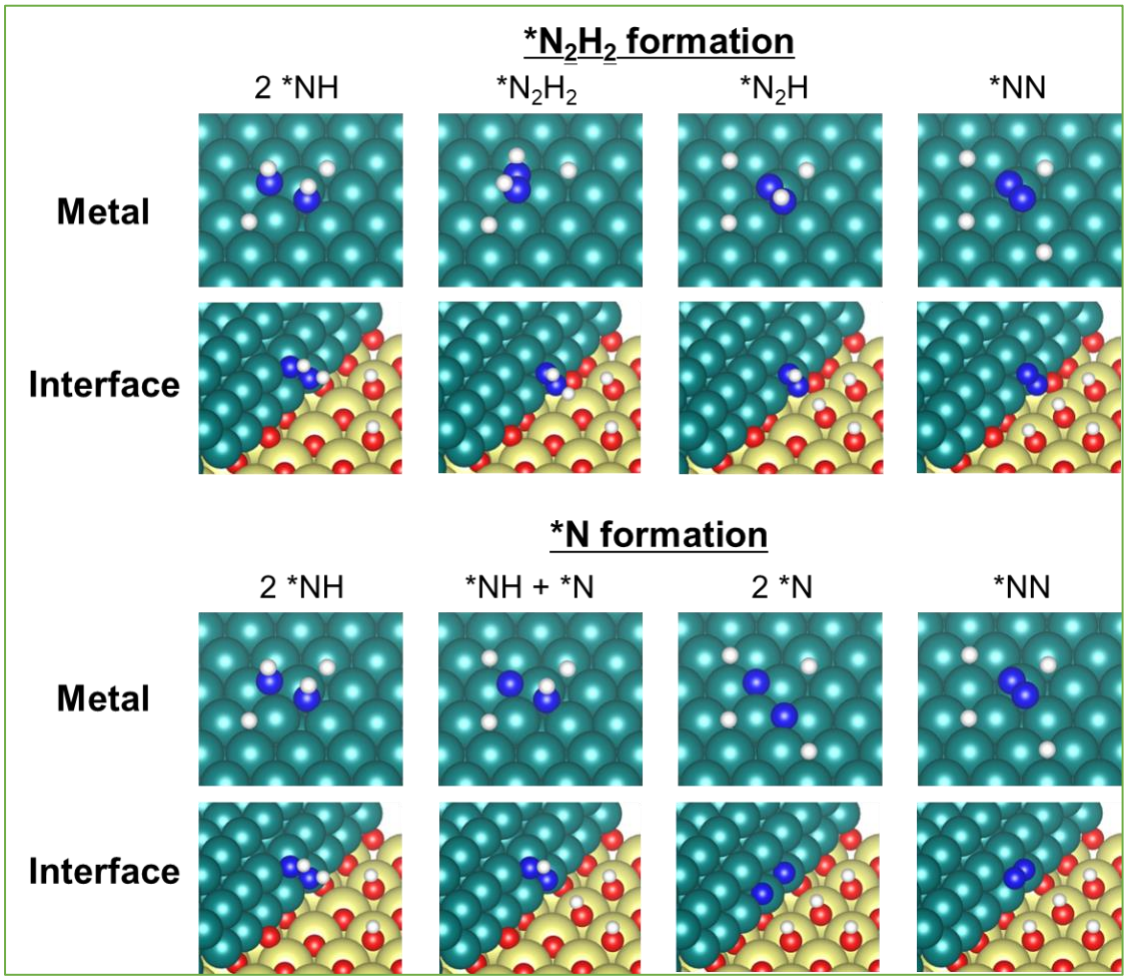

Fig. S12 Calculation model of each elementary step on H-terminate model.

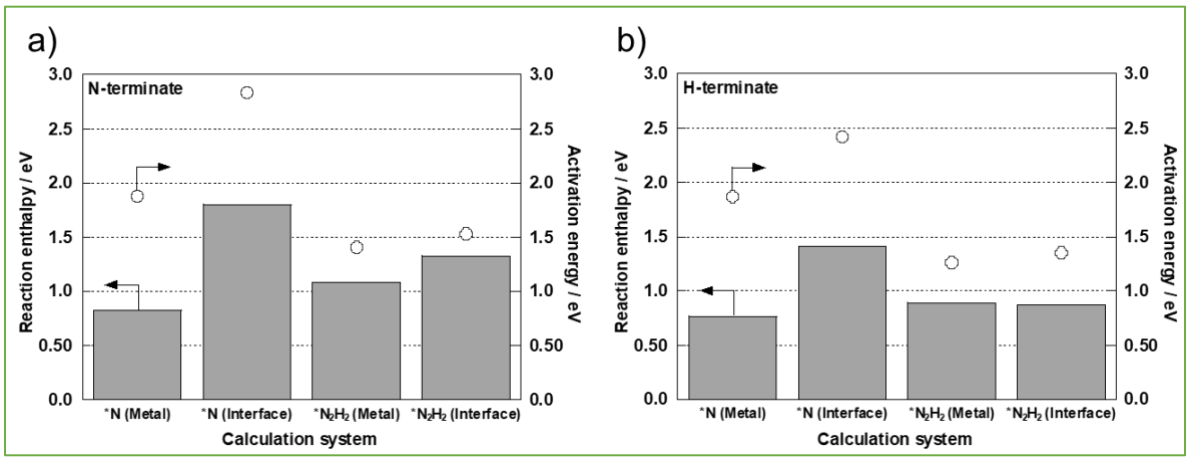

Fig. S13 Reaction enthalpy and activation energy of rate-determining step on each mechanism using (a) N-terminate model and (b) H-terminate model.

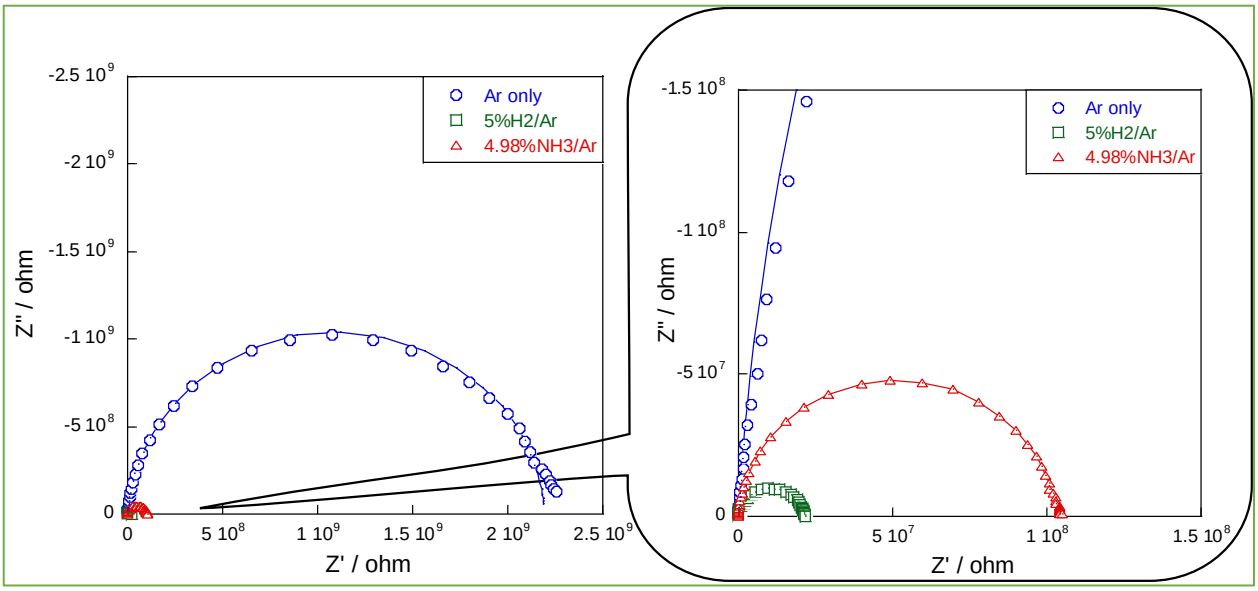

Fig. S14 The results of AC impedance measurements.

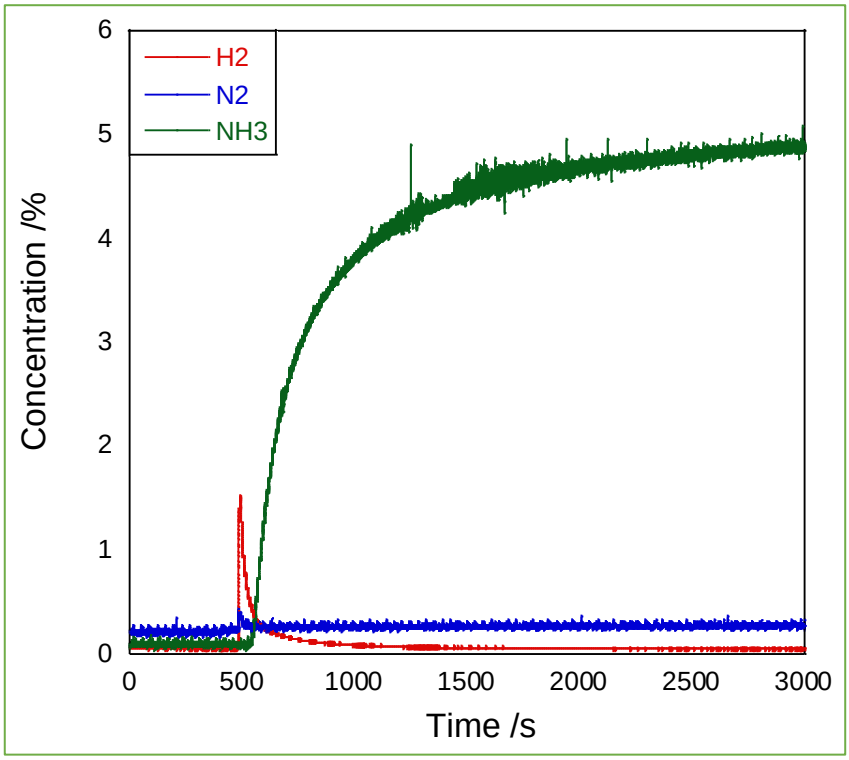

Fig. S15 NH_3 decomposition at room temperature measured by Q-MASS.

The exit gas from the ammonia inflow to 8.2 mol% Ru/CeO_2 at room temperature was analyzed by Q-MASS. The formation of H_2 and N_2 was confirmed immediately after the inflow of ammonia gas. The H_2:N_2 ratio was 4:1, indicating that the amount of H_2 was higher. It is thought that N was adsorbed on the catalyst surface and could not be desorbed. Thereafter, NH_3 decomposition did not proceed. This is thought to be due to the adsorbed N covering the catalyst surface. Therefore, it can

be said that the dehydrogenation reaction of ammonia is easy to occur at low temperatures, but the desorption of nitrogen is difficult to proceed.

Table S1. Physicochemical properties of Ru/CeO_2.

catalyst	catalyst calcination temperature K	specific surface area $m^2 g^{-1}$	Ru particle size nm	metal dispersion %
0.85mol%Ru/CeO_2	723	139.5	3.7	111
5.0mol%Ru/CeO_2	573	150.8	4.4	47.7
5.0mol%Ru/CeO_2	723	98.6	4.9	45.3
8.2mol%Ru/CeO_2	723	87.9	6.1	33.3

Ru particle size and dispersion were derived by TEM and CO pulse measurements. 0.85 mol% Ru/CeO_2 is highly dispersed with very low Ru loading, and the dispersion exceeded 100% probably due to the adsorption of CO on the CeO_2 and physical adsorption.

Table S2 The temperature dependence of NH_3 conversion over 8.2 mol%Ru/CeO_2 catalyst without EF; 100 mg catalyst, 0.1 MPa.

Catalyst-bed Temperature K	NH_3 conversion %	NH_3 decomposition rate mmol min^{-1}
376.6	0.1	0.000
476.3	2.7	0.003
526.7	9.1	0.010
546.5	13.6	0.015
576.6	30.5	0.034
596.7	47.2	0.053
626.1	73.7	0.082
651.6	88.0	0.098
677.2	90.8	0.101
779.9	95.1	0.106
729.2	94.1	0.105

Table S3 The temperature dependence of NH_3 conversion over 8.2 mol%Ru/CeO_2 catalyst in EF; 100 mg catalyst, 0.1 MPa, 6.0 mA.

Catalyst-bed Temperature K	NH_3 conversion %	NH_3 decomposition rate mmol min^{-1}	Response voltage kV
367.4	24.5	0.03	-0.14
469.5	23.9	0.02	-0.10
525.7	31.6	0.03	-0.11
570.7	40.7	0.04	-0.08
627.6	65.0	0.07	-0.07
685.0	78.7	0.08	-0.05

Table S4 The temperature dependence of NH_3 conversion over 8.2 mol%Ni/CeO_2 without EF; 100 mg catalyst, 0.1 MPa.

Catalyst-bed Temperature K	NH_3 conversion %	NH_3 decomposition rate mmol min^{-1}
370.7	0.2	0.0002
597.2	9.2	0.0095
679.2	18.3	0.0189
770.7	66.2	0.0684
883.5	86.9	0.0899

Table S5 The temperature dependence of NH_3 conversion over 8.2 mol%Ni/CeO_2 catalyst with/without EF; 100 mg catalyst, 0.1 MPa, 0 or 6.0 mA.

Catalyst-bed Temperature K	NH_3 conversion %	NH_3 decomposition rate mmol min^{-1}	Response voltage kV
348.9	17.1	0.02	-0.09
379.9	16.6	0.02	-0.09
429.6	16.7	0.02	-0.13
470.7	13.2	0.01	-0.09
565.9	9.7	0.01	-0.06
669.9	21.6	0.02	-0.06
770.0	69.1	0.07	-0.02
871.6	92.8	0.10	0.00

Table S6 The temperature dependence of NH_3 conversion over 8.2 mol%Fe/CeO_2 catalyst without EF; 100 mg catalyst, 0.1 MPa.

Catalyst-bed Temperature	NH_3 conversion	NH_3 decomposition rate
K	%	mmol min^{-1}
369.6	0.2	0.000
477.9	0.5	0.001
578.7	1.8	0.003
676.2	0.1	0.000
774.9	48.3	0.073

Table S7 The temperature dependence of NH_3 conversion over 8.2 mol%Fe/CeO_2 catalyst in EF; 100 mg catalyst, 0.1 MPa, 6.0 mA.

Catalyst-bed Temperature	NH_3 conversion	NH_3 decomposition rate	Response voltage
K	%	mmol min^{-1}	kV
356.0	21.4	0.02	-0.11
378.8	21.1	0.02	-0.11
472.4	21.3	0.02	-0.12
570.2	15.4	0.02	-0.10
668.2	12.9	0.01	-0.07
769.8	49.7	0.05	-0.02

Table S8 The temperature dependence of NH_3 conversion over 8.2 mol%Co/CeO_2 catalyst without EF; 100 mg catalyst, 0.1 MPa.

Catalyst-bed Temperature	NH_3 conversion	NH_3 decomposition rate
K	%	mmol min^{-1}
374.6	0.0	0.000
471.0	0.0	0.000
573.0	1.0	0.001
673.0	16.6	0.017
772.2	76.0	0.078

Table S9 The temperature dependence of NH_3 conversion over 8.2 mol%Co/CeO_2 catalyst in EF; 100 mg catalyst, 0.1 MPa, 0 or 6.0 mA.

Catalyst-bed Temperature	NH_3 conversion	NH_3 decomposition rate	Response voltage
K	%	mmol min^{-1}	kV
338.1	4.2	0.00	-0.06
373.1	5.6	0.01	-0.06
471.1	4.7	0.00	-0.06
573.1	3.2	0.00	-0.05
669.5	13.3	0.01	-0.02
770.0	69.4	0.07	0.00

Table S10. The temperature dependence of NH_3 conversion over CeO_2 catalyst in EF; 100 mg catalyst, 0.1 MPa, 6.0 mA.

Catalyst-bed Temperature	NH_3 conversion	NH_3 decomposition rate	Response voltage
K	%	mmol/min	kV
372.2	6.4	0.007	-0.08
422.1	6.7	0.007	-0.08
472.3	6.5	0.007	-0.08
521.2	2.8	0.003	-0.07
571.7	0.1	0.000	-0.06
622.6	0.2	0.000	-0.05
672.6	0.4	0.000	-0.03
723.1	1.0	0.001	-0.02

The low activity of CeO_2 only indicates that an active metal is required for the ammonia decomposition reaction. Due to the presence of protons on CeO_2, it is slightly active in the low temperature range of the electric field reaction, but not the main activity.

Table S11. Physicochemical properties of 8.2 mol% Ru/CeO_2 structure before and after the electric field test. 5%NH_3/Ar = 50 SCCM, 100 mg cat, 0.1 MPa, 6.0 mA.

catalyst state	specific surface area	Ru particle size	metal dispersion	Crystallite size			
				CeO_2 (200)	CeO_2 (311)	CeO_2 (222)	CeO_2 (422)
	$m^2 g^{-1}$	nm	%	Å	Å	Å	Å
Before EF test	108.6	6.5	29.4	103.6	80.3	64.7	76.2
After EF test	88.4	6.2	27.1	99.0	83.6	67.3	78.9

Ru particle size and Ru dispersion were derived by TEM and CO pulse measurements.

Table S12 Data for Arrhenius plots on NH_3 decomposition rates over 0.85 mol%Ru/CeO_2 catalyst without EF.

Catalyst-bed Temperature	NH_3 conversion	NH_3 decomposition rate	1/*T*	Ln*r*
K	%	mmol min^{-1}	10^{-3} K^{-1}	(mol g^{-1} h^{-1}) / -
572.9	2.2	0.01	1.7	8.6
475.2	0.1	0.00	2.1	5.7
619.0	9.7	0.02	1.6	10.1
670.6	29.9	0.08	1.5	11.2
717.6	55.7	0.14	1.4	11.9

Table S13 Data for Arrhenius plots on NH_3 decomposition rates over 0.85 mol%Ru/CeO_2 catalyst in EF.

Catalyst-bed Temperature	NH_3 conversion	NH_3 decomposition rate	Response voltage	1/*T*	Ln*r*
K	%	mmol min^{-1}	kV	10^{-3} K^{-1}	(mol g^{-1} h^{-1}) / -
346.7	9.3	0.04	-0.18	2.9	2.4
353.1	10.2	0.04	-0.18	2.8	2.5
364.0	11.0	0.05	-0.19	2.7	2.6
373.0	11.0	0.05	-0.19	2.7	2.6
383.5	10.1	0.04	-0.18	2.6	2.5
394.0	10.3	0.04	-0.18	2.5	2.5
426.7	7.5	0.03	-0.12	2.3	2.2
469.0	7.6	0.03	-0.11	2.1	2.2
568.4	16.1	0.07	-0.10	1.8	3.0
619.4	30.7	0.13	-0.10	1.6	3.6
663.8	60.6	0.25	-0.07	1.5	4.3

Table S14. Data used for TOF calculation.

Metal (Ru) loading amount	Catalyst calcination temperature	Ru particle size	NH_3 conversion	
			with EF (473 K)	without EF (573 K)
mol%	K	nm	%	%
0.85	723	3.7	6.1	5.4
5.0	573	4.4	17.8	29.2
5.0	723	4.9	20.1	23.3
8.2	723	6.1	20.8	29.8

Ru particle size was derived by TEM measurements.

Table S15. Low-temperature adsorbed species trap test. 5%NH_3/Ar = 50 SCCM, 300 mg 8.2 mol% Ru/CeO_2, 0.1 MPa, 0 or 6.0 mA.

	Catalyst-bed Temperature K	NH_3 conversion %	NH_3 decomposition rate mmol/min	Response voltage kV	Desorption at 493 K H_2/N_2 ratio -
without EF	572.8	45.1	0.046	0	0.47
with EF	366.7	44.3	0.045	-0.22	1.43

Table S16 Reaction enthalpy and activation energy of each reaction step.

		N-terminate		H-terminate	
Mechanism	Reaction step	Metal	Interface	Metal	Interface
*N formation	*NH + *NH → *NH + *N + *H	0.42 (1.37)	-0.27 (0.00)	0.35 (1.33)	-0.03 (0.00)
	*NH + *N + *H → 2 *N + 2 *H	-0.49 (0.42)	-1.25 (0.83)	-0.63 (0.31)	-0.76 (0.82)
	2 *N + 2 *H → *NN + 2 *H	0.82 (1.88)	1.80 (2.83)	0.77 (1.87)	1.41 (2.42)
*N_2H_2 formation	*NH + *NH → *NHNH	1.08 (1.41)	1.33 (1.52)	0.89 (1.26)	0.87 (1.35)
	*NHNH → *NNH + *H	-0.17 (1.25)	-0.41 (0.18)	-0.16 (1.12)	-0.22 (0.27)
	*NNH + *H → *NN + 2 *H	-0.15 (0.75)	-0.10 (1.16)	-0.24 (0.73)	-0.12 (1.11)

Numbers in () indicate the activation energy.

Table S17 Results of AC impedance measurements.

Condition -	Temp. K	R 10^8 W	C 10^{-10} F	s 10^{-10} S cm^{-1}	e 10^{-11} F cm^{-1}	e_r 10^2
Ar only	472.6	22	2.2	0.46	2.2	2.5
4.98%NH_3/Ar	472.8	1.0	2.0	9.8	2.1	2.3
5%H_2/Ar	473.3	0.21	2.3	47	2.3	2.6