

Ammonia synthesis using a stable electrone as an electron donor and reversible hydrogen store

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Supplementary Methods

Preparation of Ru catalyst on various supports

Ru/ γ -Al₂O₃: γ -Al₂O₃ was heated at 500 °C for 5 h in air. The obtained powder was dispersed in a solution of Ru₃(CO)₁₂ in tetrahydrofuran (THF) for 4 h at room temperature. After evaporation and drying, the sample was heated at 450 °C for 2 h in vacuum and reduced in a stream of H₂ at 400 °C for 4 h.

Ru/CaO, Ru/CaO–Al₂O₃ (CA): CA powders were synthesized by conventional solid-state reaction using a stoichiometric mixture of high purity CaCO₃ and α -Al₂O₃ at 1300 °C for 12 h in air. Ru loading on CA and CaO was achieved using the same

method as that for Ru/C12A7:e⁻.

Cs-Ru/MgO, Ba-Ru/activated carbon (AC): The alkali-promoted catalysts Cs-Ru/MgO and Ba-Ru/AC were prepared according to previous reports^{11,33}. Cs and Ba oxide species deposited near Ru particles on MgO and AC donate electrons to Ru. The Cs-Ru/MgO catalyst was prepared by the following procedure. MgO was heated in high vacuum at 500 °C for 6 h and then dispersed in a solution of Ru₃(CO)₁₂ in THF for 4 h at room temperature. After evaporating the solvent at 40 °C, the obtained powder was slowly heated to 450 °C in high vacuum to decompose the carbonyl precursor. The dark gray powder obtained was dispersed in a solution of Cs₂CO₃ in absolute ethanol by stirring for 3 h, after which the solvent was evaporated and the catalyst was dried in vacuum. The atomic ratio of Cs/Ru in the catalyst was 1.0. The Ba-Ru/AC catalyst was prepared by the following procedure. The AC support was impregnated with a solution of Ru₃(CO)₁₂ in THF in a rotary evaporator at room temperature. After evaporating the solvent at 40 °C, the obtained powder was heated to 450 °C in high vacuum and reduced in a stream of H₂ at 400 °C for 4 h. The promoter was introduced using the wet impregnation method with an aqueous solution of Ba(NO₃)₂ at room temperature. The sample impregnated with the promoter was dried in air at 120 °C for 10 h. The molar ratio of Ba/Ru in the catalyst was 6.2.

Measurement of the electron density of Ru/C12A7:e⁻

An iodometric titration method¹ was used to confirm the presence of electrons and quantify the electron concentration (N_e) in the Ru/C12A7:e⁻ catalyst. Approximately 10 mg of catalyst was dispersed in an aqueous I₂ solution (5.0×10^{-3} M, 3 mL), and then 0.1 mL of HCl was poured into the solution. After confirming complete dissolution of the sample, the amount of residual I₂ was titrated using sodium thiosulfate solution (5.0×10^{-3} M). Observation of the endpoint was enhanced by adding a few drops of starch solution, which induces a violet coloration. The average electron density was obtained from three independent measurements.

Kinetic analysis

The kinetic analyses on Ru/C12A7:e⁻ are based on references published elsewhere^{2,3}. The reaction orders with respect to N₂ and H₂ were obtained at a constant flow rate (60 mL min⁻¹), using Ar gas as a diluent and that for NH₃ was determined with (3H₂+N₂) by changing the synthesis gas flow rate. The constituent gases of the reactant (N₂, H₂, Ar) were as follows in mL min⁻¹: (5, 15, 0), (10, 30, 0), (15, 45, 0), and (20, 60, 0) for NH₃ order; (6, 30, 24), (10, 30, 20), (15, 30, 15), and (20, 30, 10) for N₂ order, (10, 20, 30),

(10, 30, 20), (10, 40, 10), (10, 50, 0) for H₂ order. These analyses were performed for Ru/C12A7:e⁻ and Ru/MgO at 360 °C under 0.1 MPa.

Supplementary Results

Supplementary Table S1: Catalytic performance of Ru catalysts on various supports.

Catalyst	Surface area (m ² g ⁻¹)	Ru loading (wt%) ^a	Dispersion (%) ^b	Particle size (nm) ^b	NH ₃ synthesis rate (μmol g ⁻¹ h ⁻¹) ^c	TOF (s ⁻¹) ^d	TOF (x10 ³ Ru atom ⁻¹ s ⁻¹) ^e	NH ₃ (vol.%) ^f	Ea (kJ mol ⁻¹) ^g
Ru/γ-Al ₂ O ₃	170	6.0	12.5	10.6	51	0.0002	0.02	0.01	64.4
Ru/CaO	3	1.5	4.9	27.2	158	0.006	0.30	0.02	120.1
Ba-Ru/AC	310	1.0	25.2	5.3	148	0.003	0.42	0.02	88.8
	310	9.1	14.3	9.3	2228	0.003	0.69	0.30	72.5
Cs-Ru/MgO	12	1.0	50.3	2.7	2264	0.013	6.36	0.31	85.8
	12	6.0	18.6	7.2	3353	0.008	1.57	0.46	73.0
Ru/C12A7:O ²⁻	1~2	1.2	3.4	39.2	546	0.038	1.28	0.11	104.6
	1~2	0.1	15.6	8.5	715	0.161	25.09	0.10	53.6
Ru/C12A7:e ⁻	1~2	0.3	4.1	32.9	1027	0.274	11.09	0.14	40.0
	1~2	1.2	3.2	41.3	2757	0.197	6.29	0.38	49.1
	1~2	4.0	2.0	68.5	2122	0.076	1.49	0.29	56.0

^aRu content was determined by ICP-AES. ^bDispersion and particle size were calculated on the basis of CO chemisorption values, assuming spherical metal particles and the stoichiometry of Ru/CO = 1. ^cNH₃ synthesis conditions: catalyst (0.2 g), synthesis gas (H₂/N₂ = 3, 60 mL min⁻¹), reaction temperature (400 °C), pressure (0.1 MPa). ^dTOF was calculated from the rate of ammonia synthesis divided by the number of CO atoms chemisorbed on the Ru surfaces. ^eTOF was also calculated from the rate of ammonia synthesis divided by the number of Ru atoms deposited on the catalysts. ^fNH₃ mole fraction in the reactor effluent. ^gEa is the apparent activation energy calculated from Arrhenius plots of the ammonia synthesis rate in the temperature range of 320-400 °C.

Supplementary Table S2: Catalytic performance of various 1 wt% Ru-loaded catalysts under a low reaction temperature.

Catalyst	NH ₃ synthesis rate ($\mu\text{mol g}^{-1} \text{h}^{-1}$) ^a	TOF (s^{-1}) ^b	NH ₃ (vol.%) ^c
Ru/ γ -Al ₂ O ₃	10	4.0×10^{-5}	0.001
Ru/CaO	12	4.6×10^{-4}	0.002
Ba-Ru/AC	14	1.6×10^{-4}	0.002
Cs-Ru/MgO	618	3.5×10^{-3}	0.084
Ru/C12A7:O ²⁻	59	4.1×10^{-3}	0.008
Ru/C12A7:e ⁻	838	6.0×10^{-2}	0.114

^aNH₃ synthesis conditions: catalyst (0.2 g), synthesis gas (H₂/N₂ = 3, 60 mL min⁻¹), reaction temperature (320 °C), pressure (0.1 MPa). ^bTOF was calculated from the rate of ammonia synthesis divided by the number of CO atoms chemisorbed on the Ru surfaces. ^cNH₃ mole fraction in the reactor effluent.

Supplementary Table S3: Orders of reaction for ammonia synthesis over various Ru catalysts^a.

Catalyst	$\alpha(\text{N}_2)$	$\beta(\text{H}_2)$	$\gamma(\text{NH}_3)$	Reference
Ru/C12A7:e ⁻	0.46	0.97	-1.0	this work
Ru/MgO	0.82	-0.38	-0.68	this work
Ru-Cs/MgO	1.0	-1.2	-0.1	(40)
Ru/MgO	0.8	-0.5	-0.6	(13)
Ru-La/MgO	0.85	-0.15	-0.17	(21)
Ru powder	0.96	-0.72	-0.15	(39)
Co ₃ Mo ₃ N	0.99	0.8	-1.34	(41)
Fe(KM1)	0.9	2.2	-1.5	(40)

^a Where the rate expression is $r = kP_{\text{N}_2}^\alpha P_{\text{H}_2}^\beta P_{\text{NH}_3}^\gamma$

Supplementary Table S4: Catalytic performance of used Ru catalysts at 400 °C under pure N₂ atmosphere.

Catalyst	Yield of NH ₃ ($\mu\text{mol g}^{-1}$) ^a
Cs-Ru/MgO	0
Ru/C12A7:e ⁻	15.7

^a This reaction was performed under pure N₂ atmosphere (26.7 kPa) using a closed gas-circulation system [Reaction conditions: catalyst (0.9 g), pressure of N₂ (26.7 kPa), reaction temperature (400 °C), reaction time (6 h)]. Before the reaction, these catalyst was heated in a silica glass flow setup at 400 °C under a pressure of 0.1 MPa (H₂:N₂ = 3:1).

References

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