

Electronic supplementary information (ESI)

Sub-nanometer Ru clusters on Sm₂O₃ obtained from a room temperature ion adsorption method for ammonia synthesis

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Table S1Properties of Ru/Sm₂O₃ catalysts.

Sample	Ru loading ^a (wt%)	Surface area ^b (m ² g ⁻¹)
Sm(OH) ₃	–	58.3
2% Ru/Sm ₂ O ₃	1.9	41.0
3% Ru/Sm ₂ O ₃	2.6	49.6
4% Ru/Sm ₂ O ₃	3.3	54.3
5% Ru/Sm ₂ O ₃	5.6	56.2

^a Determined by ICP-OES^b Determined by Nitrogen adsorption/desorption isotherms.

Table S2EXAFS data fitting results of Ru foil and Ru/Sm₂O₃ samples with different Ru loading.

Sample	Ru–Ru		Ru–O		D. W.	ΔE_0 (eV)	R factor
	R (Å)	CN	R (Å)	CN			
Ru foil	2.648±0.00				0.0024±0.0008	-3.9±1.1	0.024
	6	6	–	–			
	2.696±0.00	6					
3% Ru/Sm ₂ O ₃		6			0.0053±0.0015 (O)	-4.4±1.6 (O)	0.012
	2.75±0.03	1.9±0.9	2.00±0.01	5.4±0.6	0.0104±0.0049 (Ru)	1.5±3.0 (Ru)	
4% Ru/Sm ₂ O ₃		6			0.0032±0.0019 (O)	-6.6±2.4 (O)	0.018
	2.70±0.01	2.6±0.9	1.99±0.01	4.3±0.7	0.0048±0.0028 (Ru)	-6.9±2.3 (Ru)	
5% Ru/Sm ₂ O ₃		6			0.0054±0.0017 (O)	-6.4±2.0 (O)	0.014
	2.72±0.01	2.0±0.8	1.98±0.01	5.4±0.7	0.0059±0.0034 (Ru)	-2.0±2.5 (Ru)	

R, distance between absorber and backscatter atoms; *CN*, coordination number; *D. W.*, Debye-Waller factor; ΔE_0 , inner potential correction to account for the difference in the inner potential between the sample and the reference compound. R factor is used to value the goodness of the fitting.

Table S3

Catalyst activities for ammonia synthesis over various catalysts operated under similar conditions.

Catalysts	Ru loading (wt%)	Temperature (°C)	Pressure (MPa)	WHSV (mL g _{cat} ⁻¹ h ⁻¹)	NH ₃ synthesis rate (μmol g _{cat} ⁻¹ h ⁻¹)	Ref.
Ru/Sm ₂ O ₃	5.0	400	1.0	24000	23040	This work
Ru/Sm ₂ O ₃	4.0	400	1.0	24000	22570	This work
Ru/Sm ₂ O ₃	4.0	400	1.0	18000	20590	This work
Ru/Sm ₂ O ₃	5.0	400	1.0	24000	19100	1
Ru/Sm ₂ O ₃	5.0	400	1.0	24000	32000	1
Ru-Ba/AC	9.1	400	1.0	18000	8285	2
Ru-Cs/MgO	6.0	400	1.0	18000	12117	2
Ru/C12A7:e ⁻	4.0	400	1.0	18000	6089	2
Ru/Pr ₂ O ₃	5.0	400	1.0	18000	19000	3
Ru/La _{0.5} Ce _{0.5} O _{1.75}	5.0	400	1.0	72000	64000	4
Ru/BaTiO _{2.5} H _{0.5}	4.3	400	5.0	66000	20700	5
Ru/CaH ₂	2.0	340	0.1	36000	4002	6
Ru/Ca ₂ N:e ⁻	1.8	340	0.1	36000	3386	7

Table S4

The chloride content in the reduced and activated 4% Ru/Sm₂O₃ sample was determined by XRF

sample	Sm ₂ O ₃ (wt%)	Ru (wt%)	Cl (wt%)
Reduced 4% Ru/Sm ₂ O ₃	94.84	4.15	0.26
Activated 4% Ru/Sm ₂ O ₃	94.32	4.26	0.27

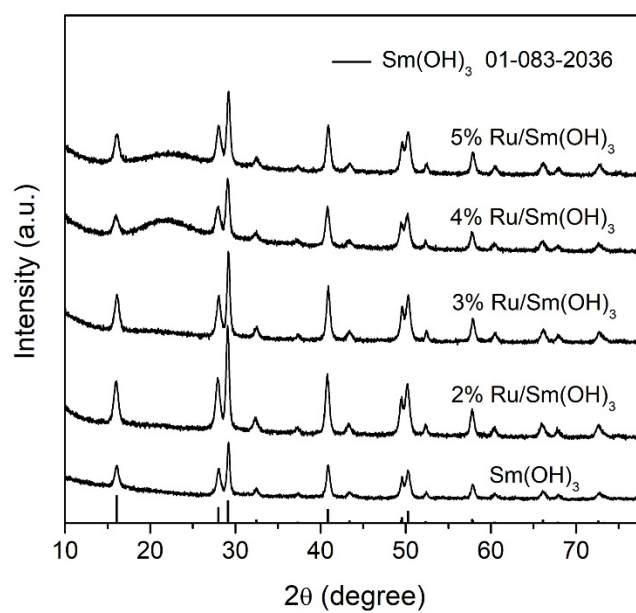


Fig. S1. XRD patterns of Sm(OH)₃ and Ru/Sm(OH)₃ composites with different Ru mass loading.

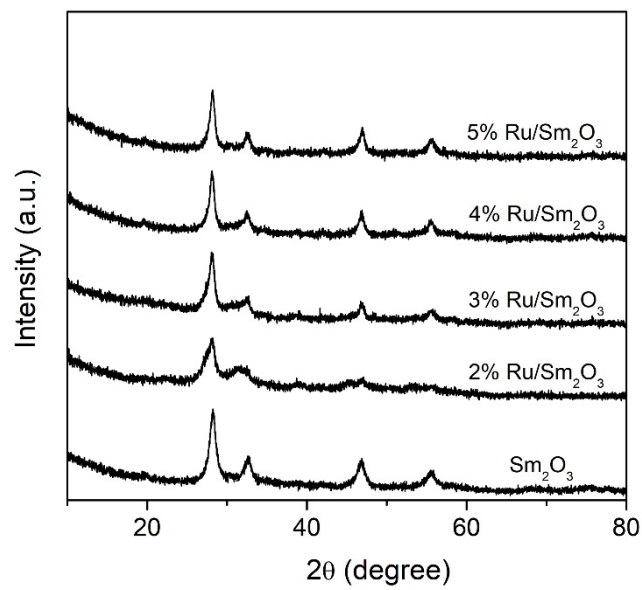


Fig. S2. XRD patterns of Sm₂O₃ and Ru/Sm₂O₃ samples with different Ru mass loading.

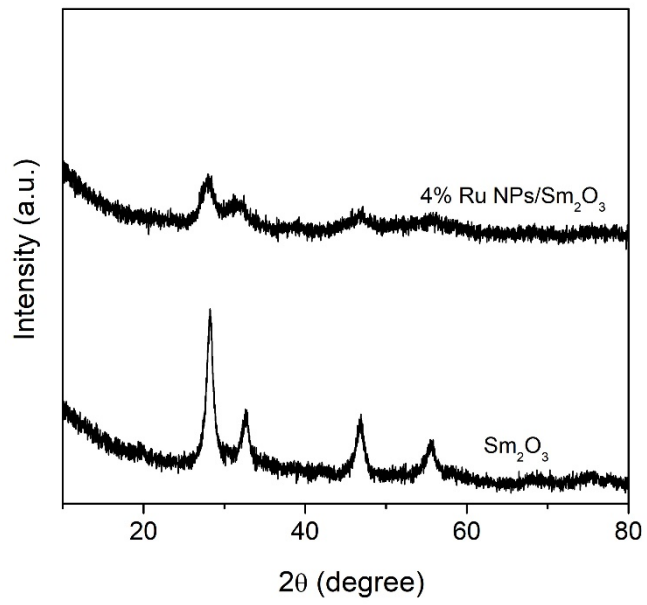


Fig. S3. XRD patterns of Sm₂O₃ and 4% Ru NPs/Sm₂O₃ sample.

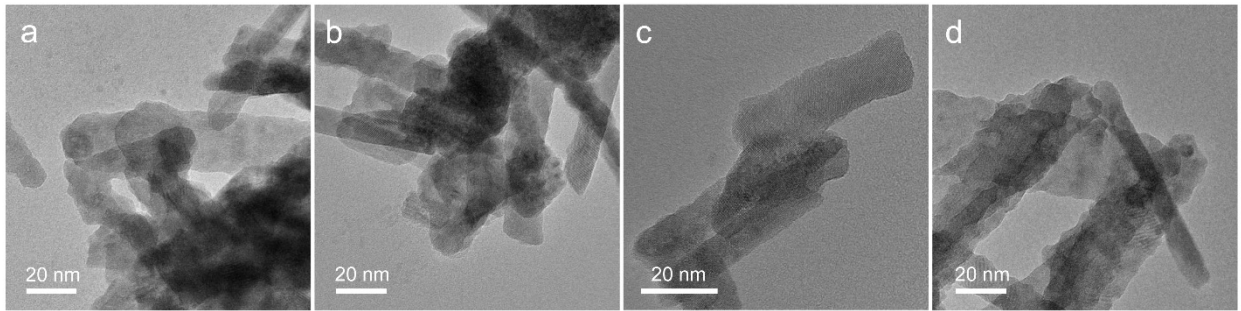


Fig. S4. TEM images of 2% Ru/Sm₂O₃ (a), 3% Ru/Sm₂O₃ (b), 4% Ru/Sm₂O₃ (c) and 5% Ru/Sm₂O₃ (d).

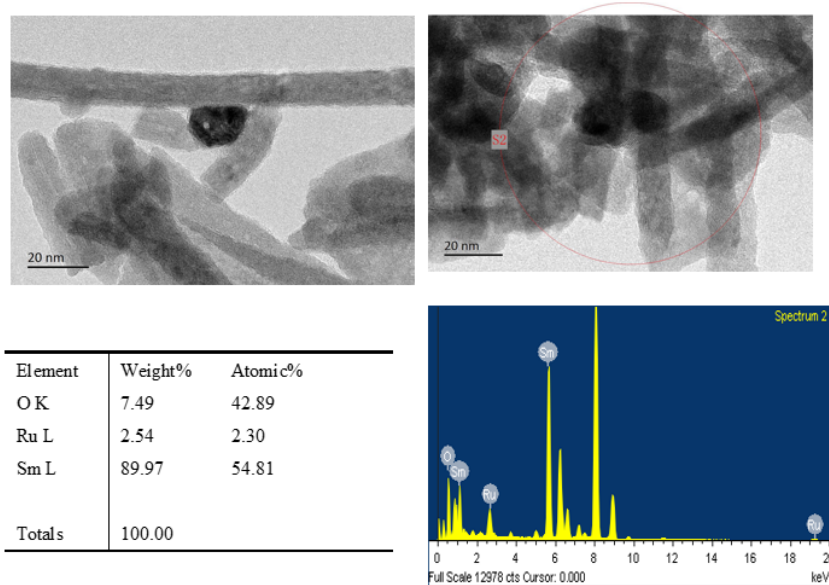


Fig. S5. TEM images and Energy Dispersive X-Ray (EDX) spectrum of Ru NPs/Sm₂O₃ catalyst.

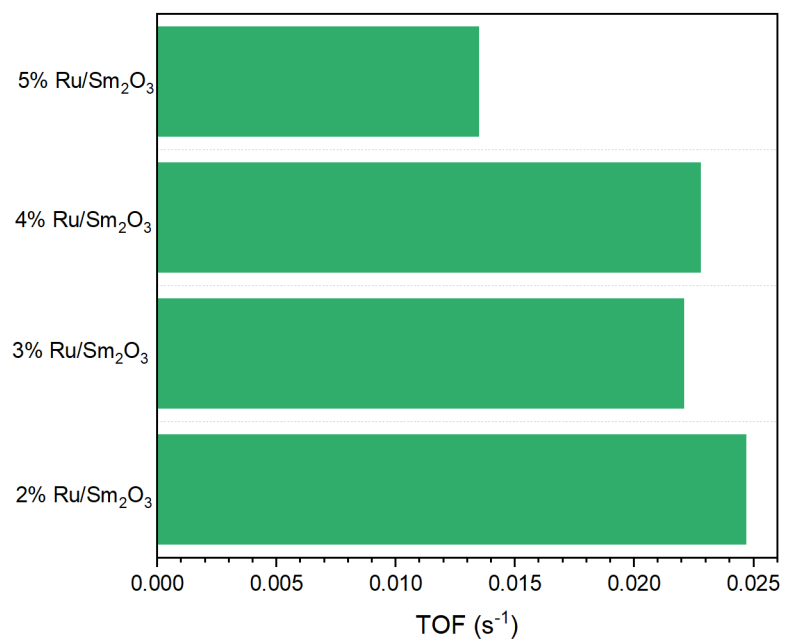


Fig.S6. TOF_{NH₃} of 2% Ru/Sm₂O₃, 3% Ru/Sm₂O₃, 4% Ru/Sm₂O₃ and 5% Ru/Sm₂O₃ at 400 °C under 1.0 MPa.

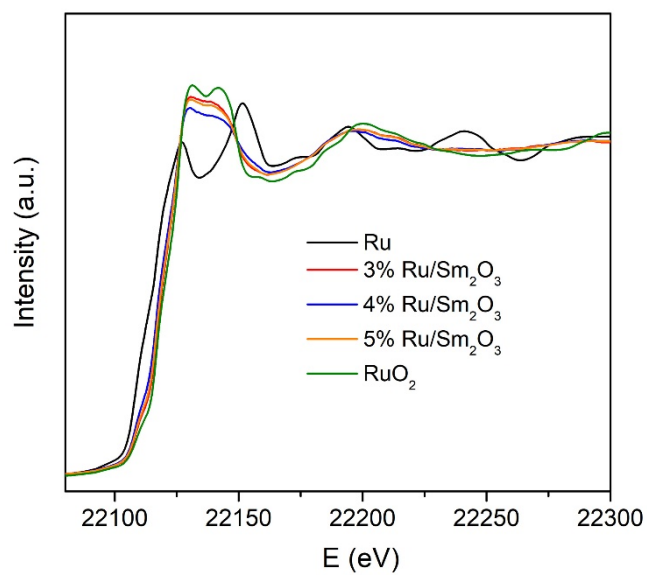


Fig. S7. The normalized Ru K-edge XANES profiles of 3% Ru/Sm₂O₃, 4% Ru/Sm₂O₃ and 5% Ru/Sm₂O₃. Ru foil and RuO₂ were included as references.

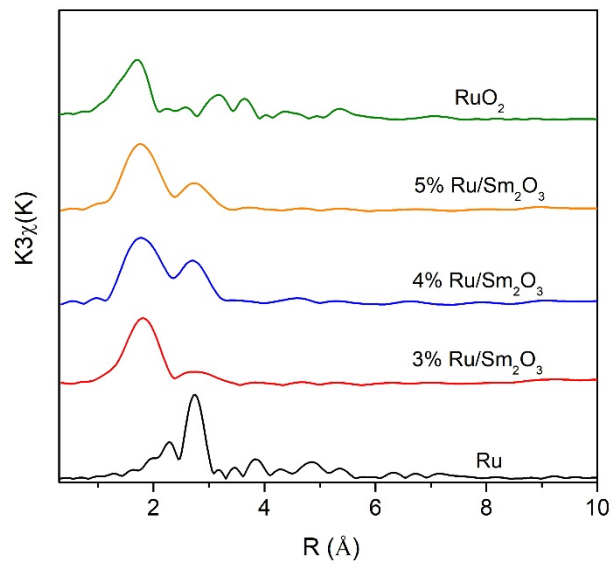


Fig. S8. Ru K-edge EXAFS spectra of 3% $\text{Ru}/\text{Sm}_2\text{O}_3$, 4% $\text{Ru}/\text{Sm}_2\text{O}_3$ and 5% $\text{Ru}/\text{Sm}_2\text{O}_3$. Ru foil and RuO_2 were included as references.

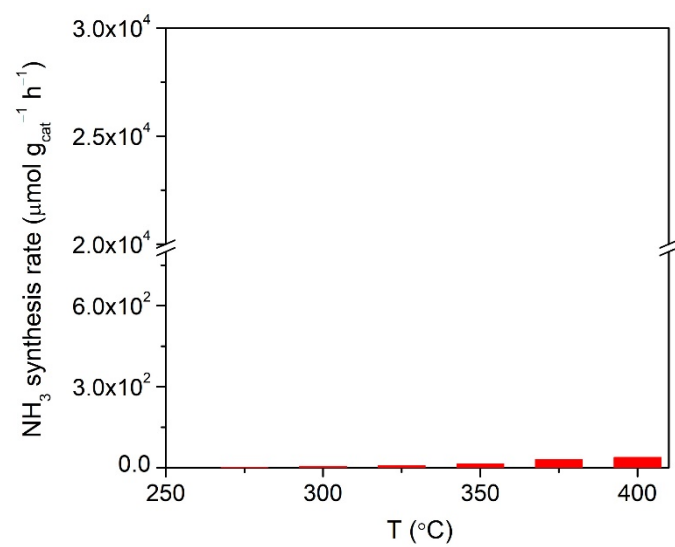


Fig. S9. Catalytic performance of bare Sm₂O₃ support under 1.0 MPa as a function of temperature.

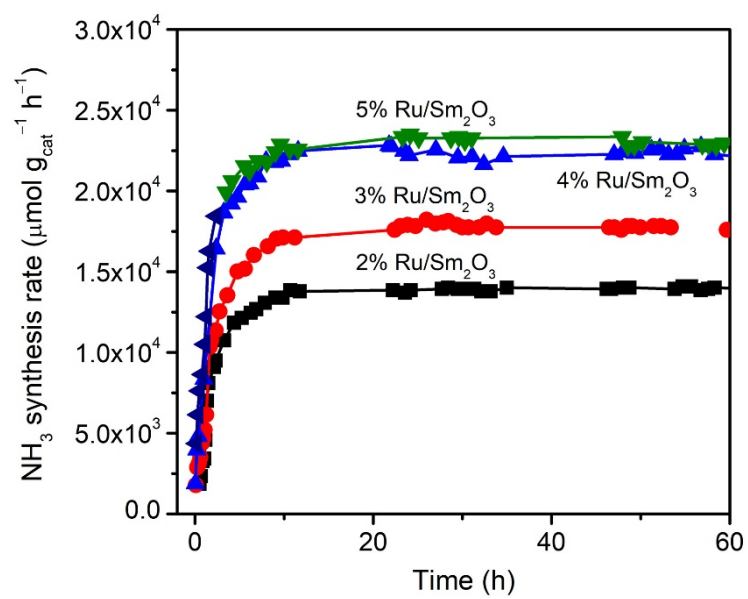


Fig. S10. Catalytic behavior of Ru/ Sm_2O_3 samples at 400 °C under 1.0 MPa as a function of time.

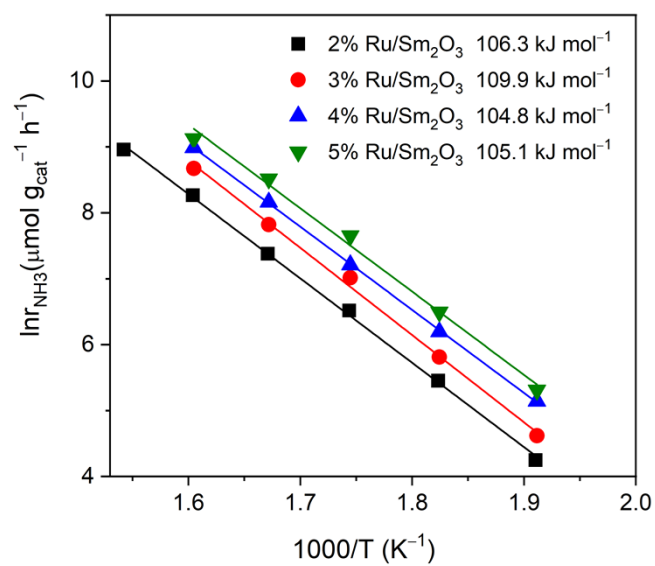


Fig. S11. Arrhenius plots of 2% Ru/ Sm_2O_3 (■), 3% Ru/ Sm_2O_3 (●), 4% Ru/ Sm_2O_3 (▲) and 5% Ru/ Sm_2O_3 (▼).

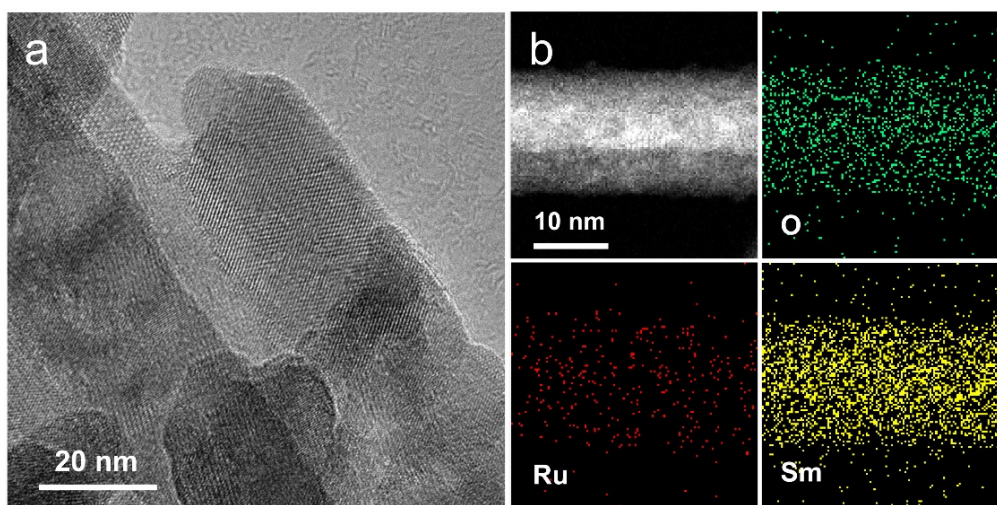


Fig. S12. (a) TEM image of activated 4% Ru/Sm₂O₃ sample. (b) HAADF-STEM image and the corresponding STEM-EDX elemental maps of activated 4% Ru/Sm₂O₃ sample.

References

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