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Electronic supplementary information

# Efficient ammonia synthesis over Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub> pre-reduced at high temperature

Yuta Ogura,<sup>1</sup> Katsutoshi Sato,<sup>1,2</sup> Shin-ichiro Miyahara,<sup>1</sup> Yukiko Kawano,<sup>1</sup> Takaaki Toriyama,<sup>3</sup> Tomokazu Yamamoto,<sup>4</sup> Syo Matsumura,<sup>3,4</sup> Saburo Hosokawa,<sup>2</sup> and Katsutoshi Nagaoka<sup>1</sup>\*

- <sup>[1]</sup> Department of Integrated Science and Technology, Faculty of Science and Technology, Oita University, 700 Dannoharu, Oita 870-1192, Japan
- Elements Strategy Initiative for Catalysts and Batteries, Kyoto University, 1-30
   Goryo-Ohara, Nishikyo-ku, Kyoto 615-8245, Japan
- <sup>[3]</sup> The Ultramicroscopy Research Center, Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan
- <sup>[4]</sup> Department of Applied Quantum Physics and Nuclear Engineering, Kyushu University,
   Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan

#### 1. Details of experimental methods

#### Catalyst preparation

The La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub> support was prepared at room temperature by means of a co-precipitation method from a suspension formed by the addition of a solution containing La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Wako Pure Chemical, Japan) and Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Kanto Chemical, Japan) to a 28 wt % ammonia solution (Wako). The precipitate was held in the suspension for at least 1 h with stirring and was then filtered, washed with distilled water, dried at 80 °C for at least a half day, and calcined at 700 °C in static air for 5 h. The CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, Pr<sub>6</sub>O<sub>11</sub>, and MgO supports were prepared by precipitation at room temperature from the corresponding nitrates in a manner similar to that described for the La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub> support. Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Kanto Chemical) and Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Wako) were used as precursors for Pr<sub>6</sub>O<sub>11</sub> and MgO, respectively.

All of the supports were impregnated with  $Ru_3(CO)_{12}$  (Furuya Metal, Japan) in tetrahydrofuran (THF, Wako). The Ru loading was fixed at 5 wt % for each catalyst. A THF suspension containing  $Ru_3(CO)_{12}$  and the support was stirred for 12 h, and then the solvent was removed by rotary evaporation. The obtained powder was kept at 80 °C for 18 h under air and then heated to 500 °C under an Ar stream and kept at that temperature for 5 h to remove the CO ligand from the  $Ru_3(CO)_{12}$ . Doping of Ru/MgO with  $Cs_2O$  was carried out as described previously.<sup>S1</sup> In addition, Ru/MgO was impregnated with  $Cs_2CO_3$  (Wako) in absolute ethanol (Wako) as follows. A suspension of  $Cs_2CO_3$  and MgO in ethanol was stirred for 3 h, and then the solvent was removed by rotary evaporation. The obtained powder was kept under a vacuum for 18 h. The Cs/Ru atomic ratio was fixed at 1.0.

#### Ammonia-synthesis activity tests

Ammonia-synthesis rates were measured with a conventional flow system under either atmospheric pressure or high pressure, as described previously.<sup>S2</sup> Briefly, powdered catalysts

were pressed into pellets at 20 MPa for 5 min, crushed, and sieved to grains with diameters of 250–500  $\mu$ m. A tubular Inconel reactor (i.d. = 7 mm) was packed with quartz wool, and then 100 mg of catalyst was added. Research-grade gases (>99.99%) were supplied from high-pressure cylinders without further purification. On the other hand, only for long-term test, inline gas purifier (MicroTorr MC50-904FV, SAES Pure Gas, USA) was used, and then concentration of impurities (H<sub>2</sub>O, O<sub>2</sub>, CO<sub>2</sub>) in gas mixture was reduced to below 100 ppt. The catalysts were reduced in a flow of pure H<sub>2</sub> (60 NmL min<sup>-1</sup>) at 450, 500, 650, or 800 °C for 1 h at 0.1 MPa and then cooled to 300 °C in an Ar stream. After the pressure was adjusted to 0.1, 0.5, 1.0, or 3.0 MPa at 300 °C, a 3:1 (mol/mol) H<sub>2</sub>/N<sub>2</sub> mixture (space velocity = 72,000 NmL h<sup>-1</sup> g<sup>-1</sup>) was fed to the catalyst. The temperature of the catalyst was then heated to 400 °C in 25 °C increments. The ammonia-synthesis rate was determined from the rate of decrease of electron conductivity (CM-30R, DKK-TOA, Japan) of a dilute sulfuric acid solution (1–100 M) used to trap the ammonia produced under the reaction conditions.

#### Kinetic analysis

Reaction kinetics were analyzed by a reported method.<sup>S3,S4</sup> In brief, the reaction orders with respect to the N<sub>2</sub>, H<sub>2</sub>, and NH<sub>3</sub> were determined by measuring N<sub>2</sub>, H<sub>2</sub>, and NH<sub>3</sub> pressure dependence for the ammonia-synthesis rates with the assumption of the rate expression (1). Equations (2) to (5) were also used for these analyses.

$$r = kP_{N_2}^{n}P_{H_2}^{h}P_{NH_3}^{a} \quad (1)$$

$$r = \frac{(1/w)dy_{o}}{d(1/q)} \quad (2)$$

$$\log y_{o} = \log\left(\frac{C}{q}\right)^{\frac{1}{m}} \quad (3)$$

$$r = \left(\frac{1}{w}\right) \left(\frac{C}{m}\right) y_0^{(1-m)} \qquad (4)$$
$$C = k_2 P_{\rm H_2}^h P_{\rm N_2}^n \qquad (5)$$

*r*, *w*,  $y_0$ , *q*, *C*, and (1-*m*) denotes ammonia-synthesis rate, catalyst mass, ammonia mole fraction at the reactor outlet, flow rate, constant and *a*. Kinetic analyses were performed at 350 °C and 0.1 MPa. Other reaction conditions are described in Table S1 and Fig S1. To avoid the contribution of the reverse reaction, kinetic measurements were carried out at a GHSV value where the ammonia concentration at the reactor exit was far away from the thermodynamic equilibrium concentration.

#### Characterisation of the supported Ru catalysts

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and energy dispersive X-ray (EDX) elemental maps were obtained with a JEM-ARM200CF electron microscope (JEOL, Japan) operated at 120 or 200 kV. Electron energy loss spectroscopy was performed at an acceleration voltage of 80 kV to reduce damage to the sample by the electron beam. For STEM and electron energy loss spectroscopy, powdered catalyst samples reduced in a quartz reactor at 650 °C under a H<sub>2</sub> flow were crushed and deposited on TEM grids coated with a thin carbon film in a glove box. The samples thus prepared were transferred from the glove box to the inside of the TEM column without being exposed to the air by means of a special holder with a gas cell. For other measurements, samples were dispersed in ethanol under ambient conditions, and the dispersion was dropped onto a carbon-coated copper grid and then dried under a vacuum at ambient temperature for 24 h.

X-ray diffraction (XRD) analysis was performed with a SmartLab X-ray diffractometer (Rigaku, Japan) equipped with a Cu K $\alpha$  radiation source. For *in situ* measurements, the sample was

placed in a reactor chamber (XRK 900, Anton Parr, Austria) and heated at 500 or 650 °C for 1 h under a stream of H<sub>2</sub> or a stream of 1:4 (v/v)  $O_2/N_2$ , and then the diffraction patterns were observed at 500 or 650 °C under the corresponding gas stream. PDXL2 software (Rigaku) with ICDD, COD,<sup>S5</sup> and AtomWork<sup>S6</sup> databases was used to analyse the XRD patterns

The specific surface areas of the catalysts after  $N_2$  treatment at 300 °C were determined by the Brunauer–Emmett–Teller method using a BELSORP-mini instrument (BEL Japan Inc., Japan).

 $H_2$  chemisorption capacity was measured to estimate the Ru dispersion of the catalysts.  $H_2$  was fed to each sample at 60 NmL min<sup>-1</sup>, and the temperature was increased from room temperature to 500, 650, or 800 °C. The sample was maintained at the desired temperature for 1 h in the  $H_2$ flow and was then purged with a stream of Ar for 30 min, cooled to -78 °C, and flushed with Ar for 60 min. After this pretreatment,  $H_2$  chemisorption analysis was carried out at -78 °C in an Ar stream (60 NmL min<sup>-1</sup>) by means of a pulsed-chemisorption technique.

The  $O_2$  absorption capacity of the catalyst, which is a measure of the degree of catalyst reduction, was measured by means of a pulse injection method. The amount of  $O_2$  absorbed on the reduced catalyst was sequentially measured at 25, 450, and 800 °C as follows. A catalyst sample (200 mg) was reduced *in situ* at 500, 650, or 800 °C for 1 h, kept in Ar at corresponding temperature for 30 min and then cooled to room temperature under Ar. At the temperature, pulses of pure  $O_2$  (124 µmol/pulse) were injected into the catalyst bed until the level of  $O_2$  detected by a thermal conductivity detector stabilised, an indication that the maximum amount of  $O_2$  had been adsorbed on the catalyst. After the  $O_2$  absorption measurement, the catalyst was heated to 450 °C in an Ar flow, and  $O_2$  absorption at 450 °C was again measured by means of the above-described method. In addition, each catalyst was heated to 800 °C in an Ar flow, and

O<sub>2</sub> absorption at 800 °C was measured by the same method.

Infrared spectra of adsorbed N<sub>2</sub> were measured with a spectrometer (FT/IR-6600, JASCO, Japan) equipped with a mercury–cadmium–tellurium detector at a resolution of 4 cm<sup>-1</sup> as described previously.<sup>S2</sup> Samples (~20 mg) were pressed into self-supporting disks (10 mm in diameter). Each disk was placed in a silica-glass cell equipped with CaF<sub>2</sub> windows and was then connected to a closed gas-circulation system. The disk was pretreated with circulated H<sub>2</sub> (80 kPa) that had been passed through a liquid N<sub>2</sub> trap. The disk was heated from room temperature to 500 or 650 °C and then kept at that temperature for 1 h. After the reduction, the cell containing the disk was evacuated at the same temperature for 0.5 h to remove the H<sub>2</sub>. After this pretreatment, the disk was cooled to room temperature under a vacuum. Pure N<sub>2</sub> (>99.9995%) was supplied to the system via a liquid N<sub>2</sub> trap. <sup>15</sup>N<sub>2</sub> (98%) was used without purification. The infrared spectrum of the sample at room temperature before N<sub>2</sub> adsorption was used as the background, and difference spectra were obtained by subtracting the background spectra from the spectra of the samples containing adsorbed N<sub>2</sub>.

## 2. Supporting Results



Fig. S1. Graphs for estimating reaction orders over  $Ru/La_{0.5}Ce_{0.5}O_{1.75}_{-650}$  and  $Cs^+/Ru/MgO_500$  red at 350 °C and 0.1 MPa. (a) and (d) N<sub>2</sub>. (b) and (e) H<sub>2</sub>. (c) and (f) NH<sub>3</sub>. Figs (a)-(c) are for  $Ru/La_{0.5}Ce_{0.5}O_{1.75}_{-650}$  red; and figs (d)-(f) are for  $Cs^+/Ru/MgO_500$  red.

# Table S1. Reaction conditions and ammonia-synthesis rates for kinetic analyses over

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Weight		J	Flow rate GHSV NH <sub>3</sub> synt		NH <sub>3</sub> synthesis rate	Yield/Yield Eq.	Orders	
(mg)		$(NmL min^{-1})$		$(NL h^{-1}g^{-1})$	$(mmol h^{-1} g^{-1})$	(-)		
		$N_2$	$\mathrm{H}_{2}$	Ar	-			
5.0	for N <sub>2</sub>	24	120	96	2,880	18.75	0.04	
		40	120	80	2,880	23.79	0.03	0.76
		60	120	60	2,880	30.64	0.04	<i>(n)</i>
		80	120	40	2,880	36.41	0.05	
	for H <sub>2</sub>	40	80	120	2,880	32.16	0.06	
		40	120	80	2,880	33.22	0.04	0.15
		40	160	40	2,880	33.22	0.04	(h)
		40	200	0	2,880	36.05	0.05	
	for NH <sub>3</sub>	20	60	0	960	20.91	0.05	
		40	120	0	1,920	25.24	0.03	-0.36
		60	180	0	2,880	27.76	0.02	<i>(a)</i>
		80	240	0	3,840	30.28	0.02	

Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub>\_650red

Cs<sup>+</sup>/Ru/MgO\_500red

Weight		Flow rate		GHSV	NH <sub>3</sub> synthesis rate	Yield/Yield_Eq.	Orders	
(mg)		(NmL min <sup>-1</sup> )		$(NL h^{-1}g^{-1})$	$(\text{mmol } h^{-1} g^{-1})$	(-)		
		$N_2$	$\mathrm{H}_{2}$	Ar	-			
50.0	for N <sub>2</sub>	24	120	96	288	4.09	0.09	
		40	120	80	288	7.07	0.09	1.07
		60	120	60	288	9.67	0.12	<i>(n)</i>
		80	120	40	288	12.64	0.16	
	for H <sub>2</sub>	40	80	120	288	8.24	0.16	
		40	120	80	288	6.67	0.09	-0.76
		40	160	40	288	5.38	0.07	<i>(h)</i>
		40	200	0	288	4.52	0.06	
	for NH <sub>3</sub>	20	60	0	96	6.32	0.16	
		40	120	0	192	7.44	0.10	-0.15
		60	180	0	288	7.81	0.07	<i>(a)</i>
		80	240	0	384	7.44	0.05	



Fig. S2. Time course of ammonia formation rate over Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub>\_650red with and without using gas purifier. Reaction conditions: catalyst, 100 mg; synthesis gas,  $H_2/N_2 = 3$  with a flow rate of 120 NmL min<sup>-1</sup>; pressure, 3.0 MPa; reaction temperature, 350 °C. When inline gas purifier is used, concentration of impurities (H<sub>2</sub>O, O<sub>2</sub>, CO<sub>2</sub>) in gas mixture is reduced to below 100 ppt.

Ammonia-synthesis rate of Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub>\_650red was stable for 50 h when inline gas purifier was used. On the other hand, the rate decreased gradually without using gas purifier, indicating that the impurities in the  $H_2/N_2$  mixture degraded the catalyst.



Fig. S3. HAADF-STEM images of Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub>\_650red without exposure to air.



Fig. S4. Ammonia-synthesis rates over Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub>\_500red, Ru/CeO<sub>2</sub>\_500red, and Ru/La<sub>2</sub>O<sub>3</sub>\_500red. Reaction conditions: catalyst, 100 mg; pre-reduction temperature, 500 °C, reactant gas, 3:1 H<sub>2</sub>/N<sub>2</sub> at a flow rate of 120 NmL min<sup>-1</sup>; pressure, 1.0 MPa; temperature, 350 °C.



Fig. S5. XRD patterns of fresh Ru/La<sub>2</sub>O<sub>3</sub> (red), fresh Ru/CeO<sub>2</sub> (green), and fresh Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub> (black).  $\Diamond$ , LaOOH;  $\blacksquare$ , La(OH)<sub>3</sub>;  $\checkmark$  La<sub>2</sub>O<sub>3</sub>;  $\bigcirc$ , CeO<sub>2</sub>.



Fig. S6. Lattice constants as a function of La/(Ce + La) molar ratios for fresh  $Ru/La_yCe_{1-y}O_{2-0.5y}$  ( $0 \le y \le 0.5$ ). Lattice constants were calculated by assuming a cubic fluorite structure and using the *d* value of the (311) plane.

Catalyst	Reduction	Specific surface	H/Ru <sup>a</sup>	Mean Ru	NH <sub>3</sub> -synthesis rate at
	temperature	area		particle size <sup>b</sup>	350 °C and 1.0 MPa
	(°C)	$(m^2 g^{-1})$	(-)	(nm)	$(\text{mmol g}^{-1} \text{ h}^{-1})$
Ru/La <sub>2</sub> O <sub>3</sub>	500	18	0.13	7.8	10.6
Ru/CeO <sub>2</sub>	500	24	0.27	2.4	12.8
Ru/CeO <sub>2</sub>	650	20	0.17	3.1	17.2

Table S2. Physicochemical properties and catalytic performances of supported Ru catalysts

 $^{a}$  Estimated from the H<sub>2</sub> chemisorption capacity.

<sup>b</sup> Estimated from the STEM images shown in Fig. S9.



Fig. S7. O<sub>2</sub> absorption capacity of Ru/La<sub>2</sub>O<sub>3</sub>\_500red, Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub>\_500red, Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub>\_650red, and Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub>\_800red. After the catalysts were pre-reduced at the specified temperature, O<sub>2</sub> absorption was measured sequentially at room temperature (r.t.), 450 °C, and 800 °C.

To estimate the degree of reduction of  $Ce^{4+}$  to  $Ce^{3+}$  in the Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub> after pre-reduction, we determined the O<sub>2</sub> absorption capacity of the reduced catalysts by pulsing O<sub>2</sub> into the catalyst bed first at 25 °C and then sequentially at 450 and 800 °C. The O<sub>2</sub> absorption capacities and calculated values for the degree of reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup> are shown in Fig. S7 and Table 1, respectively. Note that mass spectroscopic analysis of the exit gas did not reveal any other products (such as H<sub>2</sub>O) during the experiments. At room temperature, Ru/La<sub>2</sub>O<sub>3</sub>\_500red adsorbed O<sub>2</sub> at 107 µmol g<sup>-1</sup>. After the initial O<sub>2</sub> absorption measurement, the catalyst was heated to 450 °C in Ar and then exposed to another O2 pulse. During the second exposure,  $O_2$  adsorption was 361  $\mu$ molg<sup>-1</sup>. Finally, the catalyst was heated to 800 °C in Ar and again exposed to O2 pulses. During this third exposure, only trace amounts of O2 (4.43 µmol  $g^{-1}$ ) were taken up. The total O<sub>2</sub> absorption capacity of Ru/La<sub>2</sub>O<sub>3</sub>\_500red was nearly equal to the theoretical amount of  $O_2$  uptake for oxidation of Ru to RuO<sub>2</sub> (495 µmol g<sup>-1</sup>). These results indicate that only the Ru atoms near the surface of large Ru particles (mean diameter, 7.8 nm) were oxidised at room temperature and that the Ru atoms in the bulk were not oxidised until the temperature reached 450 °C. In contrast, at room temperature, Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub>\_500red took up more O<sub>2</sub> than the amount required for oxidation of Ru. These results indicate that some of the  $Ce^{4+}$  in  $La_{0.5}Ce_{0.5}O_{1.75}$  was reduced to  $Ce^{3+}$  during pre-reduction with H<sub>2</sub> and that oxidation of La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75-x</sub> increased the amount of O<sub>2</sub> absorption at room temperature. During the O<sub>2</sub> absorption measurements at 450 and 800 °C, only trace amounts of O2 were taken up. These results demonstrate that Ru and La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75-x</sub> were nearly fully oxidised to RuO<sub>2</sub> and La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub> at room temperature and that the resulting material was thermally stable. Total O<sub>2</sub> absorption capacity increased as the pre-reduction temperature of Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub> was increased from 500 to 800 °C, an indication that the degree of reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup> increased with increasing pre-reduction temperature. Assuming that complete oxidation to  $La_{0.5}Ce_{0.5}O_{1.75}$  and RuO<sub>2</sub> occurred, the values of the degree of reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup> after pre-reduction at 500, 650, and 800 °C were determined to be 23%, 43%, and 63%, respectively.



**Fig. S8. STEM images and EDX maps for Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub>\_500red, \_650red and \_800red.** (a)–(c) STEM images. (d)–(f) Reconstructed overlay EDX maps of Ru-L (green), La-L (red), and Ce-L (blue). (g)–(i) Ru particle size distributions. Panels (a), (d), and (g) are for Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub>\_500red; panels (b), (e), and (h) are for Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub>\_650red; and panels (c), (f), (i) are for Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub>\_800red.



**Fig. S9. STEM images and EDX maps of supported Ru catalysts.** (a)–(c) STEM images. (d)–(f) Reconstructed overlay EDX maps of Ru-L (green), La-L (red), and Ce-L (blue). (g)–(i) Ru particle size distributions. Panels (a), (d), and (g) are for Ru/La<sub>2</sub>O<sub>3</sub>\_500red; panels (b), (e), and (h) are for Ru/CeO<sub>2</sub>\_500red; and panels (c), (f), (i) are for Ru/CeO<sub>2</sub>\_650red.



Fig. S10. In situ XRD patterns for Ru/La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub> after various treatments. (a) In situ XRD patterns measured after treatment of the catalyst in a flow of H<sub>2</sub> or air at 500 or 650 °C for 1 h (b) Detail showing diffraction peaks of the (311) plane. (c) Temperature dependence of the lattice constant calculated by assuming cubic fluorite structure using the *d* value of the (311) plane. The dotted line indicates the lattice constant of La<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>1.75</sub> measured at room temperature in an air flow.

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## 4. Author contributions

K.N. directed and conceived this project. K.S. coordinated the experimental work. O.Y., S. Miyahara, and Y.K. prepared the catalysts, carried out several characterisations, and measured the catalyst activities. T.T., T.Y., and S. Matsumura conducted HAADF-STEM observations and measured EEL and EDX spectra. S.H. conducted the XRD analysis. All the authors discussed the results and commented on the study. O.Y., K.S., and K.N. co-wrote the manuscript.