Electronic Supplementary Information

Ammonia synthesis from nitrogen and steam using electrochemical cell with hydrogen-permeable membrane and Ru/Cs⁺/C catalysts

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Elemental analysis of electrolyte after NH_3 synthesis

To investigate the cause of degradation in the electrochemical cell, the electrolyte after synthesis of NH_3 using the electrochemical cell for several days was investigated using X-ray fluorescence analysis (XRF, Malvern Panalytical Epsilon 1). The cell was disassembled, and the cathode and anode were peeled off from the electrolyte disk. Elemental analysis using XRF was conducted on both sides of the electrolyte disk. Table S1 presents the elemental composition ratios obtained by XRF. Elements constituting the electrolyte, specifically Si, P, and Cs, were detected on both the cathode and anode sides. Ti was detected on both sides, but the amount was notably higher at 64% on the anode side. This suggests that Ti leached out from the Pt-plated Ti-sintered fibres used in the anode substrate into the electrolyte. For a more stable and prolonged operation, it was suggested that a more precious metal is required for the anode substrate.

The NH_3 production rate with varying H_2/N_2 ratio

In our previous report,[15] we investigated the optimum flow rate of N_2 for NH_3 synthesis using the electrochemical system and found the appropriate H_2/N_2 ratio from the current density, where Ru catalysts supported on MgO or CeO_2 were investigated. However, in this work, carbon-based materials were studied for the supports of Ru catalysts. It is necessary to confirm whether the optimal ratio found in the previous paper, H_2/N_2 = 0.07, is applicable to the catalysts in this study. The deviation of optimal H_2/N_2 ratio from the stoichiometric ratio of 3 is attributed to the fact that the ammonia synthesis reaction is negative-order the NH_3 formation rate of with respect to the partial pressure of H_2. However, there is a possibility that the poisoning effect on hydrogen is dependent on the catalyst type.

Therefore, investigated NH_3 synthesis from mixtures of N_2 and H_2 with varying the H_2/N_2 ratio using a vertical fixed-bed reactor with 30wt%-Ru/Cs^+/VXC72R. The Fig. S1 illustrates the NH_3 production rates at 250°C and 0.1 MPa with varying the H_2/N_2 ratio. The H_2 flow rate was set at 1.0 or 2.0 cm^3_{STP} min^{-1}, while the N_2 flow rate was varied as stated H_2/N_2 ratios. NH_3

Table S1. Elemental composition ratios of the electrolyte after electrochemical synthesis.

Element	Elemental composition / atom%	
	Cathode side	Anode side
Si	9	1
P	22	18
Ti	5	64
Cs	64	10
Pt	0	7

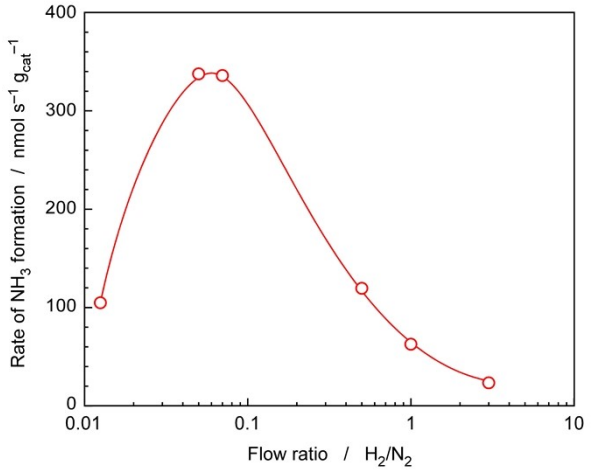

Fig. S1. Dependence of rate of NH_3 formation on the flow ratio of H_2/N_2 at 250°C and 0.1 MPa using a vertical fixed-bed reactor with 30 wt%-Ru/Cs^+/VXC72R.

production rates were in the range of 336 to 338 nmol s^{-1} g^{-1} at H_2/N_2 ratios of 0.07 to 0.05, with the maximum production rate achieved. The optimal H_2/N_2 ratio of Ru catalyst supported on the carbon material was almost similar to that supported on MgO or CeO_2.