

Electronic Supplemental Information

Electrochemical-catalytic NH₃ synthesis from H₂O and N₂ using an electrochemical cell with a Ru catalyst, Pd-Ag membrane cathode, and NaOH-KOH molten salt electrolyte at 250°C

Raisei Sagara, Rika Hayashi, Aika Hirata, Shintaroh Nagaishi, Jun Kubota*

1. Catalyst preparation

A carbon support material, a carbon black sample called VULCAN XC-72R (Cabot Co.), was obtained. The carbon support material was calcined at 400°C for 1 h in air to remove impurities. A tetrahydrofuran (THF, FUJIFILM Wako Pure Chemical Co.) solution of triruthenium dodecacarbonyl (Ru₃(CO)₁₂, provided by TANAKA Kikinzoku Kogyo K.K.) was then prepared at a predetermined concentration. The carbon support was immersed in a solution of Ru₃(CO)₁₂ and THF for 4 h with continuous stirring. The solvent was then evaporated from the suspension using a rotary evaporator at 40°C under reduced pressure to prevent decomposition of Ru₃(CO)₁₂. The resulting powder was then calcined at 400°C under vacuum conditions to obtain Ru/C. Ru/C was then immersed in an ethanol solution containing Cs carbonate (Cs₂CO₃, FUJIFILM Wako Pure Chemical Co.) for 4 h, with continuous stirring. In this study, the molar ratio of Cs to Ru was adjusted to 1:1. The solvent was evaporated using a rotary evaporator, followed by calcination at 400°C in a stream of H₂ at a rate of 50 cm³_{STP} min⁻¹ for 2 h. STP is an abbreviation for standard temperature and pressure, defined as 0°C and 0.101 MPa. The resulting catalyst was labelled as Ru/Cs⁺/C, with Cs in an unknown chemical state,

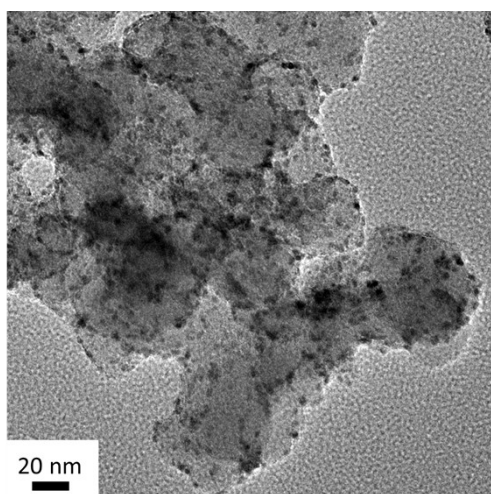


Fig. S1 TEM image of 30 wt%-Ru/C.

indicating that it may exist in forms such as carbonate, hydroxide or oxide. The catalyst was formed into discs using a hydraulic press, crushed and the granules, 600 to 800 μm in size, were sieved and used for experiments.

Transmission electron microscope (TEM) image of carbon supported Ru catalyst is shown in Fig. S1. It was found that Ru particles of approximately 5 nm in diameter were broadly dispersed on the carbon support surfaces.

2. Gas lines

The gas lines for the NH₃ synthesis are shown in Fig. S2. The gas system regulated the gas flow rates on both the cathode and anode sides using mass flow controllers individually between 0.10 and 1.0 MPa as absolute pressures. Due to domestic legal regulations, experiments exceeding 1.1 MPa cannot be conducted. Ar was supplied to the anode side, while N₂ and H₂ were connected to the cathode side. H₂ was only used for catalyst pretreatment at the same temperature as NH₃ synthesis for several hours, prior to NH₃ synthesis experiments, and for leak check of the system with a hydrogen detector. Liquid H₂O was injected into an evaporation chamber using a plunger pump (FLOM, SP-22-12S). To prevent condensation of steam in the tubes, the gas lines were placed in an oven. The temperatures of evaporation chamber and electrochemical cell were controlled with respective heaters. Back-pressure regulating valves were

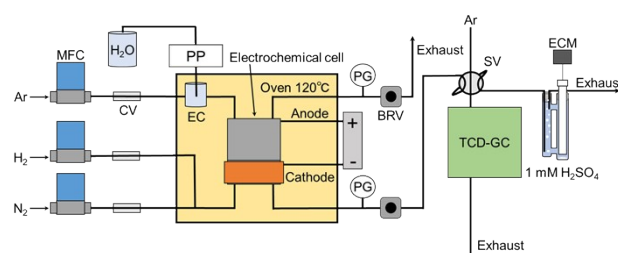


Fig. S2 Illustration of the gas system for NH₃ synthesis. The abbreviations listed below are: mass flow controller (MFC), check valve (CV), plunger pump (PP), evaporation chamber (EC), pressure gauge (PG), back-pressure regulating valve (BRV), 6-way sampling valve (SV), gas chromatograph with a thermal conductivity detector (TCD-GC), and electroconductivity meter (ECM).

used to regulate the individual pressure of the cathode and anode sides.

The electrochemical cell was connected to a regulated power supply with constant current mode (Matsusada Precision Inc., P4K40-06), which could control the small current ranging in 0.1 mA. The current and voltage of cell were recorded by a data logger (Graphtec Co., GL100-N).

The exhaust gas from the cathode side was bubbled into a 25 mL solution of 1.0 mM H_2SO_4 , which was placed in a constant temperature bath at 30°C, with stirring to monitor the electroconductivity of the solution using an electroconductivity meter (DKK-TOA, CM-31P). The electroconductivity had been calibrated against amount of NH_3 , so that it could be estimated the absolute amount of NH_3 . The method of measuring the amount of NH_3 through neutralization absorption into aqueous H_2SO_4 solution and subsequent measurement with an electroconductivity meter is commonly used in studies of ammonia synthesis catalysts. Unlike methods involving indicator reagents or ion chromatography, this method has lower sensitivity, making it unlikely to detect ammonia in the environment. H_2 concentration in the exhaust gas from the cathode side was analysed by gas chromatography with a thermal conductivity detector (GL Sciences, GC-3200). The area ratio of H_2 to N_2 peaks was measured by the gas chromatograph, and the amount of H_2 was determined relative to the flow rate of N_2 . As a result, the rate and the current efficiency for H_2 formation were significantly influenced by the instability and uncertainty of the flow rate of N_2 , leading to a considerable amount of error in their determination.

3. Typical experiment procedures

To assemble the electrochemical cell, a small amount of silicone grease was applied to both sides of the GORE sheet gasket. Before heating the electrochemical cell in the oven, the tubing was connected and the system pressurized with H_2 . A gas leak detector (Testo SE & Co. KGaA, testo 316-2), were used to check for leaks at various points in the cell.

The electrochemical cell was initially heated from room temperature to 120°C and then increased by 20°C every hour until it reached 250°C. This is to prevent NaOH-KOH from scattering into the tubing due to rapid boiling of the electrolyte.

Before NH_3 synthesis experiments, 10 $\text{cm}^3_{\text{STP}} \text{min}^{-1}$ of H_2 was flowed into the cathode side for 3-5 h for pretreatment of Ru catalysts. After the pretreatment, H_2 flow was stopped and N_2 was flowed with predetermined rate.

Due to the very low flow rate of N_2 , ranging from 3 $\text{cm}^3_{\text{STP}} \text{min}^{-1}$ for 10 mA cm^{-2} to 30 $\text{cm}^3_{\text{STP}} \text{min}^{-1}$ for 100 mA cm^{-2} , it took 2 to 3 h for the composition of the cell outlet gas to stabilize.

The 1.0 mM H_2SO_4 solution exhibited an electroconductivity of 82.1 mS m^{-1} . Upon absorption of NH_3 into the 1.0 mM H_2SO_4 solution of 25 cm^3 , the electroconductivity decreased by 0.990 mS m^{-1} per μmol of NH_3 . Within the range of 82.1 to approximately 30 mS m^{-1} , there was a linear relationship between electroconductivity and the amount of absorbed NH_3 . Typically, electroconductivity measurements were recorded

every 3 or 5 min for a duration of 30 to 60 min to estimate the amount of NH_3 . Due to the sensitivity of conductivity measurements to temperature changes, it was necessary to place the conductivity cell in a thermostatic bath and further enclose it in a box to prevent exposure to air conditioning airflow in the laboratory.