

Supporting information

Effect of the ruthenium precursor on the low-temperature ammonia synthesis activity over Ru/CeO₂

Yuichi Manaka,^{*ab} Yuki Nagata,^{ac} Keisuke Kobayashi,^a Daisuke Kobayashi^c and Tetsuya Nanba^{*a}

^a *Renewable Energy Research Center, National Institute of Advanced Industrial Science and Technology, 2-2-9 Machiikedai, Koriyama, Fukushima, 963-0298 JAPAN*

E-mail: Yuichi.manaka@aist.go.jp, tty-namba@aist.go.jp

^b *School of Material and Chemical Technology, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa, 226-8502 JAPAN*

^c *Department of Applied Chemistry, Tokyo Denki University, 5 Senju-Asahicho, Adachi-ku, Tokyo 120-8551, JAPAN*

Catalyst preparation

CeO₂ (167 m²/g) was purchased from Daiichi-Kigenso. Ru(NO₃)₃, Ru(NH₃)₆Cl₃, and RuCl₃ were purchased from TANAKA KIKINZOKU KOGYO K.K. Na₂RuO₄, Ru(dpm)₃, Ru(acac)₃, and Ru₃(CO)₁₂ were purchased from Furuya Metal Co., Ltd. Ru(NO)(NO₃)₃ was purchased from Strem Chemicals, Inc. [Ru(OH)(NO)(NH₃)₄](NO₃)₂ was purchased from N.E. CHEMCAT. All chemicals were used as received without further purification.

The Ru precursors were diluted with water or ethanol (for Ru(acac)₃ and Ru(dpm)₃) or THF (for Ru₃(CO)₁₂) to ensure that the CeO₂ support was immersed in a volume of Ru solution twice as large as the support void volume (the concentration of Ru was adjusted to 1wt% loading). Ru was loaded on CeO₂ via the incipient wetness method. Ru/CeO₂ was dried overnight at 100 °C. Ru/CeO₂ was calcined using a tubular furnace under a 10% H₂ stream at 300 °C for 1 h. The calcined Ru/CeO₂ was sized to a particle size of 150–250 μm.

Catalytic reaction

The catalytic activity was measured in a fixed-bed flow reactor. A portion of the catalyst (0.2 g) was set on quartz glass wool in the middle of the reactor, and the thermocouple was set up in the catalyst bed. Pretreatment was performed under a 30 mL/min flow of H₂ gas and 10 mL/min of N₂ gas at 600 °C for 30 min. Ammonia production was measured under atmospheric pressure conditions between 300 and 600 °C. An H₂/N₂ gas ratio of 3 and an SV 40,000 h⁻¹ were employed. To carry out measurements in the steady state, the amount of ammonia produced was measured 90 min after each reaching the measurement temperature. The product gases were analysed by FT-IR spectrophotometry (Nicolet iS50 FT-IR spectrophotometer, Thermo Fisher Scientific) with a multi-reflection gas cell (optical path length = 2.4 m, measured wavelength = 4000 to 600 cm⁻¹, interval = 0.5 cm⁻¹). The NH₃ concentration was quantified using the calibration curve prepared with standard gas. The FT-IR absorbance band at 1122 cm⁻¹ represented the peak of NH₃. Because the amount of Ru differs for each catalyst, the ammonia concentration was calculated in units of (1 wt% Ru, 2.0 g). The reproducibility of the catalytic reaction was confirmed, as shown in Fig. S4.

Characterization

Nitrogen adsorption-desorption measurements were performed at -196 °C using a BELSORP-mini II instrument (Microtrac BEL). The samples were degassed under vacuum at 100 °C for 3 h prior to measurement. The pore size distributions were calculated using the Brunauer–Joyner–Halenda (BJH) method, and the specific surface areas of the samples were estimated using the Brunauer–Emmett–Teller (BET) method. Pulse CO chemisorption measurements were performed using a ModelR6015H instrument (Ohkura Riken). O₂ gas at 400 °C was employed for the oxidation process, and H₂ gas at 600 °C was employed for the reduction process. The CO/Ru ratio was calculated using the following equation:

$$\text{CO/Ru (\%)} = \text{adsorbed CO amount (mol)} / \text{loaded Ru amount (mol)} \times 100$$

H₂-temperature-programmed reduction (TPR) measurements were performed using a handmade setup with a JMS-MT3010HRGA INFITOF instrument (JEOL Ltd.) using a catalyst loading of 0.15 g. For oxidising pretreatment, a flow of 10% O₂/He gas was used at 200 °C for 1 h. For measurement, a flow of 1% H₂/He

was employed between -70 and 900 °C at a heating rate of 10 °C min^{-1} . X-ray diffraction (XRD) patterns were recorded on a RINT Ultima+ instrument (RIGAKU) with $\text{CuK}\alpha$ radiation at 45 keV and 200 mA.

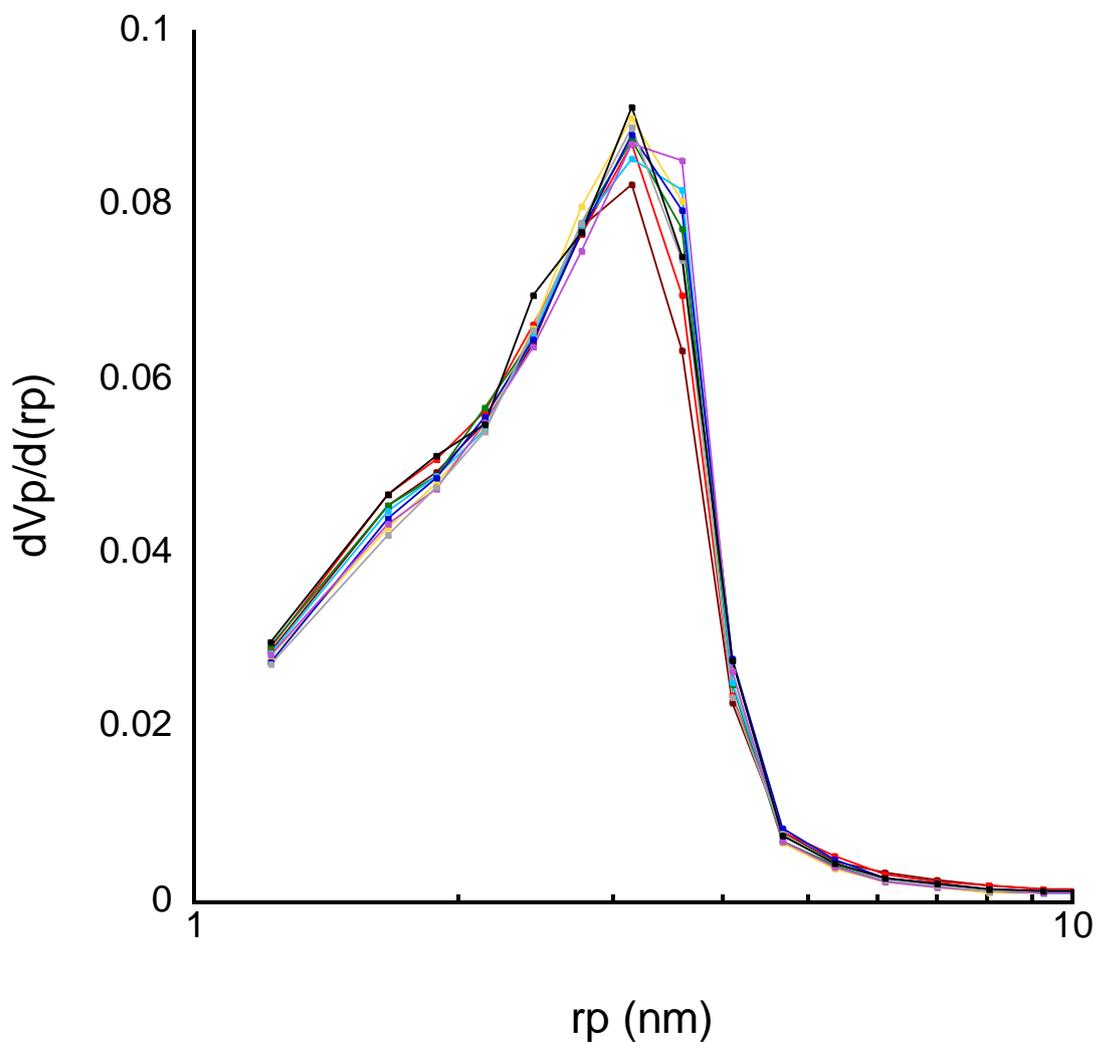


Fig. S1. BJH plot of each of the Ru/CeO₂ catalysts calculated using the adsorption-desorption method. Different precursors are indicated by the differently colored lines: Brown: Ru(NO)(NO₃)₃, Red : Ru(acac)₃, Yellow: Ru(CO)₁₂, Green: Ru(dpm)₃, Pale blue: [Ru(OH)(NO)(NH₃)₄](NO₃)₂, Blue: Ru(NO₃)₃, Purple: RuCl₃, Gray: Ru(NH₃)₆Cl₃, Black: CeO₂. Measurement conditions are described in the experimental section.

Table S1. Properties of Ru/CeO₂ catalysts

Ru precursor	Pore volume (cm ³ /g)	Pore radius (nm)	S _{BET} / (m ² /g)
Ru(NO)(NO ₃) ₃	0.24	5.9	162
Ru(acac) ₃	0.25	6.0	167
Ru(CO) ₁₂	0.24	5.7	166
Ru(dpm) ₃	0.24	5.7	169
[Ru(OH)(NO)(NH ₃) ₄](NO ₃) ₂	0.24	5.8	165
Ru(NO ₃) ₃	0.24	6.0	162
RuCl ₃	0.24	5.8	165
Ru(NH ₃) ₆ Cl ₃	0.24	5.9	163
- (CeO ₂)	0.24	5.8	167

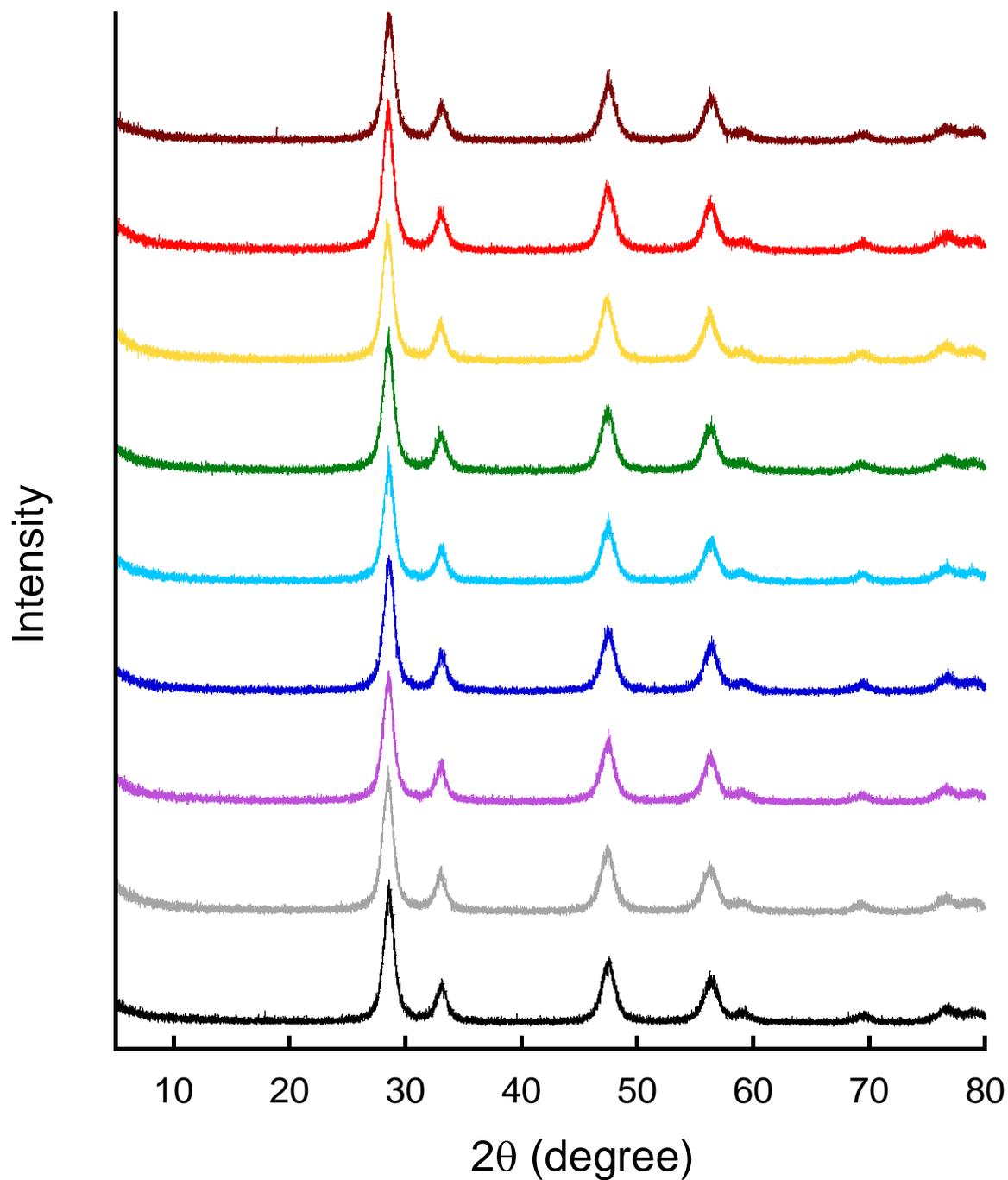


Fig. S2. XRD patterns of the Ru/CeO₂ catalysts. Different precursors are indicated by the differently colored lines: Brown: Ru(NO)(NO₃)₃, Red: Ru(acac)₃, Yellow: Ru(CO)₁₂, Green: Ru(dpm)₃, Pale blue: [Ru(OH)(NO)(NH₃)₄](NO₃)₂, Blue: Ru(NO₃)₃, Purple: RuCl₃, Gray: Ru(NH₃)₆Cl₃, Black: Na₂RuO₄. Measurement conditions are described in the experimental section.

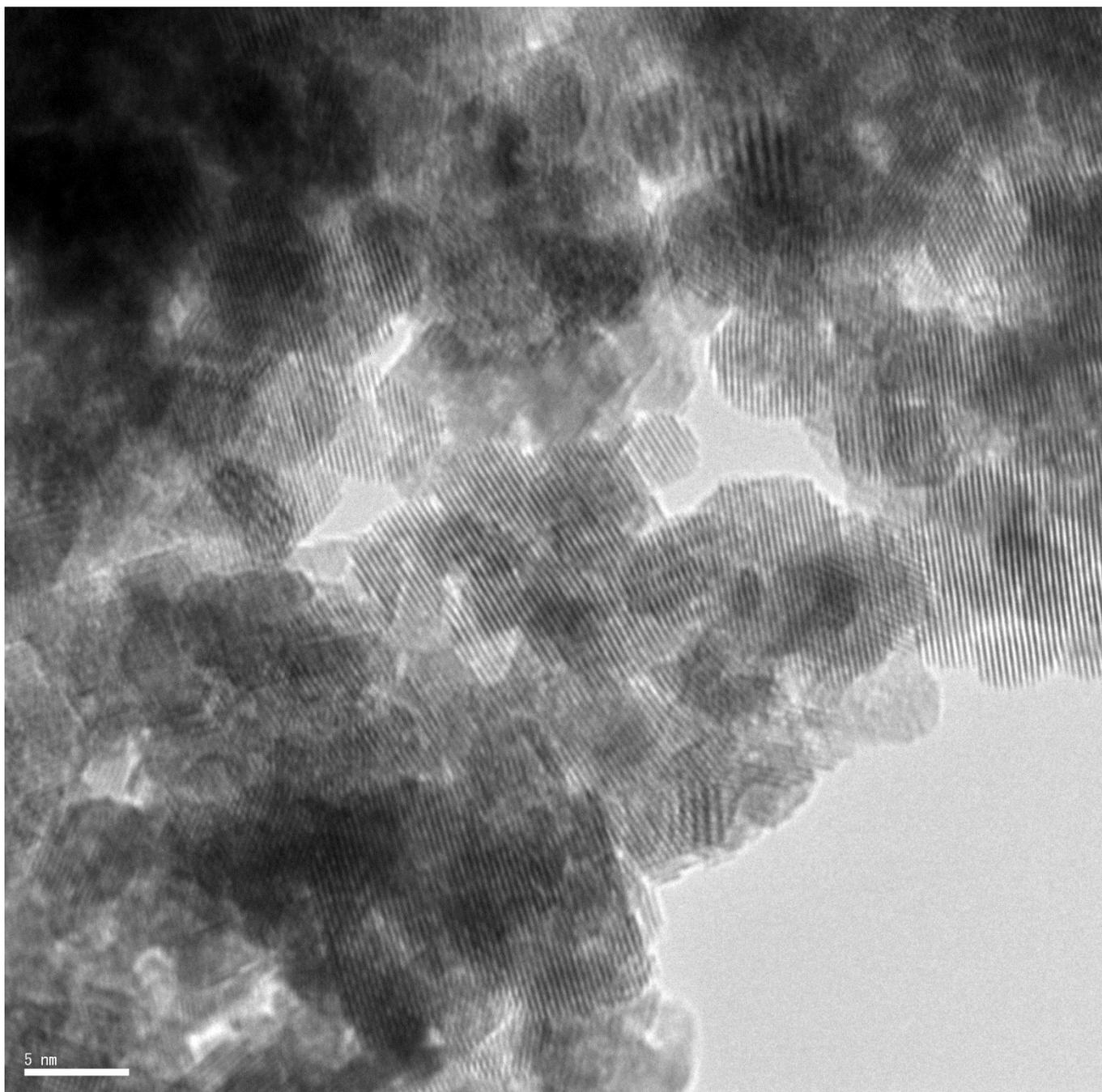


Fig. S3(a). TEM measurement for the Ru/CeO₂ catalysts. (a) Ru(NO)(NO₃)₃ as precursor.

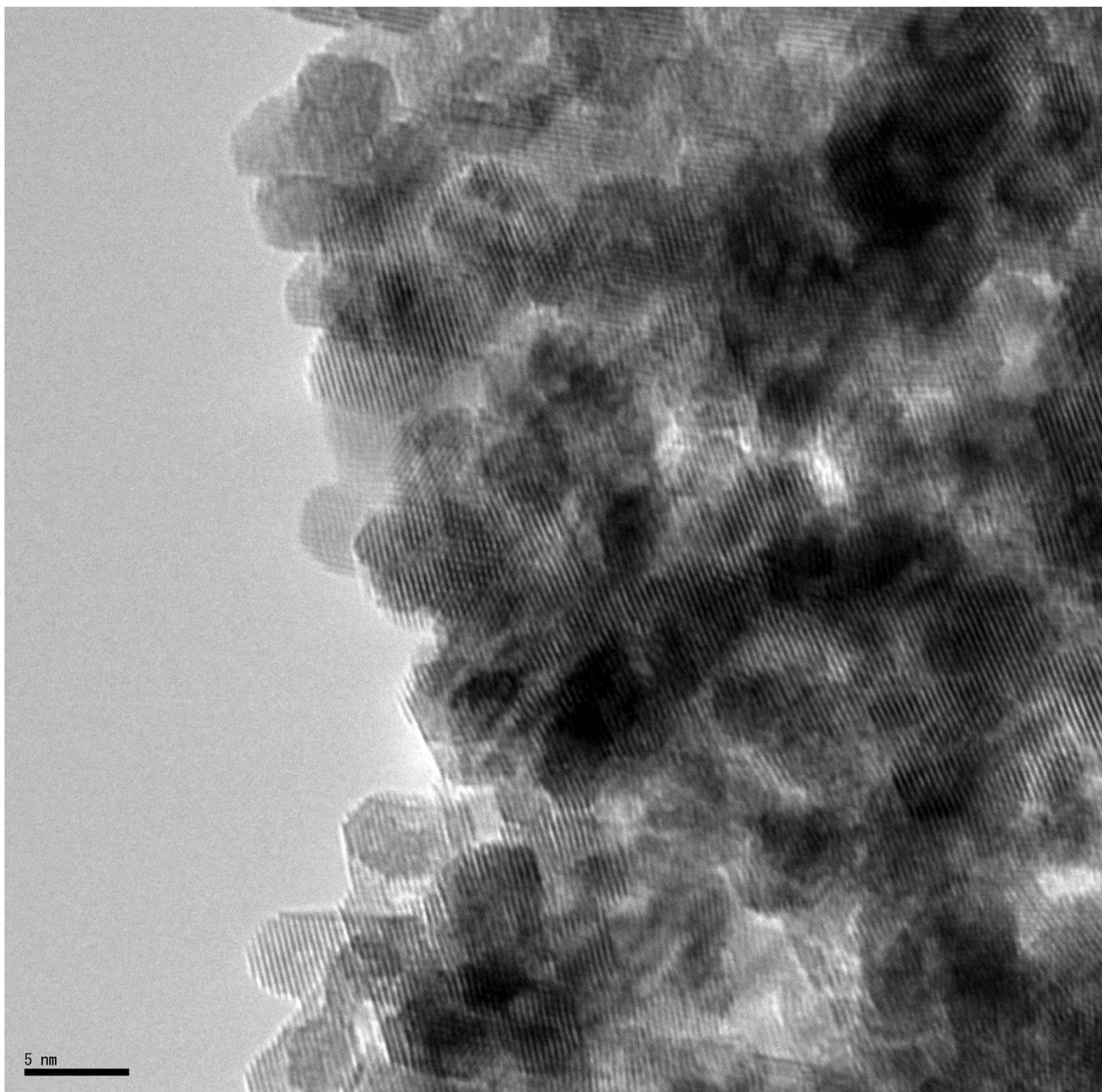


Fig. S3(b). (b)Ru(CO)₁₂ as precursor.

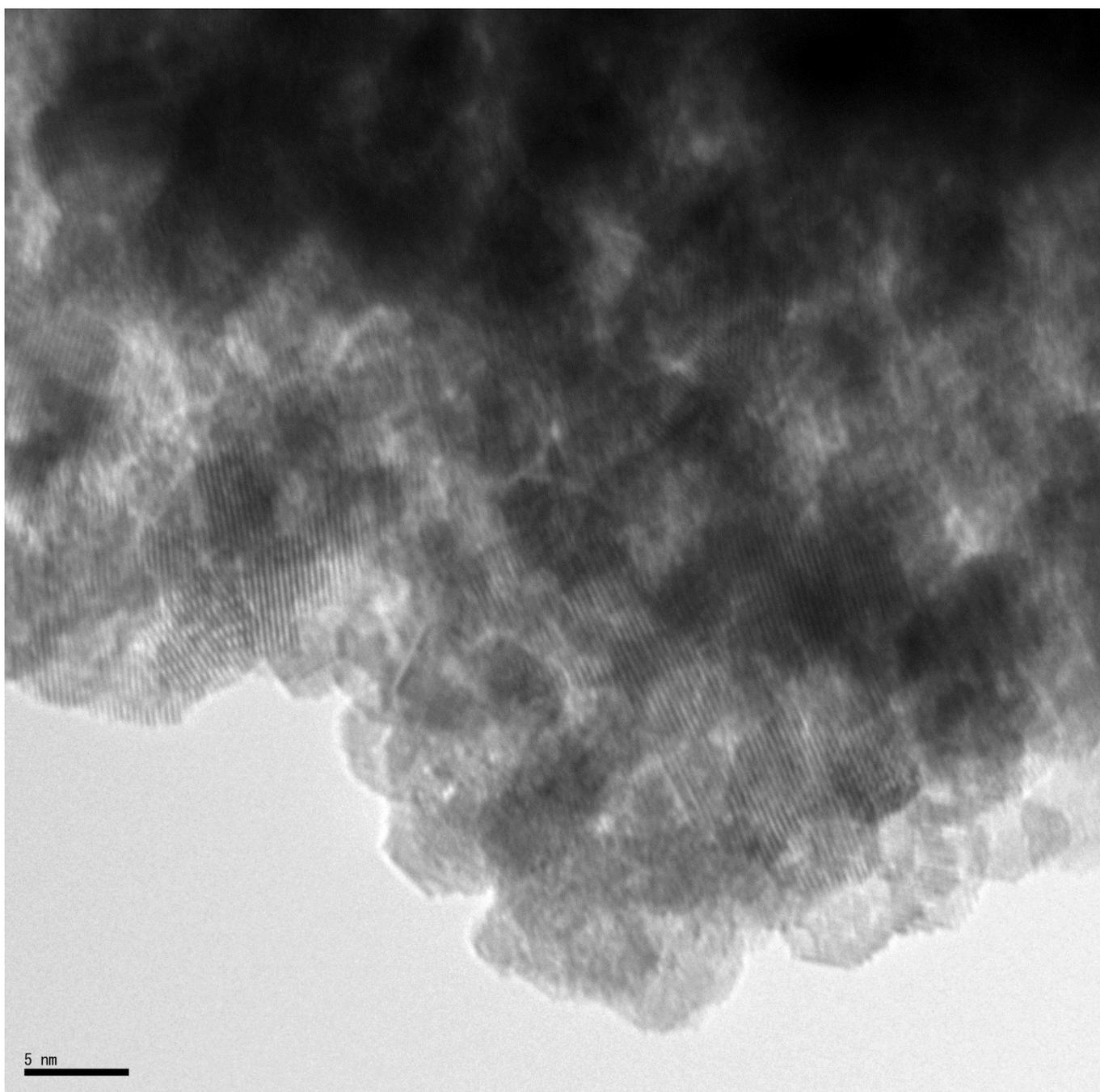


Fig. S3(c). (c)RuCl₃ as precursor.

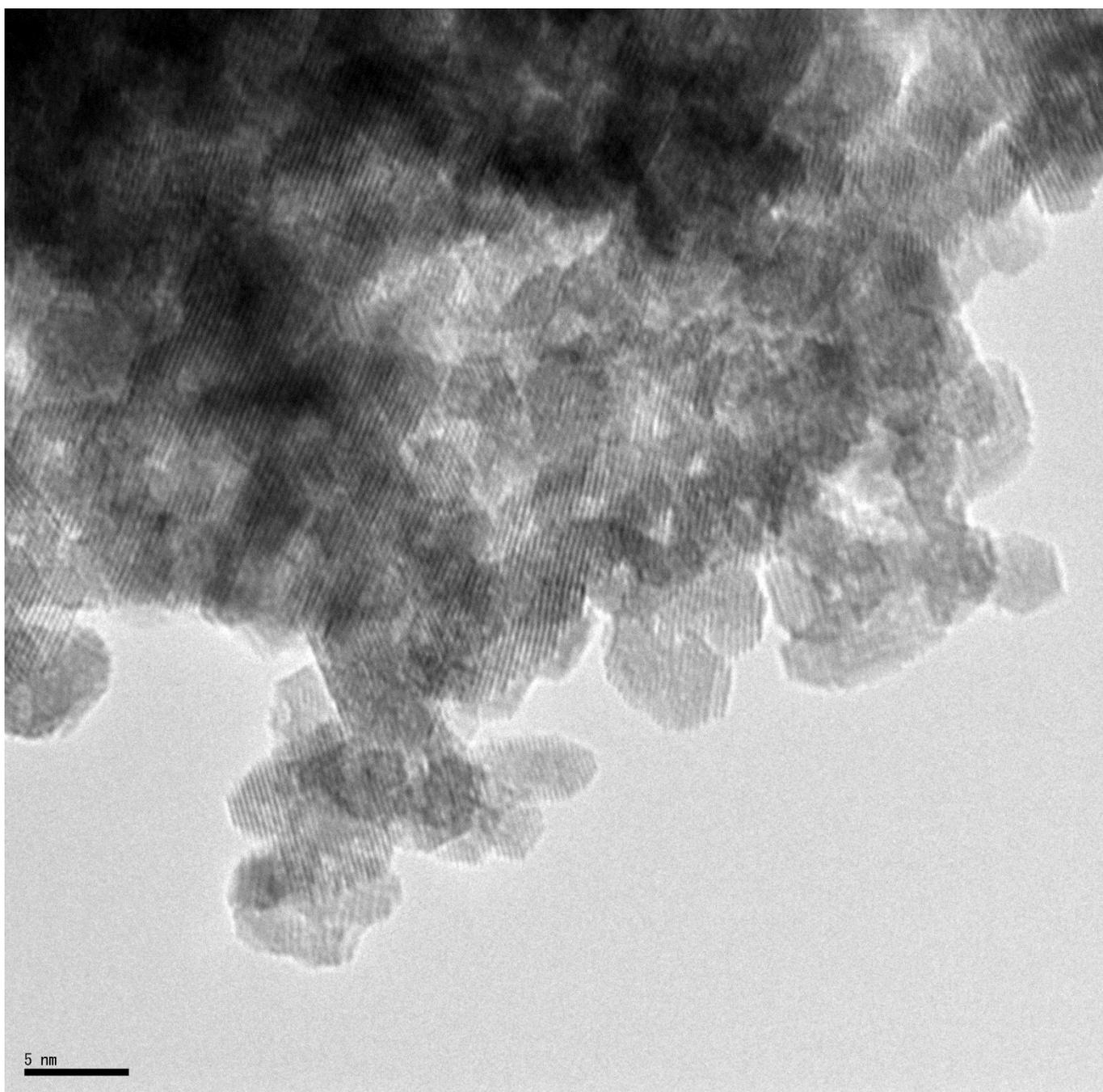


Fig. S3(d). (d)Ru(NH₃)₆Cl₃ as precursor.

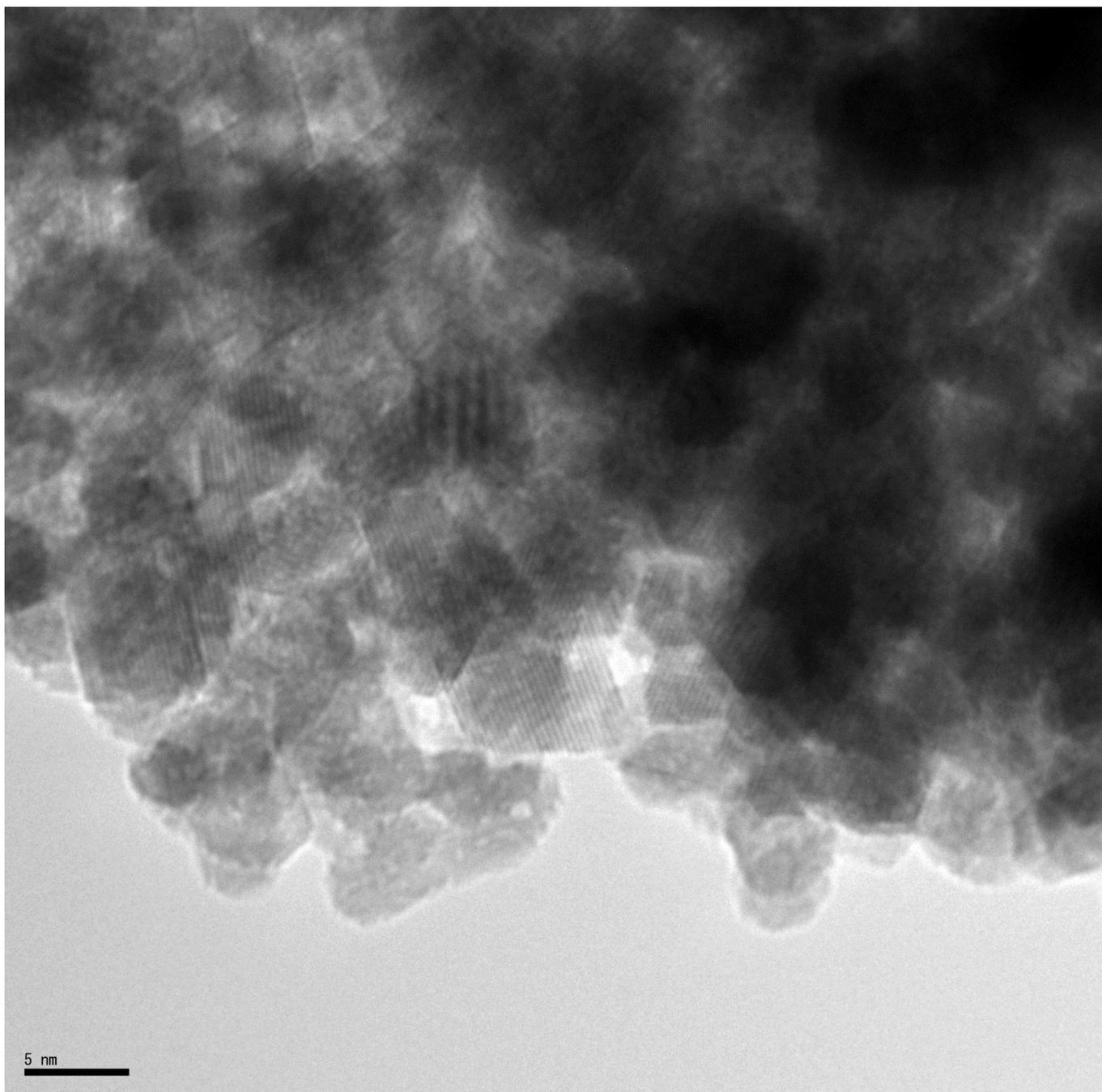


Fig. S3(e). (e)Na₂RuO₄ as precursor.

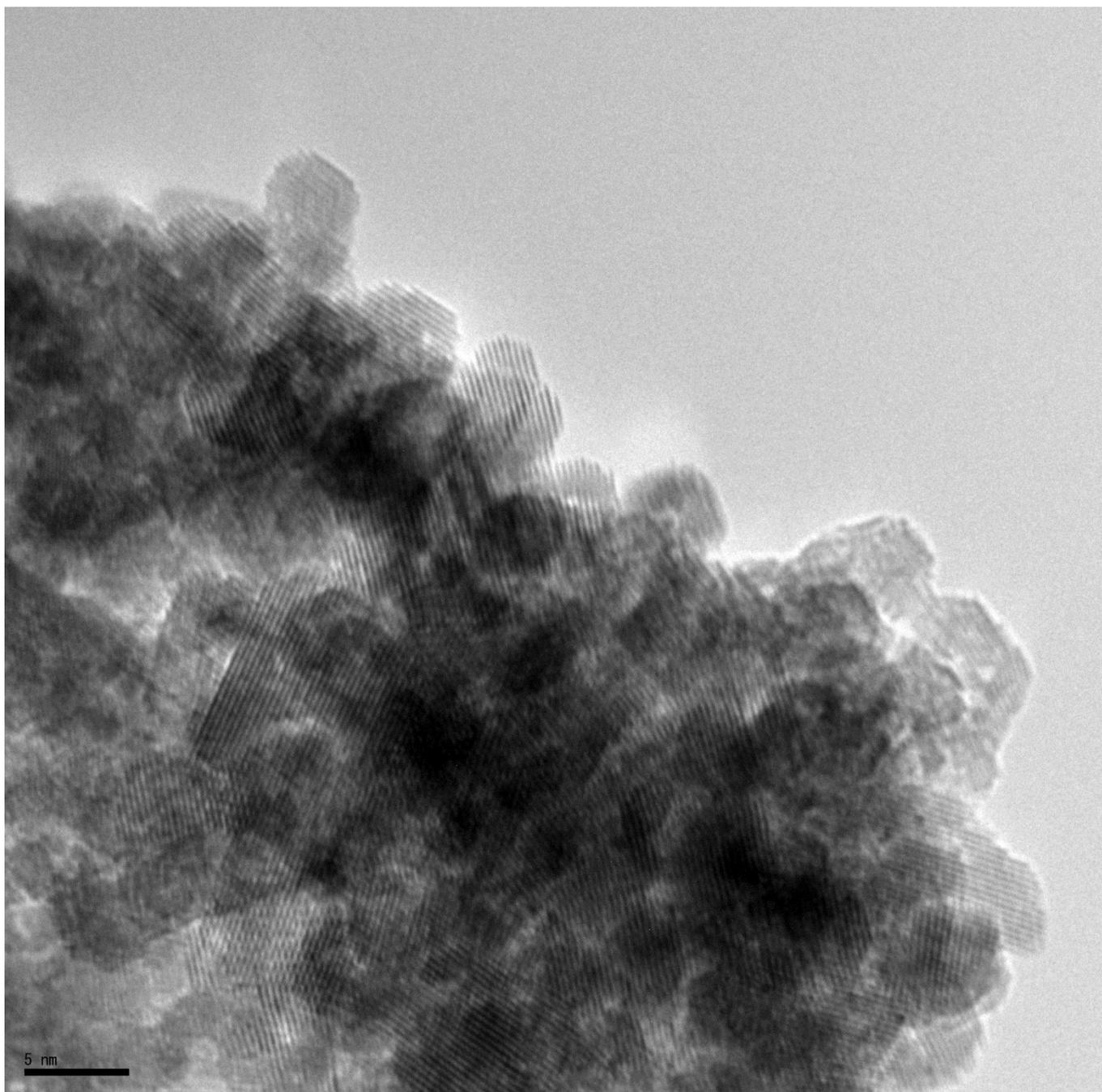


Fig. S3(f). TEM measurement for the CeO₂.

Table S2. The relationship between Ru condition and catalytic activity

Ru precursor	Particle size (Å)	Ru dispersion (%)	Ammonia synthesis ability@350 °C (ppm)
Ru(NO)(NO ₃) ₃	7.2	127.4	809.2
Ru(acac) ₃	5.8	158.2	753.5
Ru(CO) ₁₂	6.0	154.2	788.7
Ru(dpm) ₃	15.8	58.2	726.8
[Ru(OH)(NO)(NH ₃) ₄](NO ₃) ₂	14.2	64.8	433.8
Ru(NO ₃) ₃	8.6	107.6	450.3
RuCl ₃	20.3	45.4	584.7
Ru(NH ₃) ₆ Cl ₃	12.2	75.7	468.9

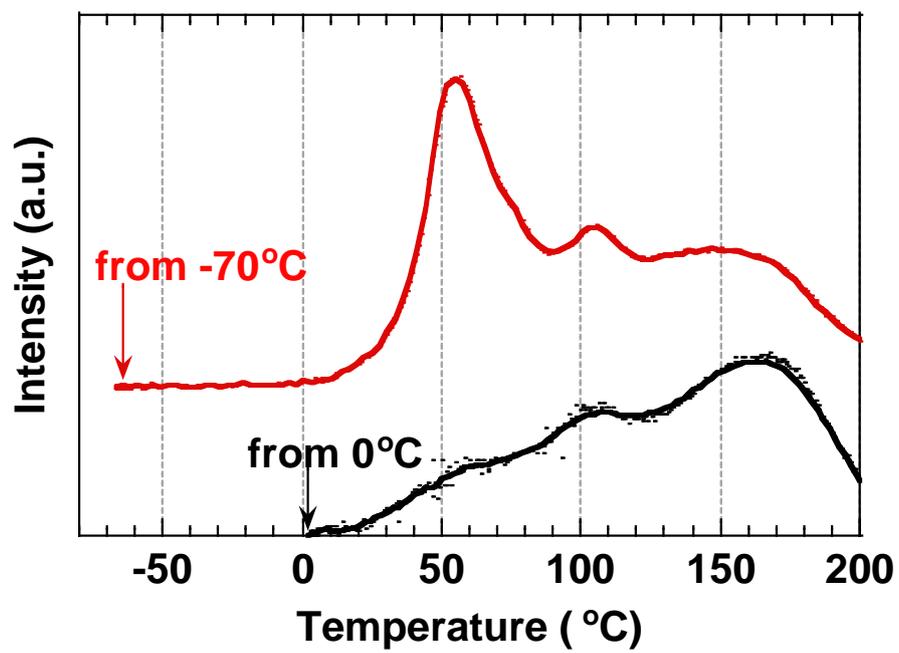


Fig. S4. H₂-TPR profiles of the Ru/CeO₂ catalyst using Ru(acac)₃ as the precursor. Red line: measurement started at -70 °C, Black line: measurement started at 0 °C.

Table S3. ICP-analysis results

Ru precursor	Loading Ru amount (wt%)	Measured Ru amount (wt%)
$\text{Ru}(\text{NO})(\text{NO}_3)_3$	1	1.03
$\text{Ru}(\text{acac})_3$	1	1.05
$\text{Ru}(\text{CO})_{12}$	1	0.85
$\text{Ru}(\text{dpm})_3$	1	0.94
$[\text{Ru}(\text{OH})(\text{NO})(\text{NH}_3)_4](\text{NO}_3)_2$	1	0.82
$\text{Ru}(\text{NO}_3)_3$	1	0.92
RuCl_3	1	0.74
$\text{Ru}(\text{NH}_3)_6\text{Cl}_3$	1	0.91
Na_2RuO_4	1	1.32

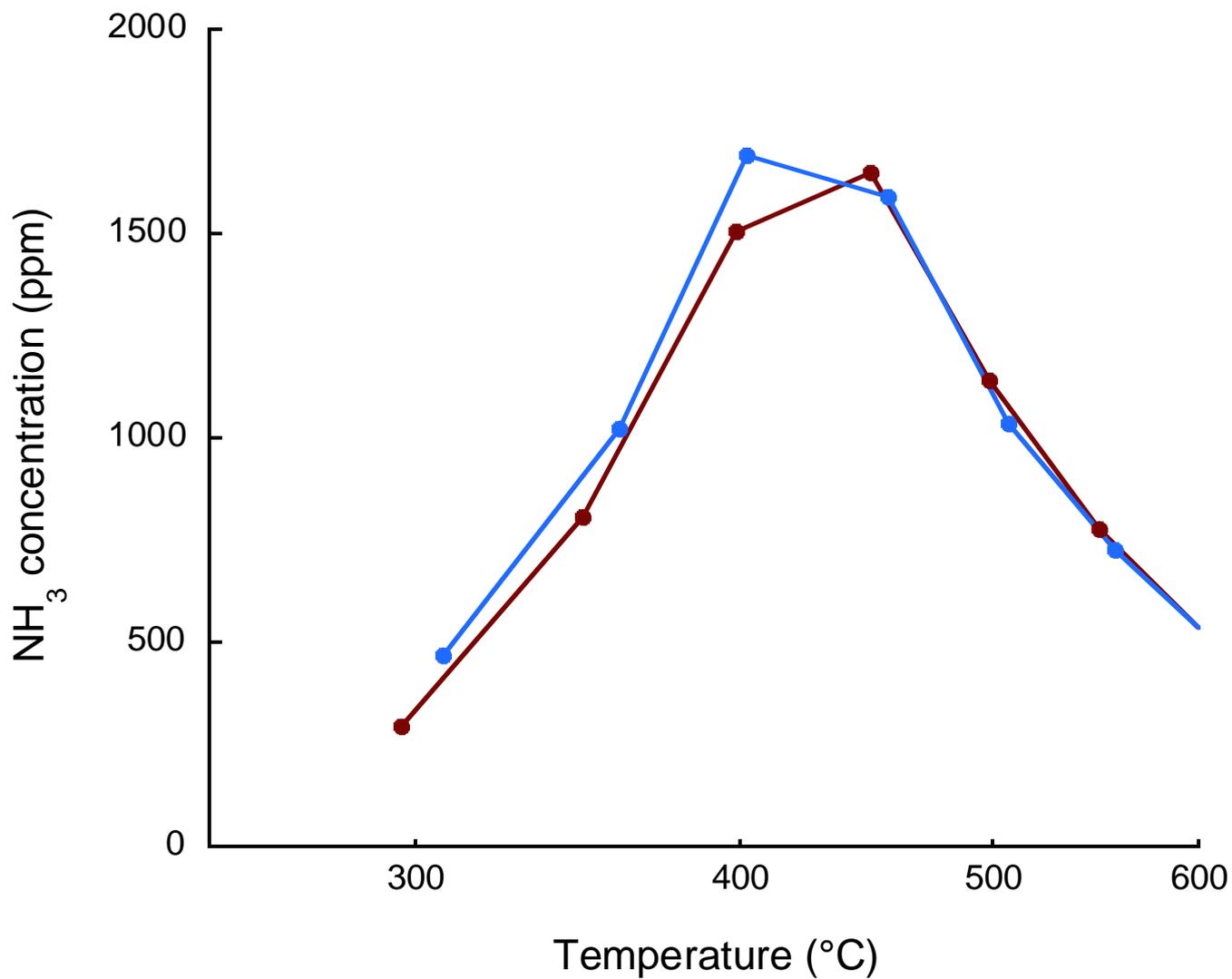


Fig. S4. The reproducibility of the catalytic reaction. Brown line: Ru(NO)(NO₃)₃ precursor. Blue line: remeasurement result.