

Supporting Information for

**Ammonia Decomposition by Ruthenium Nanoparticles Loaded on Inorganic Electride
 C12A7:e⁻**

Fumitaka Hayashi,¹ Yoshitake Toda,¹ Yoshimi Kanie,¹ Masaaki Kitano,² Yasuhiro Inoue,³ Toshiharu Yokoyama,¹ Michikazu Hara,³ Hideo Hosono^{1,2,3*}

1 Frontier Research Center, Tokyo Institute of Technology, 4259-S2-13 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan.

2 Materials Research Center for Element Strategy, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

3 Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan.

* corresponding author: hosono@msl.titech.ac.jp

Table S1. Activity and apparent activation energy for ammonia decomposition on previously-reported Ru-loaded catalysts reported^a

Entry	Catalyst	Ru Cont. / wt%	Ru Disp. / %	Temp. / °C	WHSV / mL _{NH₃} g _{cat} ⁻¹ h ⁻¹	Conv. of NH ₃ / %	E _a / kJ mol ⁻¹	TOF / s ⁻¹	Dec. rate of NH ₃ / kg _{NH₃} kg _{cat} ⁻¹ h ⁻¹	Refs.
1	Ru/Carbon nanotube	4.7	25.6	400	30000	17.7	69.2	0.60	3.65	S1
2	Ru-K/Carbon nanotube	4.5	27.0	400	150000	7.5	56.1	1.22	7.70	S1
3	Ru/MgO	5.0	11.0	400	150000	4.8	62.3	0.45	4.89	S1
4	Ru/TiO ₂	4.8	^{-b}	400	150000	3.8	63.3	^{-b}	3.92	S1
5	Ru/Al ₂ O ₃	5.0	11.5	400	150000	3.4	64.6	0.47	3.47	S1
6	Ru/Al ₂ O ₃	5.0	10.6	400	150000	1.2	80.4	0.43	1.19	S1
7	Ru/nano MgO	2.8	17.8	400	30000	17.5	^{-b}	0.90	3.61	S2
8	Ru-Cs/nano MgO	2.8	17.8	400	30000	23.0	^{-b}	1.18	4.74	S2
9	Ru/Al ₂ O ₃	1.6	77.0	410	3840	40.0	87.8	0.014	1.06	S3

^a When the space velocities were extremely-high, or the catalyst was diluted with silica or alumina, a part of previous data was excluded from Table S1 to compare fairly. ^b Not reported.

Table S2. Reaction orders with respect to ammonia and hydrogen for ammonia decomposition on previously-reported Ru-loaded catalysts

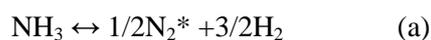
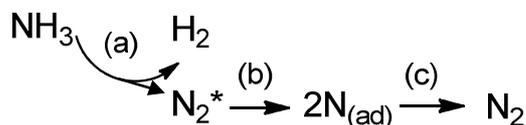
Entry	Catalyst	Temp. / °C	α	γ	$-\gamma/\alpha$	Refs.
1	Ru/Carbon	350-450	0.69-0.75	1.6-2.0	2.1-2.9	S3
2	Ru film	270-465	1.2	2.0	1.67	S4
3	Ru/Al ₂ O ₃	350-400	0.6	0.9	1.5	S5

References

- S1 S. F. Yin, Q. H. Zhang, B. Q. Xu, W. X. Zhu, C. F. Ng, C. T. Au, *J. Catal.* **2004**, *224*, 384-396.
 S2 J. Zhang, H. Xu, Q. Ge, W. Li, *Catal. Commun.* **2006**, *7*, 148-152.
 S3 M. C. J. Bradford, P. E. Fanning, M. A. Vannice, *J. Catal.* **1997**, *172*, 479-484.
 S4 S. R. Logan, C. Kemball, *Trans. Faraday Soc.* **1960**, *56*, 144-153
 S5 A. Amano, H. Taylor, *J. Am. Chem. Soc.* **1954**, *76*, 4201-4204.

Derivation of Temkin-Pyzhev equation^{S6,S7}

Temkin and Pyzhev assumed that the decomposition of ammonia consists of the following three processes (a)-(c), and that the processes (a) and (b) is fast, and the process (c) is slow and rate-limiting. Here N_2^* and $N_{(ad)}$ represent the imaginary species of nitrogen in the gas phase and nitrogen adatom. In this mechanism, $N_{(ad)}$ is not in equilibrium with N_2^* during the overall reaction, but, instead, is in equilibrium with the gas phase H_2 and NH_3 .



For equilibrium (a), we obtain $P_{N_2^*} = K P_{NH_3}^2 / P_{H_2}^3$ (1), where K is the thermodynamic equilibrium constant for process (a). For process (b), we obtain Eq. 2 using the Frumkin-Temkin isotherm, where θ is the fraction of surface covered by nitrogen adatom, and f and a_0 stand for constants.

$$\theta = (1/f) \ln a_0 P_{N_2^*} \quad (2)$$

Since the nitrogen desorption rate for process (c) is expressed by the Elovich equation, we get $R_d = k_d \exp(h\theta)$ (3), where R_d is the N_2 desorption rate, and k_d and h are constants. On the present assumption, the ammonia decomposition rate is equal to the N_2 desorption rate, and thus we get Eq. 4, which is known as the Temkin-Pyzhev equation, by substituting Eqs. 1 and 2 into Eq. 3. Here k and n are constants.

$$-d(P_{NH_3})/dt = k (P_{NH_3}^2 / P_{H_2}^3)^n \quad (4)$$

References

S6 M. Temkin, V. Pyzhev, *Acta Physicochim. USSR* **1940**, 12, 327-356.

S7 J. M. Thomas, W. J. Thomas, In *Principles and practice of heterogeneous catalysis*; VCH: Cambridge, **1997**, pp. 548-551.

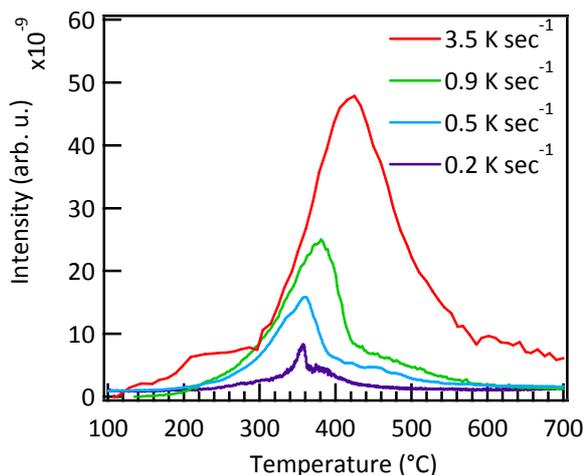


Figure S1. TPD ($m/z = 14$) profile of N_2 for 2 wt%-Ru loaded MgO after heating in a flow of N_2 - H_2 mixture at 360 °C for 5 h, annealed in N_2 flowing at 300 °C for 5 h, and cooled to room temperature in N_2 flowing. The peak area is proportional to the heating rate when the peak intensity is integrated with respect to the temperature.

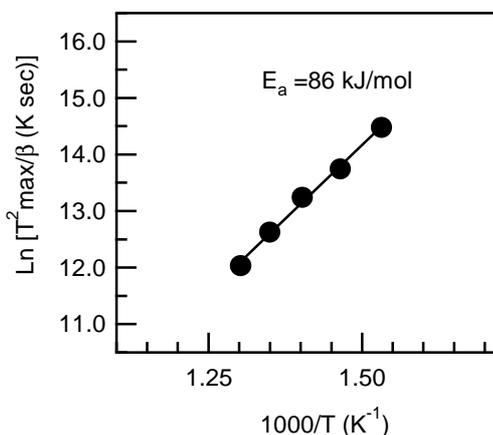


Figure S2. Activation energy estimation of N_2 desorption on Ru-K/C using the Redhead equation. T_{max} : Temperatures corresponding to the peak of N_2 desorption band, the maximum of N_2 desorption rate.

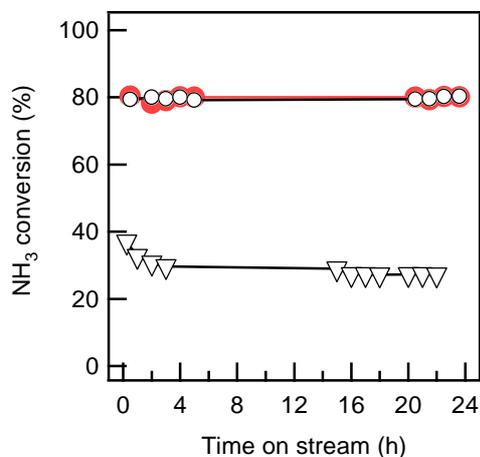


Figure S3. Stability test in NH_3 decomposition under the condition of 600 °C and $WHSV=120,000$ $ml_{NH_3} g_{cat}^{-1} h^{-1}$: ●, Ru/C12A7:e⁻; ○, Ru/C12A7:O²⁻; ▽, Ru-K/C.