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Electronic Supplementary Information (ESI)

Key factor for the anti-Arrhenius low-temperature heterogeneous catalysis induced by H^+ migration: H^+ coverage over support

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Table of Contents

1. Experimental Procedures

Preparation of 1wt%Ru/CeO_2

As a catalyst support, CeO_2 (JRC-CEO-01) was used. Ruthenium was loaded on the CeO_2 using an impregnation method. First, CeO_2 was dispersed in acetone. Then it was stirred at room temperature for 2 h. An acetone solution of $Ru(acac)_3$ was added to the CeO_2 slurry and was stirred at room temperature for 2 h. After the solution was heated to evaporate the acetone, it was dried at 393 K for 24 h. The obtained sample was reduced at 723 K under H_2 (50 SCCM) and Ar (50 SCCM) flow for 2 h. Finally, the prepared catalysts were molded into 355–500 μm granules.

Activity test

In all activity tests, a fixed-bed flow-type reactor was used. A schematic image of the apparatus is shown in Fig. S1. Two 2 mm-diameter stainless steel rods were attached to the catalyst bed as electrodes. The catalyst bed temperature was observed with a thermocouple inserted into the reactor and attached to the catalyst bed. Using a power supply device, 0–12 mA direct current was applied to the catalyst bed. The response voltage waves were detected using a digital oscilloscope (TDS 2001C; Tektronix Inc.). All activity tests were conducted with 100 mg catalyst. The catalyst was pre-reduced at 723 K under N_2 (60 SCCM) and H_2 (180 SCCM) for 2 h to activate ruthenium before the activity test. The synthesized ammonia was trapped in distilled water and was analyzed quantitatively using an ion chromatograph (IC-2001; Tosoh Co. Inc.).

The NH_3 synthesis rates with and without the electric field (Fig. 1(a), Fig. S4 and Table S1-S2) were detected under N_2 60 SCCM and H_2 180 SCCM. P_{H2} dependence measurements (Fig. 1(b), Fig. S2 and Table S3-S6) were conducted under constant total flow (240 SCCM) and N_2 flow (60 SCCM) while the respective flows of H_2 and He were changed.

In-situ FT-IR measurement in transmission mode

In-situ FT-IR measurements in transmission mode (FT-IR 6200; Jasco Corp.) were conducted with a CaF_2 window and MCT detector. The pelletized 1wt%Ru/CeO_2 (10 mmϕ, 50 mg, 40 kN, 1 min) was used as a sample. The measurement flow was shown in Fig. S3. Firstly, the catalyst was pre-reduced at 723 K under N_2 (5 SCCM) and H_2 (15 SCCM) for 2 h. Afterward, the catalyst was purged under Ar (20 SCCM) at 673 K for 1 h to remove hydrogen over lattice oxygen (O_{lat}) of CeO_2 surface. The complete desorption of hydrogen with purge was confirmed before this consideration (not shown here). Furthermore, the gas lines of Ar and N2+H2(D2) were separated, and the gas line was well purged by Ar for 1 h in between the H/D exchange test. Then, background spectrum was measured under Ar (20 SCCM) at each objective temperature (323, 373, 423, 473, 573, and 673 K). O_{lat}-D^+ stretching peaks were detected with N_2 (5 SCCM) and D_2 (15 SCCM) supply at each temperature. Before all O_{lat}-D^+ stretching peaks observation, the catalyst was purged under Ar (20 SCCM) at 673 K for 1h.

***In-situ* DRIFTS measurements**

In-situ DRIFTS measurements (FT-IR 6200; Jasco Corp.) with/without the electric field (0 or 6 mA) at 323 K and 473 K were conducted with ZnSe window and MCT detector. The 1wt%Ru/CeO_2 granules were used as a sample. The cell for DRIFTS measurements with the electric field does not have enough thermotolerance. Therefore, the experiments were conducted at lower than 473 K. Firstly, the catalyst was pre-treated at 473 K under N_2 (5 SCCM) and H_2 (15 SCCM) for 2 h. Then, the catalyst was purged under Ar (20 SCCM) at 473 K for 1 h. After that, background spectrum was measured under Ar (20 SCCM) at 323 and 473 K. O_{lat}-D^+ stretching peaks were detected with N_2 (5 SCCM) and D_2 (15 SCCM) supply at each temperature with/without the electric field (0 or 6 mA). Before all O_{lat}-D^+ stretching peaks observation, the catalyst was well purged under Ar (20 SCCM) at 473 K for 1h.

Characterizations

The phase and morphology of CeO_2, 1wt%Ru/CeO_2 (as made and after the activity test) were analyzed by X-ray diffraction (XRD, MiniFlex 600, Cu Kα; Rigaku Corp.).

2. Supplementary Figures and Tables

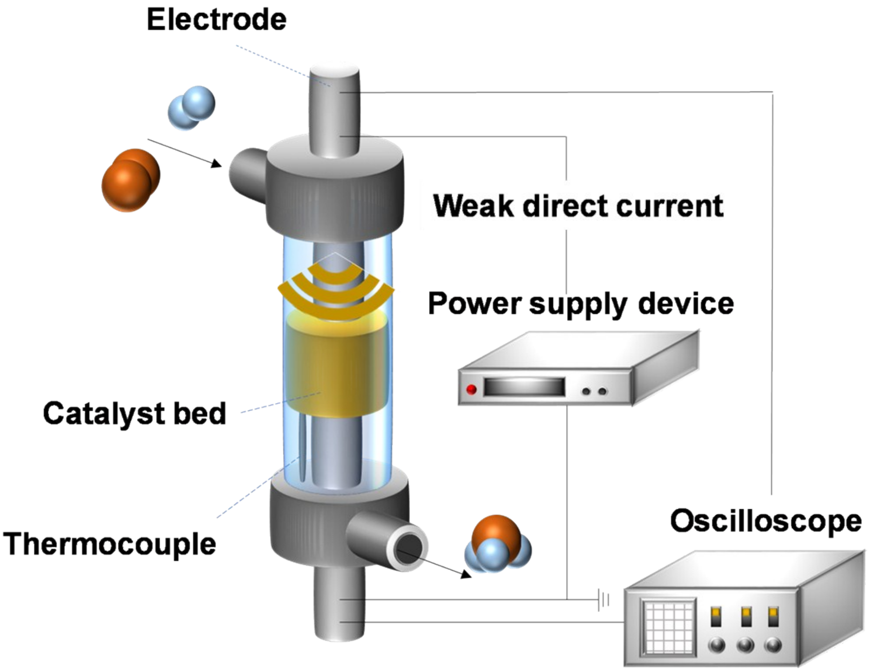

Fig. S1 Schematic image of the reactor for ammonia synthesis in the electric field.

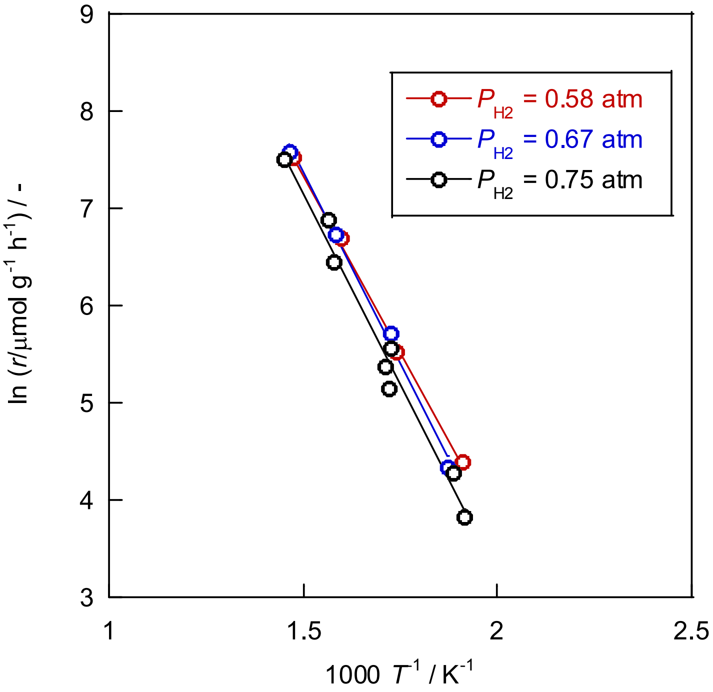

Fig. S2 Arrhenius plots for NH_3 synthesis rate (r) over 1wt%Ru/CeO_2 under several P_{H2} (0.58, 0.67 and 0.75 atm) without the electric field.

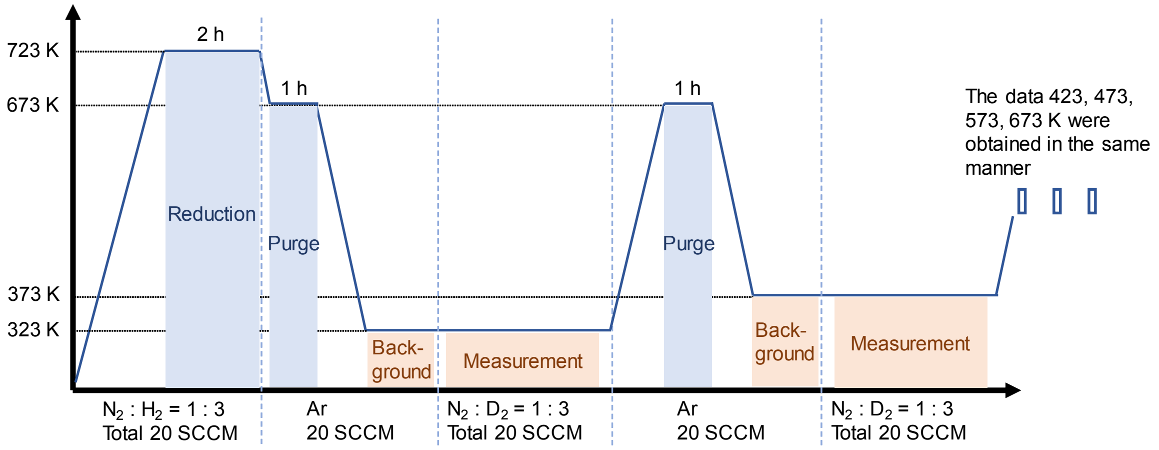

Fig. S3 Flow of *in-situ* IR measurement in transparent mode.

In-situ DRIFTS measurements with/without the electric field was conducted. As for both setting temperatures (323 and 473 K), the application of the electric field resulted in slight decrease of the O_{lat}-D^+ peak intensity. It will be caused by the temperature increase by the Joule heat. However, the decrement of the peak intensity by the electric field was smaller than that by the increase of the setting temperatures. Therefore, we concluded that the proton coverage without the electric field can use for the consideration in the main text.

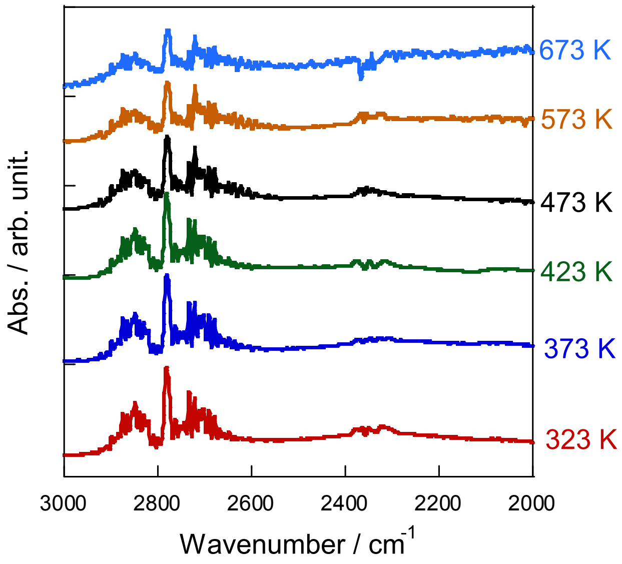

Fig. S4 *in-situ* IR measurements for 1wt%Ru/CeO$_2$ under N$_2$ 5 SCCM and D$_2$ 15 SCCM.

No peaks assigned to the surface structure change were detected during IR measurements. The catalyst was treated at high temperature (723 K) before measurements, and the temperature during the measurement did not exceed the pre-treatment temperature. Therefore, the catalyst structure was kept during the measurement. A little fluctuation was observed around 2300-2400 cm^{-1}. It was caused by the change of P_{CO2} outside the measurement cell.

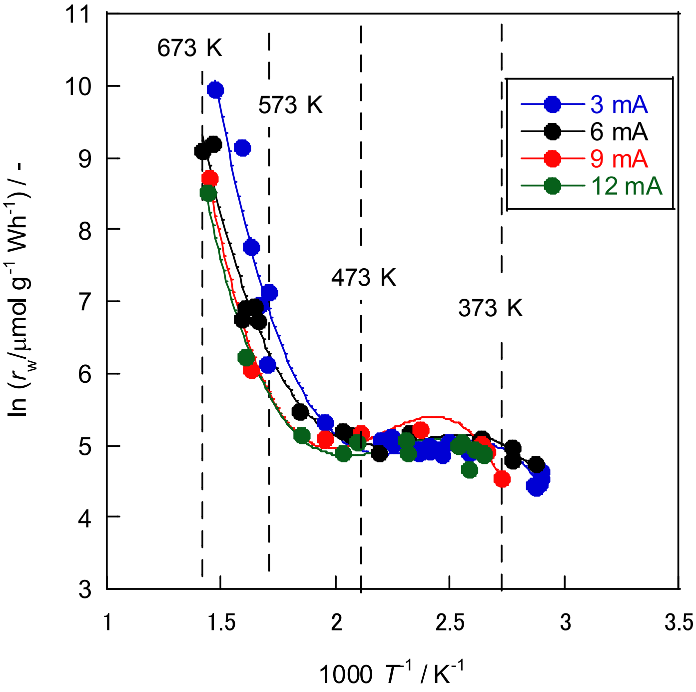

Fig. S5 Arrhenius plots for NH_3 synthesis rate per input power (r_w) over 1wt%Ru/CeO_2 with 3–12 mA direct current.

NH_3 synthesis rate per applied power (r_w) over 1wt%Ru/CeO_2 were considered. Here, r_w was calculated as shown in below

$$r_w = \frac{r}{I \times V} \qquad (S.1)$$

where I and V denotes applied current and voltage, respectively. The r_w exhibited almost constant value among all applied current. This trend corresponded to the previous studies. [Torimoto]

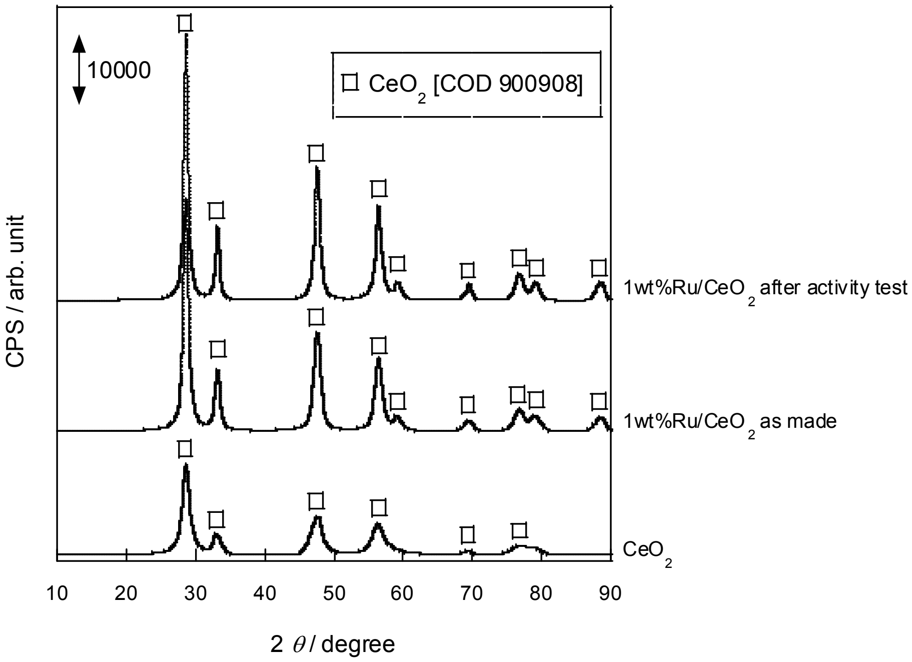

Fig. S6 XRD patterns for CeO_2 and 1wt%Ru/CeO_2 (as made and after activity test).

The effects of the electric field on phase and morphology of CeO_2 were considered using XRD measurements. As a result, no change was confirmed even after the activity tests with the electric field.

Table S1 Temperature dependence of NH_3 synthesis rate without the electric field under P_{H2} = 0.75 atm

Catalyst bed temperature / K	NH_3 synthesis rate / µmol g^{-1} h^{-1}	1000/T / K^{-1}	ln r / -
522	46.4	1.91	3.84
530	73.0	1.89	4.29
580	261.1	1.72	5.57
581	173.9	1.72	5.16
585	215.6	1.71	5.37
634	637.8	1.58	6.46
641	988.4	1.56	6.90
690	1837.9	1.45	7.52

Table S2 Temperature dependence of NH_3 synthesis rate with the electric field (6 mA) under P_{H2} = 0.75 atm

Catalyst bed temperature / K	Response voltage / kV	NH_3 synthesis rate / μmol g^{-1} h^{-1}	1000/T / K^{-1}	ln r / -
348	-0.19	131.4	2.88	4.88
360	-0.25	181.0	2.78	5.20
361	-0.24	208.3	2.77	5.34
379	-0.28	265.5	2.64	5.58
379	-0.28	266.4	2.64	5.58
430	-0.19	199.2	2.32	5.29
457	-0.20	157.7	2.19	5.06
484	-0.13	135.2	2.07	4.91
492	-0.16	168.0	2.03	5.12
541	-0.19	273.6	1.85	5.61
600	-0.08	416.5	1.67	6.03
606	-0.09	517.0	1.65	6.25
622	-0.12	716.3	1.61	6.57
629	-0.17	876.3	1.59	6.78
683	-0.03	1694.9	1.46	7.44
705	-0.05	2476.3	1.42	7.81

Table S3 Temperature dependence of NH_3 synthesis rate without the electric field under P_{H2} = 0.67 atm

Catalyst bed temperature / K	NH_3 synthesis rate / μmol g^{-1} h^{-1}	1000/T / K^{-1}	ln r / -
535.2	77.4	1.87	4.35
579.7	305.7	1.73	5.72
631.8	849.2	1.58	6.74
683.3	1985.2	1.46	7.59

Table S4 Temperature dependence of NH_3 synthesis rate with the electric field (6 mA) under P_{H2} = 0.67 atm

Catalyst bed temperature / K	Response voltage / kV	NH_3 synthesis rate / μmol g^{-1} h^{-1}	1000/T / K^{-1}	ln r / -
357.8	-0.22	212.5	2.79	5.36
389.5	-0.20	181.1	2.57	5.20
428.1	-0.20	177.8	2.34	5.18
482.2	-0.14	180.8	2.07	5.20
521.7	-0.12	176.7	1.92	5.17
566.3	-0.13	310.2	1.77	5.74
606.8	-0.10	610.1	1.65	6.41
646.7	-0.06	1254.5	1.55	7.13
689.5	-0.02	2367.4	1.45	7.77

Table S5 Temperature dependence of NH_3 synthesis rate without the electric field under P_{H2} = 0.58 atm

Catalyst bed temperature / K	NH_3 synthesis rate / μmol g^{-1} h^{-1}	1000/T / K^{-1}	ln r / -
524	81.3	1.91	4.40
576	250.4	1.74	5.52
627	805.7	1.60	6.69
678	1854.5	1.47	7.53

Table S6 Temperature dependence of NH_3 synthesis rate with the electric field (6 mA) under P_{H2} = 0.58 atm

Catalyst bed temperature / K	Response voltage / kV	NH_3 synthesis rate / μmol g^{-1} h^{-1}	1000/T / K^{-1}	ln r / -
342.5	-0.21	141.2	2.92	4.95
356.3	-0.22	173.4	2.81	5.16
364.0	-0.24	190.9	2.75	5.25
365.4	-0.19	161.3	2.74	5.08
369.3	-0.19	148.9	2.71	5.00
383.0	-0.18	143.6	2.61	4.97
404.0	-0.15	126.6	2.48	4.84
420.1	-0.18	144.0	2.38	4.97
436.7	-0.17	136.0	2.29	4.91
438.6	-0.16	131.8	2.28	4.88
472.8	-0.13	144.8	2.12	4.98
473.8	-0.14	152.6	2.11	5.03
521.7	-0.15	253.2	1.92	5.53
591.9	-0.06	466.5	1.69	6.15

639.8	-0.06	1156.5	1.56	7.05
643.7	-0.02	1371.7	1.55	7.22
684.2	-0.02	2304.3	1.46	7.74

3. References

[Torimoto] M. Torimoto, S. Ogo, D. Harjowinoto, T. Higo, J. G. Seo, S. Furukawa and Y. Sekine, *Chem*. *Commun*., 2019, **55**, 6693-6695.