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Supplementary Information

Dual Confinement Stabilizes highly dispersed Ru clusters for Efficient and Durable Ammonia Decomposition

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Characterizations

XRD test (Rigaku SmartLab, Cu Kα, λ=0.15418 nm) : Place approximately 20 mg of the powder catalyst sample on a slide, flatten it with a cover slip, and insert it into the instrument at a step speed of 10 °/min. HR-TEM (JEM-2100Plus, 200 kV): A small amount of powder sample was placed in anhydrous ethanol, ultrasonically dispersed for a certain period of time, and then dropped onto a copper mesh for TEM and EDS (Oxford X-MAX 80T) characterization. ICP-OES (Thermo Scientific iCAP PRO): Take 5 mg of the sample and place it in a hydrothermal reactor, add 1 ml of aqua regia, and put it in an oven at 160 °C to maintain for 6 hours. Filter the obtained solution and make up to 10 ml for testing. RAMAN (HORIBA XploRA Plus): Approximately 20 mg of the powder catalyst sample was flattened and placed on a slide. The test was conducted with a Laser at 532 nm and a filter at 25%. The XPS test was conducted using Thermo Scientific K-Alpha (Al-Kα excitation source), binding energy calibration standard (C 1s=284.8 eV as internal reference), and spectrum fitting method, ensuring the reproducibility and rigor of the characterization data. TPD tests were conducted on a BEL Japan BelCata II analyzer coupled with a BEL Japan BelMass mass spectrometer. A 90 mg sample was pretreated at 500°C for 30 min in a 10 vol% NH_3/Ar mixture (30 mL/min). After cooling to 50 °C, the sample was purged with the same 10% NH_3/Ar (30 mL/min) for 1 h to reach saturated NH_3 adsorption. Subsequently, the gas was switched to pure He (30 mL/min) and purged until a stable baseline was achieved. Finally, the sample was heated from room temperature to 600°C at a rate of 10°C/min under pure He flow (30 mL/min), and the TPD profile was recorded. The signals of NH_3 (m/z = 17), H_2 (m/z = 2), and N_2 (m/z = 28) were detected by mass spectrometry. In-situ DRIFTS measurements for CO adsorption were carried out on a Thermo Nicolet IS50 Fourier-transform infrared (FT-IR) spectrometer, equipped with an in-situ diffuse reflectance cell from Hefei In-Situ Technology Co., Ltd. (China), and the model of the diffuse reflectance accessory is CIS-IRDROA-SD. ZnSe windows were used, and a mercury-cadmium-telluride (MCT) detector was adopted. The test parameters were set as: wavenumber range 4000-650 cm^{-1}, resolution 4 cm^{-1}, 4 scans, and data interval 1 cm^{-1}.

Sample Nomenclature

Commercial CeO_2 powder, commercial nano-CeO_2 powder, and the CeO_2/SiO_2 support are denoted as CeO_2, CeO_2-NM, and CeO_2/SiO_2, respectively.

The Ru-supported samples were designated as Ru/ CeO_2, Ru/ CeO_2-NM, and Ru/ CeO_2/SiO_2, respectively.

Material Synthesis Method

CeO_2/SiO_2: The CeO_2/SiO_2 composite was synthesized by first adding 360 mg of fumed silica powder (Macklin, specific surface area: 400 m^2 g^{-1}) into 50 mL of deionized water under continuous stirring, followed by ultrasonic treatment until complete dispersion was achieved. Add 170 mg of $Ce(NO_3)_3 \cdot 6H_2O$ (Macklin, 99.99%) to the above solution under vigorous stirring until the solid was completely dissolved. Then, a 1 mol/L KOH solution was added dropwise to adjust the pH of the mixture to approximately 10, followed by continued stirring for 3-5 minutes. The filtered solid was collected using vacuum filtration and dried overnight at 60 °C. The resulting solid was then ground into a fine powder and calcined at 600 °C for 12 hours to obtain the final CeO_2/SiO_2 support.

Ru/CeO_2/SiO_2, Ru/CeO_2 and Ru/CeO_2-NM: The Ru/CeO_2/SiO_2 catalyst was synthesized via the incipient wetness impregnation method. A precursor aqueous solution (volume = saturated water absorption volume of the support) was prepared by dissolving $RuCl_3 \cdot xH_2O$ (Aladdin, 99.95%) in deionized water. 300 mg of CeO_2/SiO_2, cerium oxide (Aladdin, 99.9%) and nano-cerium oxide (Aladdin, 20–50 nm, 99.5%) powder was impregnated with the Ru precursor solution at mass loadings of 2%, respectively. The precursor solution was added until the solution barely covered the solid material, and the mixture was dried overnight at room temperature. The resulting solid was then calcined at 500 °C for 2 hours in a muffle furnace to obtain the final Ru/CeO_2/SiO_2, Ru/CeO_2 and Ru/CeO_2-NM catalyst powder.

The elemental contents of all Ru-loaded samples were measured using ICP-OES (as shown in Table S1).

Ammonia Decomposition Catalytic Performance Test

The evaluation of ammonia decomposition catalysts for hydrogen production was conducted in a fixed-bed reactor. A total of 100 mg catalyst was loaded into the reactor with quartz wool support. Then introduced 99.9 vol% NH_3, and the catalytic performance was evaluated within the temperature range of 300-550 °C. The reaction was carried out at atmospheric pressure with a weight hourly space velocity (WHSV) of 12000 mL $gcat^{-1}$ h^{-1}. The composition of the effluent gas was analyzed using an online gas chromatograph (GC-7960 PLUS, KAIZE) equipped with thermal conductivity detector (TCD).

$$X_{NH_3}(\%) = \frac{[NH_3]_{in} \text{ - } [NH_3]_{out}}{[NH_3]_{in}} \times 100\% \qquad (1)$$

$$r_{H_2}(mmol\ g_{Ru}{}^{-1}\ min^{-1}) = \frac{\frac{V_{NH_3}}{22.4} \times X_{NH_3} \times 1.5}{m_{Ru}} \qquad (2)$$

The ammonia conversion rate and the hydrogen production rate were calculated using above equations, where $[NH_3]_{in}$ and $[NH_3]_{out}$ represent the volumetric flow rates of ammonia entering and exiting the reactor, and X_{NH_3} denotes the ammonia conversion rate. V_{NH_3} represents the ammonia flow rate, 22.4 is the molar volume of gas under standard conditions (L/mol),) X_{NH_3} is the ammonia decomposition conversion rate, and m_{Ru} is the mass of Ru in the catalyst.

Table S1 Metal composition of supported Ru catalyst

Sample	Ru content (wt%)	Ce content (wt%)
Ru/CeO_2/SiO_2	2.26%	15.11%
Ru/CeO_2	2.23%	
Ru/CeO_2-NM	2.47%	

Catalyst	Ru (%)	T (°C)	WHSV (mL g_{cat}^{-1} h^{-1})	Conv. (%)	H_2 formation rate (mmol g_{Ru}^{-1} min^{-1})	Ref.
Ru/MgO (111)	3.1	400	30,000	69	745	[1]
Ru/MgO (111)	3.1	450	30,000	100	1,080	[1]
Ru/$La_{0.33}Ce_{0.68}$	1.8	450	6,000	100	372	[2]
Ru/$La_{0.33}Ce_{0.68}$	1.8	450	30,000	79	1,472	[2]
Ru/Ce_1	1.8	450	6,000	98	367	[2]
Ru–K/Al_2O_3	4.6	450	30,000	35	254	[3]
RuLaCs/Al_2O_3	1.0	450	5,000	99	558	[4]
RuLaCs/Al_2O_3	1.0	400	5,000	82	458	[4]
Ru/C12A7: e^-	2.2	400	15,000	70	532	[5]
Ru/C12A7: e^-	2.2	450	15,000	99	759	[5]
Ru/BHA	2.7	450	60,000	21	507	[6]
Ru/BHA	3.0	450	30,000	42	423	[6]
Ru/MgO	2.8	450	30,000	41	493	[7]
Ru/MgO	0.8	450	60,000	38	2,092	[8]
Ru/MgO	1.7	450	22,000	83	1,198	[8]
Ru/MgO-DP	3.5	450	30,000	56	540	[9]
Ru/La_2O_3	4.8	450	18,000	73	304	[10]
Ru/CeO_2	2.0	450	6,000	98	330	[11]
Ru/Sm_2O_3-p	2.0	450	30,000	56	916	[12]
Ru/c-MgO	2.9	450	30,000	75	866	[13]
Ru/CeO_2-CNTs	1.5	450	30,000	70	1,464	[14]
Ru/SiO_2	10	450	30,000	36	112	[15]
Ru/CeO_2/SiO_2	2.2	450	36,000	64	1,169	This work
Ru/CeO_2/SiO_2	2.2	450	60,000	57	1,735	This work

Table S2 Performance comparison

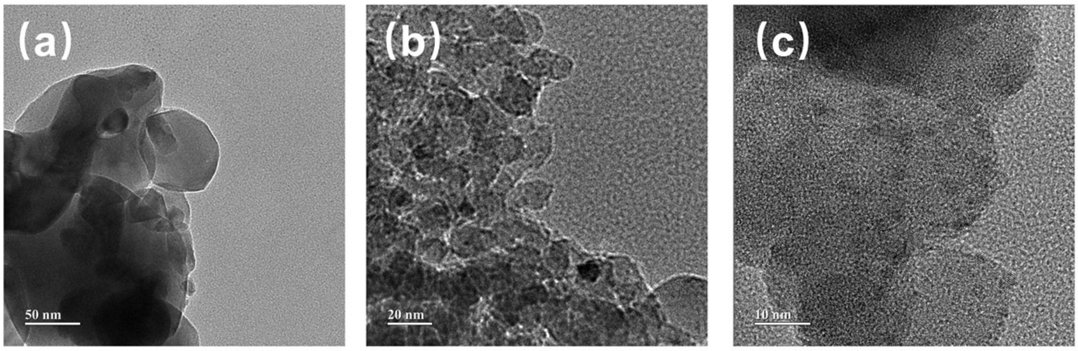

Fig. S1 TEM image of (a) 2%Ru/CeO_2; (b) 2%Ru/CeO_2-NM; (c) 2%$Ru/CeO_2/SiO_2$.

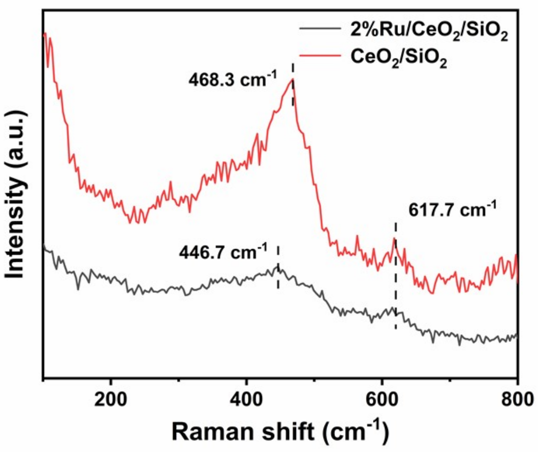

Fig. S2 Raman spectra of 2%Ru/CeO_2/SiO_2 and CeO_2/SiO_2.

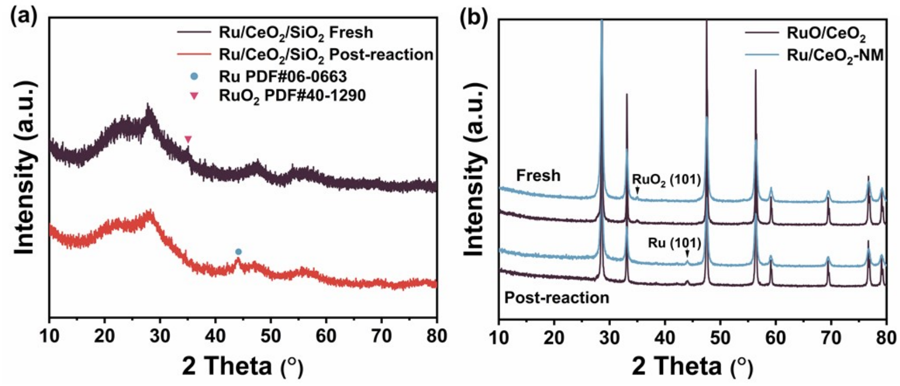

Fig. S3 The XRD patterns before and after the reaction (a) 2%Ru/CeO$_2$/SiO$_2$; (b) 2%Ru/CeO$_2$ and Ru/CeO$_2$-NM.

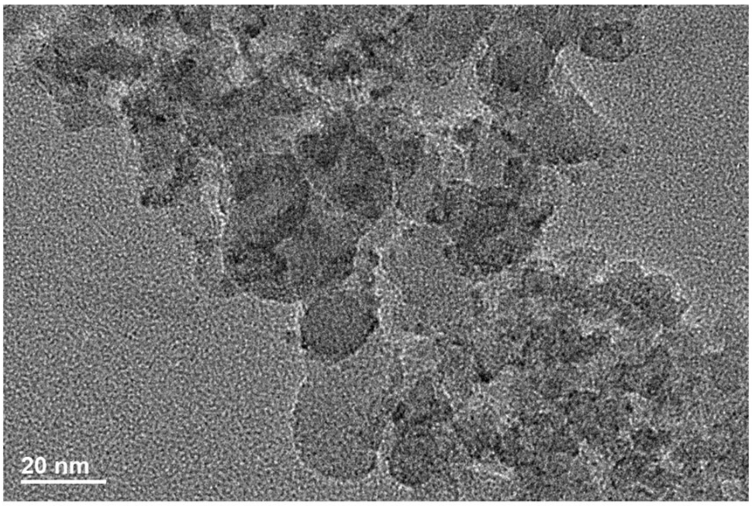

Fig. S4 TEM image of 2%Ru/CeO_2/SiO_2 catalyst after 50 hours of stability test.

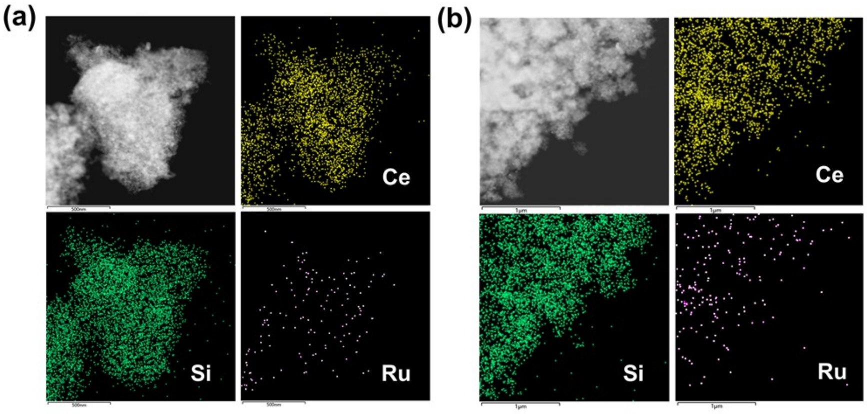

Fig. S5 EDS mapping of (a) 2%Ru/CeO_2/SiO_2; (b) 2%Ru/CeO_2/SiO_2 after 50 hours of stability test.

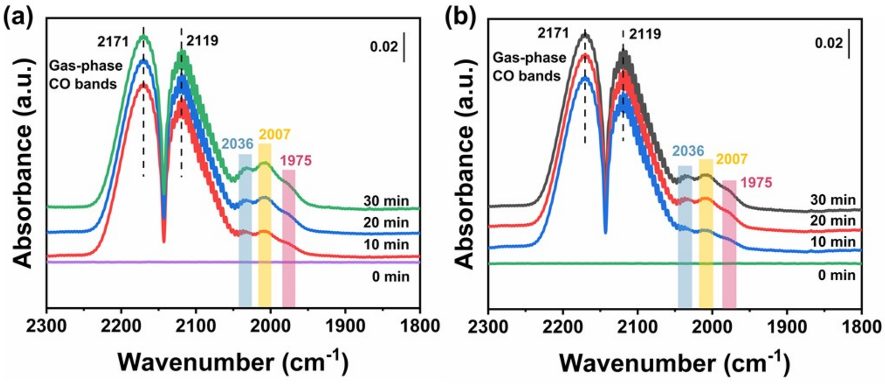

Fig. S6 In-situ DRIFTS spectrum of CO adsorption on 2%Ru/CeO_2/SiO_2 (a) Fresh sample; (b) Post-reaction sample.

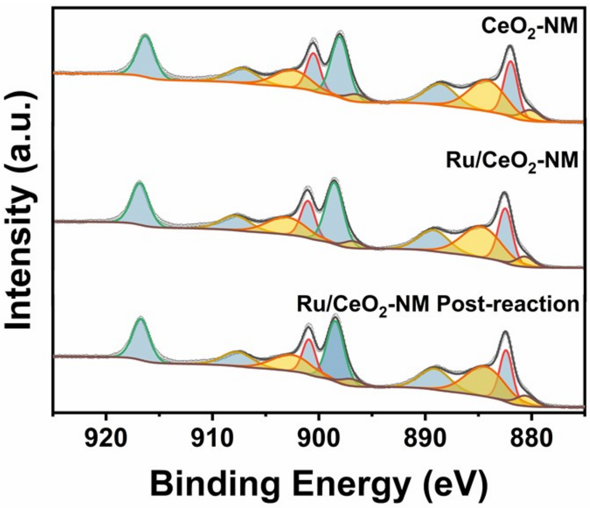

Fig. S7 XPS spectra of Ce 3d of 2%Ru/CeO$_2$-NM.

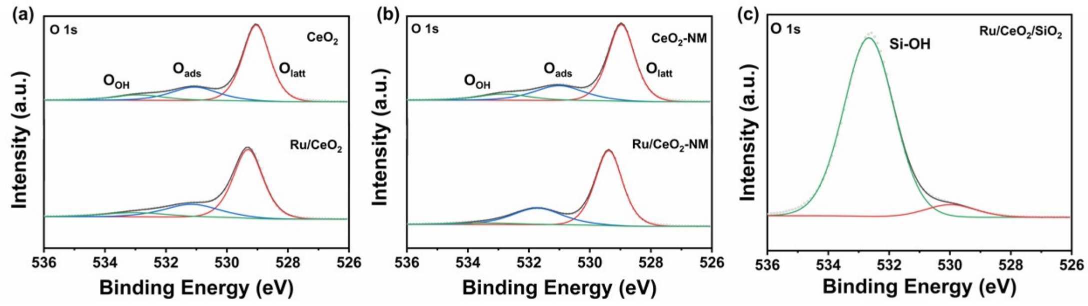

Fig. S8 XPS spectra of O 1s of (a) CeO$_2$ and 2%Ru/CeO$_2$; (b) CeO$_2$-NM and 2%Ru/CeO$_2$-NM; (c) Ru/CeO$_2$/SiO$_2$.

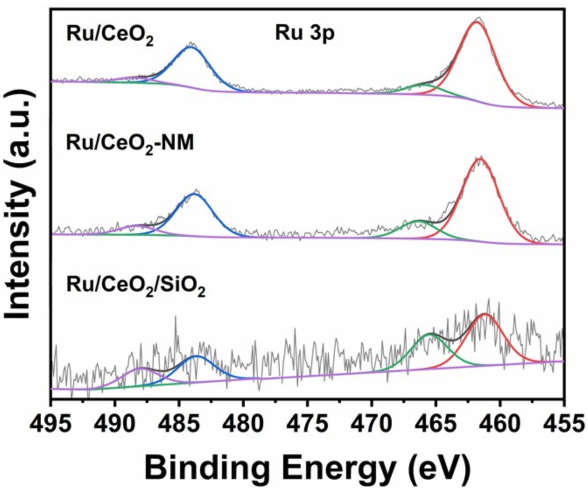

Fig. S9 XPS spectra of Ru 3p of post-reaction samples.

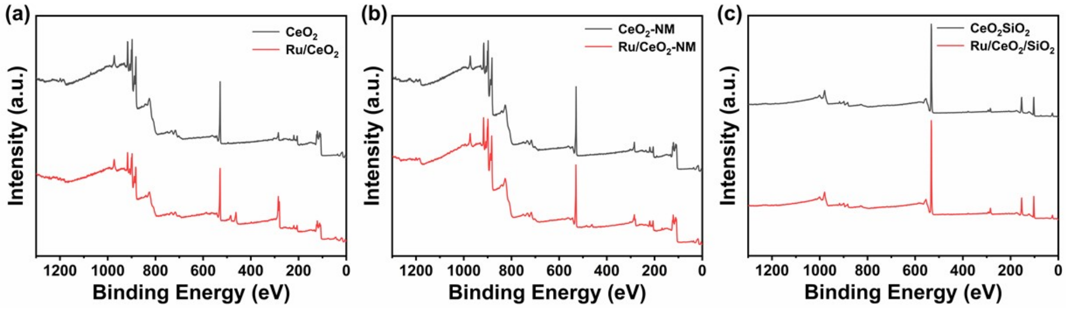

Fig. S10 The wide-scan XPS spectrum of the samples.

References

1. H. Fang, S. Wu, T. Ayvali, J. Zheng, J. Fellowes, P.-L. Ho, K. C. Leung, A. Large, G. Held, R. Kato, K. Suenaga, Y. I. A. Reyes, H. V. Thang, H.-Y. T. Chen and S. C. E. Tsang, *Nat. Commun.*, 2023, **14**.
2. T. A. Le, Y. Kim, H. W. Kim, S.-U. Lee, J.-R. Kim, T.-W. Kim, Y.-J. Lee and H.-J. Chae, *Appl. Catal. B-Environ.*, 2021, **285**, 119831.
3. Q. Su, L. L. Gu, A. H. Zhong, Y. Yao, W. J. Ji, W. P. Ding and C. T. Au, *Catal. Lett.*, 2018, **148**, 894-903.
4. Z. Wang, H. Luo, L. Wang, T. Li, S. Li and Y.-Q. Liu, *ACS Sustain. Chem. Eng.*, 2024, **12**, 5620-5631.
5. F. Hayashi, Y. Toda, Y. Kanie, M. Kitano, Y. Inoue, T. Yokoyama, M. Hara and H. Hosono, *Chem. Sci.*, 2013, **4**, 3124-3130.
6. Z. Wang, Z. Cai and Z. Wei, *ACS Sustain. Chem. Eng.*, 2019, **7**, 8226-8235.
7. J. Zhang, H. Xu, Q. Ge and W. Li, *Catal. Commun.*, 2006, **7**, 148-152.
8. X.-C. Hu, W.-W. Wang, R. Si, C. Ma and C.-J. Jia, *Sci. China:Chem.*, 2019, **62**, 1625-1633.
9. X. Ju, L. Liu, P. Yu, J. Guo, X. Zhang, T. He, G. Wu and P. Chen, *Appl. Catal. B-Environ.*, 2017, **211**, 167-175.
10. C. Huang, Y. Yu, J. Yang, Y. Yan, D. Wang, F. Hu, X. Wang, R. Zhang and G. Feng, *Appl. Surf. Sci.*, 2019, **476**, 928-936.
11. J. Feng, X. Zhang, J. Wang, X. Ju, L. Liu and P. Chen, *Catal. Sci. Technol.*, 2021, **11**, 6330-6343.
12. X. Zhang, L. Liu, J. Feng, X. Ju, J. Wang, T. He and P. Chen, *Catal. Sci. Technol.*, 2021, **11**, 2915-2923.
13. X. Ju, L. Liu, X. Zhang, J. Feng, T. He and P. Chen, *ChemCatChem*, 2019, **11**, 4161-4170.
14. L. Lv, P. Chu, T. Han, Y. Jiang, Z. Wang, Y. Liu, H. Dai, L. Wei and J. Deng, *Angew. Chem., Int. Ed.*, 2025, **64**.
15. T. V. Choudhary, C. Sivadinarayana and D. W. Goodman, *Catal. Lett.*, 2001, **72**, 197-201.