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Superior catalytic performance of Ru nanoparticles on Cs-loaded MgO superbase in ammonia synthesis

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Experimental Section

Preparation of solid base support

Cs-loaded MgO (Cs–MgO) with different CsOH loading was prepared by impregnation method. The Cs–MgO samples were denoted as xCs–MgO, where x corresponding to the weight ratio of CsOH/MgO in the Cs–MgO samples. For example, 0.1 g of CsOH was dissolved in 3.0 mL of distilled water, which was then mixed with 1.0 g of MgO. The mixture was digested under room temperature for 12 h, and then dried at 80 ºC. Finally, the obtained product was calcined at 600 ºC for 2 h under air atmosphere to get 0.1Cs–MgO.

Preparation of catalysts

The 3% Ru/xCs–MgO samples with Ru mass loading of 3% were prepared by solid milling of support with $Ru_3(CO)_{12}$ powder without use of solvent. The mixture was milled for 10 minutes. After that, the mixture was heated at 300 °C in flowing Ar for 2 h. The obtained catalysts were denoted as 3% Ru/xCs–MgO.

The 3% Ru/MgO samples with Ru mass loading of 3% was also prepared by same method, and used as reference sample for a comparison.

Characterization

Powder X-ray diffraction (XRD) patterns were recorded on an X'Pert Pro (PANAnalytical) diffractometer with Cu Kα radiation.

BET surface area was measured by nitrogen adsorption on a Micromeritics ASAP 2020 apparatus. The surface areas are determined by applying the Brunauer–Emmett–Teller (BET) method.

CO_2 temperature-programmed desorption (CO_2-TPD) measurements were conducted on a Micromeritics 2920 apparatus. Prior to the adsorption of CO_2 at 100 °C, the sample was treated at

400 °C for 2 h in a flow of He. After purging at 100 °C with He for 30 min, the sample was heated to 800 °C at a rate of 10 °C min^{-1}. The amount of CO_2 desorbed from the support was determined by gas chromatograph.

The exposed Ru surface area was measured by CO pulse chemisorption using an automated chemisorption analysis instrument from Altamira (AMI-200). The catalyst was reduced at 450 ºC for 2 h in 10% H_2 (balance with Ar) prior to the pulse CO chemisorption measurement, and then cooled down to room temperature in He. CO pulses were introduced to the sample and the CO uptake was measured using a TCD detector. The Ru dispersion was calculated assuming a CO:Ru stoichiometry of 1:1.

The morphologic characterization was performed on a JEOL 2100X transmission electron microscope.

X-ray photoelectron spectroscopy (XPS) was performed with an ESCALAB MK-II spectrometer (VG Scientific Ltd., UK) using Al Kα radiation (1486.6 eV). Charging effects were corrected by the C1s binding energy of 284.8 eV.

Catalytic performance measurement

Ammonia synthesis reaction was carried out in a fixed-bed stainless reactor. In a typical experiment, 50 mg of 3% Ru/xCs–MgO powder (20–40 mesh) was loaded into a stainless-steel reactor with an inner diameter of 9 mm. The sample was heated to 450 °C at a rate of 5 °C min^{-1} in a flow of 75% H_2/N_2 mixture (gas hourly space velocity: 24,000 mL g_{cat}^{-1} h^{-1}) under pressure of 1.0 MPa, and kept at 450 °C for 4 h. Then, the temperature of the reactor was changed to a designated temperature in the 75% H_2/N_2 mixture for activity test. The ammonia in an outlet gas was trapped with 5 mM H_2SO_4 aqueous solution, and the concentration of NH_4^+ in H_2SO_4 aqueous solution was determined with a conductivity detector.

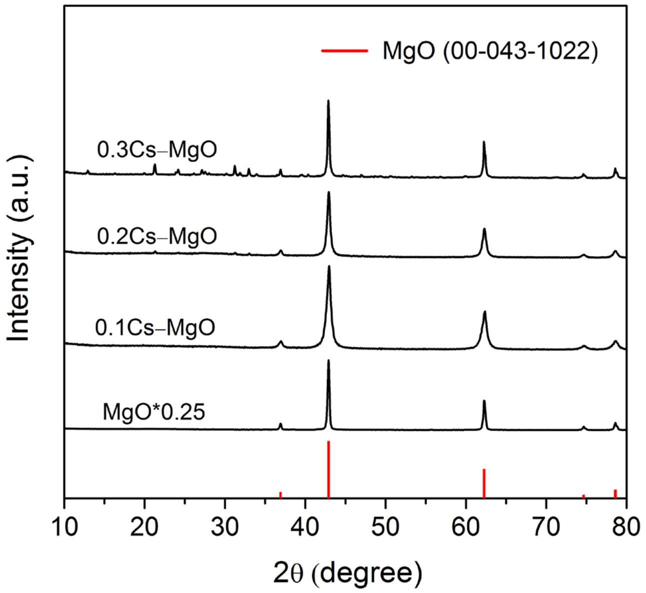

Fig. S1 XRD patterns of MgO, 0.1Cs–MgO, 0.2Cs–MgO and 0.3Cs–MgO.

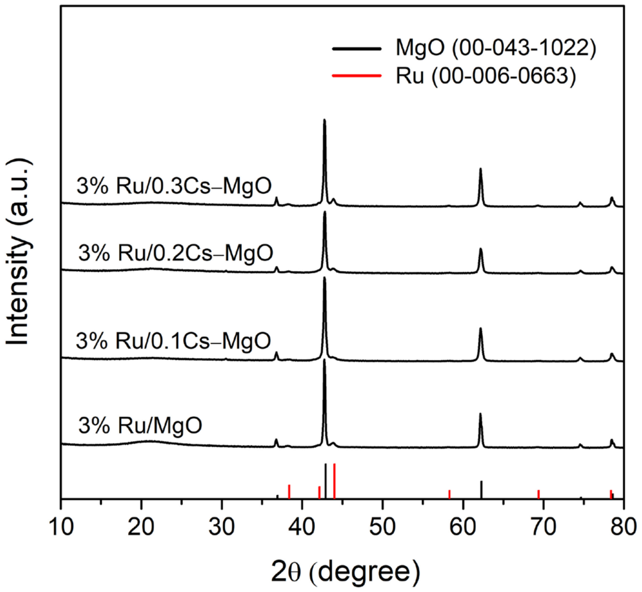

Fig. S2 XRD patterns of 3% Ru/MgO, 3% Ru/0.1Cs–MgO, 3% Ru/0.2Cs–MgO and 3% Ru/0.3Cs–MgO.

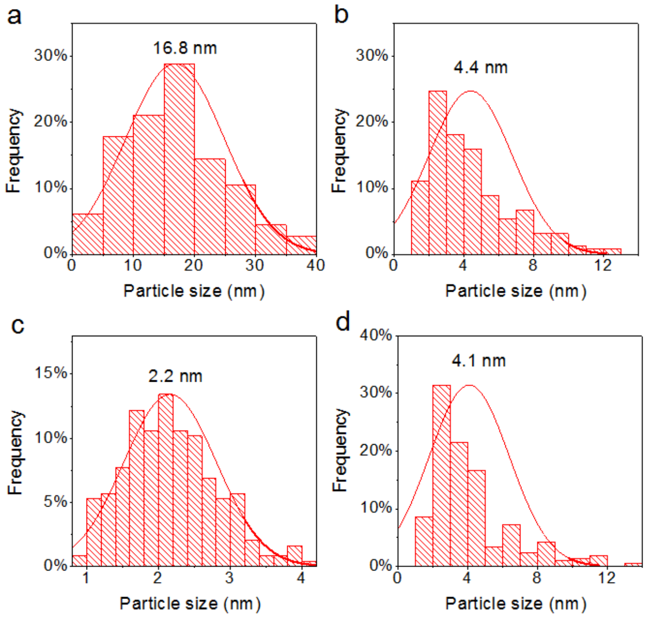

Fig. S3 Ru particle size distributions of 3% Ru/MgO (a), 3% Ru/0.1Cs–MgO (b), 3% Ru/0.2Cs–MgO (c) and 3% Ru/0.3Cs–MgO (d).

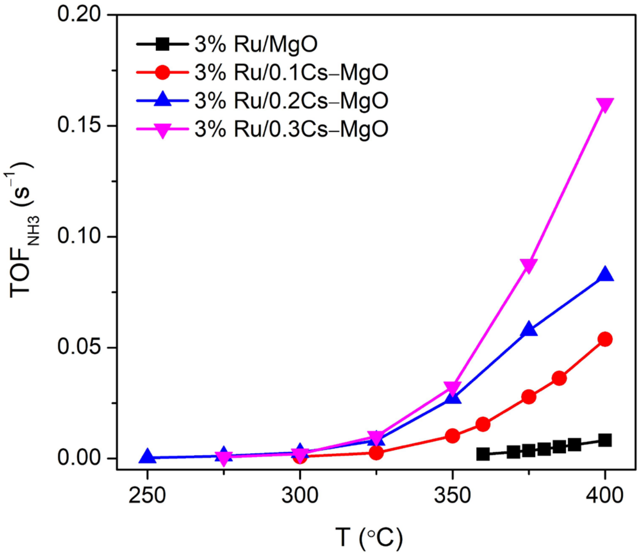

Fig. S4 TOF$_{NH3}$ of 3% Ru/MgO and 3% Ru/xCs–MgO under 1.0 MPa as a function of temperature.

Table S1 Properties of 3% Ru/xCs–MgO and 3% Ru/MgO samples.

Sample	Peak temperature (°C)	Adsorption of CO_2 (μmol g^{-1})	Surface area (m^2 g^{-1})	Density of basic sites (μmol m^{-2})
3% Ru/MgO	130	620.5	15.3	40.6
	393	934.7		61.1
3% Ru/0.1Cs–MgO	147	719.6	56.7	12.7
	496	1456.9		25.7
	640	1495.4		26.4
3% Ru/0.2Cs–MgO	90	668.7	23.2	28.8
	473	1080.7		46.6
	703	2035.5		87.7
3% Ru/0.3Cs–MgO	128	434.4	15.4	28.2
	365	1275.7		82.8
	805	2622.3		170.3

Table S2 Properties of 3% Ru/xCs–MgO and 3% Ru/MgO samples.

Sample	Ru particle size by TEM (nm)	Metal dispersion by CO chemisorption (%)	Ru particle size by CO chemisorption (nm)
3% Ru/MgO	16.8	21.9	5.1
3% Ru/0.1Cs–MgO	4.4	33.1	3.4
3% Ru/0.2Cs–MgO	2.2	24.4	4.6
3% Ru/0.3Cs–MgO	4.1	10.0	11.2

Table S3 Activities of various Ru–Cs/MgO catalysts.

Sample	Ru content (wt%)	Temperature (°C)	Pressure (MPa)	WHSV (ml g_{cat}^{-1} h^{-1})	Ammonia synthesis rate (μmol g_{cat}^{-1} h^{-1})	Reference
Ru/0.2Cs–MgO	3	400	1	24000	21504	This work
Ru–Cs/MgO	6	400	1	18000	12117	Nat. Chem., 2012, 4, 934-940.
Ru–Cs/MgO	1	400	5	66000	2740	Advanced Energy Materials, 2018, 8, 1801772.
Ru–Cs/MgO	1	400	0.1	18000	2260	ACS Catal., 2017, 7, 2313-2324.
Ru–Cs/MgO	6	400	0.1	18000	3350	
Ru–Cs/MgO	4	400	1	18000	10530	Catal. Sci. Technol., 2017, 7, 191-199.
Ru–Cs/MgO	4	390	1	18000	1500	RSC Adv., 2016, 6, 51106-51110.
Cs–Ru/MgO (111)	3.7	400	0.9	36000	24200	ACS Catal., 2020, 10, 5614-5622.
Cs–Ru/MgO (110)	3.5	400	0.9	36000	12000	
Cs–Ru/MgO (100)	3	400	0.9	36000	6800	