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Electronic Supplementary Information

Ammonia synthesis from nitrogen and water at intermediate temperatures and elevated pressures by using an electrochemical hydrogen-membrane reactor with supported Ru catalysts and phosphate electrolytes.

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This electronic supplementary Information (ESI) shows the detailed explanation for experimental setup and procedure for infrared spectroscopy of adsorbed N_2 on Ru catalysts. Thermodynamic parameters for water electrolysis and ammonia synthesis are also shown.

Experimental apparatus

Cross-sectional view of infrared spectroscopic cell is shown in Fig. S1. The cell was made of quartz glass, which had 30 and 27 mm of outer and inner diameters, respectively. A stainless steel (SUS316) tube (4 mm of outer diameter) and flexible sheath heater (1.6 mm of outer diameter, 1.7 m of length, 100 V-500 W) was wrapped around the center part of cell. The cell could be cooled to -123°C by flowing liquid N_2 in the stainless steel tube and heated to 600°C by the electric heating. To flow liquid N_2, one of the ends of stainless steel tube was evacuated by a diaphragm pump with pumping speed of 18 L min^{-1} and the other end was placed into liquid N_2 bottle. Temperature of sample disk was measured by a sheathed thermocouple which was placed in a quartz tube inside the cell close to the sample. Quartz flanges of NW(KF)25 (EVAC Glass) were equipped to both sides of the cell and CaF_2 windows of 40 mm diameter and 4 mm thick were attached to the flanges with O-rings of fluorine-contained rubber (Viton) and specialized clamps (EVAC Glass). Copper tubes (4 mm outer diameter) were wrapped around the cell near the flanges and cooling water at 20°C from a chiller was flowed continuously to maintain the temperature of flanges and windows. A sample disk of 20 mm diameter is placed vertically at the center of cell using a holder made of quartz glass. The cell was connected to a closed circulation vacuum system made of borosilicate glass (Pyrex glass). To connect quartz tube to Pyrex tube, graded seals were used.

The closed circulation vacuum system used in this work is illustrated in Fig. S2. This system was made of Pyrex glass. The ground glass cocks with a high-vacuum grease (Apiezon H) were used for this system. This vacuum system could be evacuated by a mechanical rotary pump with liquid N_2 trap to ca. 10^{-1} Pa. The system was equipped with a capacitance manometer for measuring gas pressure and Pirani vacuum gauge for checking the vacuum pressure. A glass-made circulation pump with a magnetic piston was equipped to the system for gas circulation of H_2 or O_2 in the sample pretreatments. Several gas lines, H_2, O_2, and N_2 from high-pressure gas cylinders with the purity of 99.5% were connected to the system. The gas could be temporally stored in a glass gas reservoir. All part of closed circulation vacuum system was placed on a lifter table and the infrared spectroscopic cell can be ejected from sample compartment of infrared spectrometer by lifting. A Fourier transform infrared spectrometer (JASCO, FT/IR-620) was used with a liquid nitrogen-cooled Hg-Cd-Te detector. For the present measurements, the resolution was 4 cm^{-1} and the signals for 256 scans were accumulated.

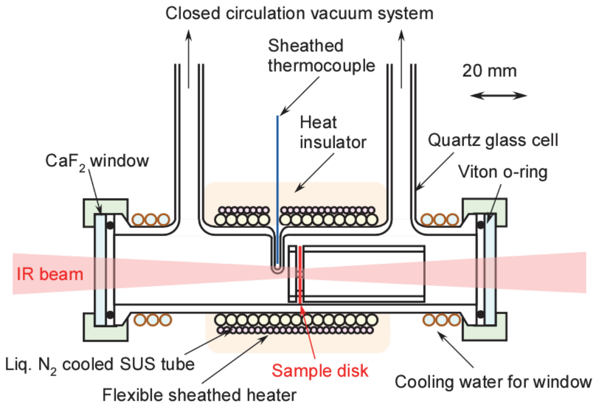

Fig. S1 Cross-sectional view of infrared spectroscopic cell for the observation of adsorbed N_2 on Ru catalysts by a transmission setup.

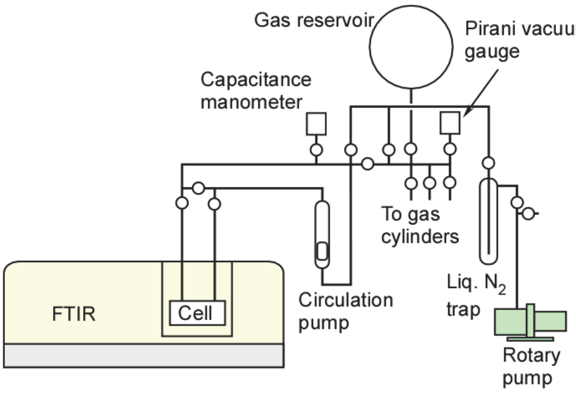

Fig. S2 Illustration of closed circulation vacuum system.

For the fabrication of sample disk, about 100 mg of sample powders were ground by a mortar and then pressed into a disk of 20 mm diameter by dies and hydraulic press. In the case of CeO_2-supported catalysts, press forming was somewhat more difficult than MgO-supported catalysts, so that pure MgO was added as a binder. The weight ratio of CeO_2-supported catalysts and binder of MgO was typically 1/4. MgO cannot adsorb N_2 at 30°C, so that it does not affect the infrared spectra. The Ru particles were intrinsically supported only on CeO_2, and MgO particles were physically mixed with CeO_2-supported catalysts. Thus, there was no possibility that MgO chemically affects Ru sites. The sample disk was placed in the infrared spectroscopic cell at upright position using a quartz sample holder. With moving the cell by the lifter table and ground glass joints, the sample disk was positioned properly in the center of infrared beam.

Experimental procedure

The infrared spectroscopic cell with the sample disk was first evacuated by the rotary pump up to ca. 10^{-1} Pa and then heated at 500°C. 10 kPa of H_2 was introduced into the cell at 500°C and circulate for 1 h. H_2 was exchanged a few times to fresh one during the H_2 treatments. The cell was evacuated again at 500°C and the immediately cooled to 30°C within 20 min. For rapid cooling, cooling air was flowed in the stainless steel tube which was wrapped around the cell.

First, reference spectrum under vacuum was acquired at 30°C. Then, N_2 gas was introduced into the cell at stated pressure followed by a measurement of sample spectrum. The ratio spectrum between sample and reference spectra showed the infrared absorption of adsorbed N_2.

Example of infrared spectra of adsorbed N_2

The infrared spectra of adsorbed N_2 on various Ru catalysts with changing N_2 pressure are shown in Fig. S3. For all catalysts, the absorption peak intensity was depending on the pressure, indicating that the adsorption of N_2 was in the equilibrium with gas phase N_2. This nature was same as that reported previously[46], and the assignment of this absorption to N≡N stretching mode of linearly bonded N_2 on the metallic Ru sites has been confirmed by isotope experiments. In our previous literature, the heat of adsorption has been obtained as 14 kJ mol^{-1} for Ru/MgO from the isotherm of adsorbed N_2.[46] Similar heat of adsorption of N_2 can be speculated for the present catalysts. The detailed work for infrared spectroscopy of adsorbed N_2 on Ru catalysts for the present electrochemical reactor will appear in a forthcoming paper.

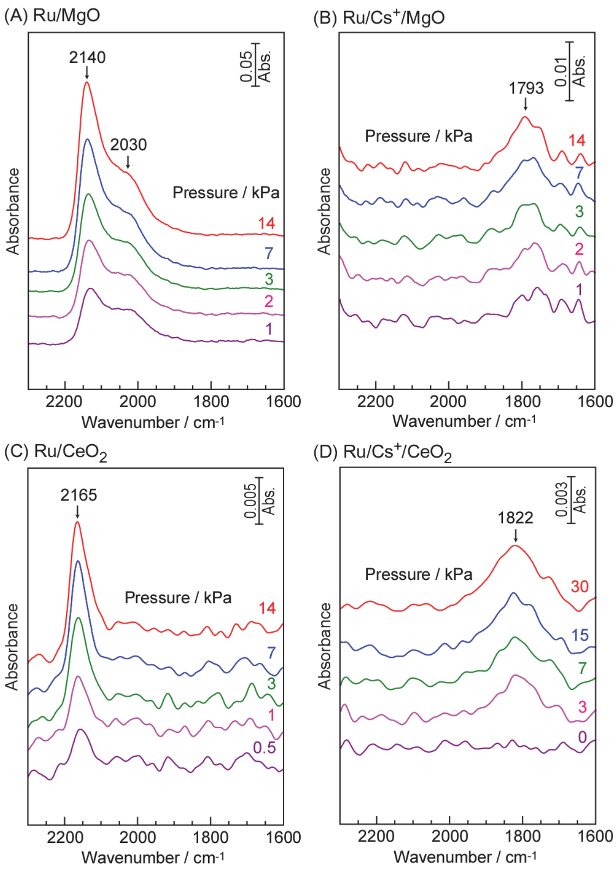

Fig. S3 Infrared spectra of adsorbed N_2 on various Ru catalysts with changing the N_2 pressure at 30°C. (A) Ru/MgO, (B) Ru/Cs^+/MgO, (C) Ru/CeO_2, and (D) Ru/Cs^+/CeO_2.

Thermodynamic parameters and calculations

The heats of formation for H_2O and NH_3, which are corresponding to the following chemical reaction equations, are listed in Table S1.

$$H_2 + 1/2\ O_2 \rightarrow H_2O$$

$$1/2\ N_2 + 3/2\ H_2 \rightarrow NH_3$$

Table S1 Thermodynamic parameters for H_2O and NH_3.

Molecules	$\Delta_f H°$		$\Delta_f G°$	
	liquid kJ mol^{-1}	gas kJ mol^{-1} (kJ mol^{-1}-H_2)	liquid kJ mol^{-1}	gas kJ mol^{-1} (kJ mol^{-1}-H_2)
H_2O	-285.8	-241.8	-237.1	-228.6
NH_3		-45.9 (-30.6)		-16.4 (-10.9)

Thus, for the reaction for NH_3 synthesis from N_2 and H_2O, the standard enthalpies and standard Gibbs energies are derived as follows.

$$H_2O + 1/3\ N_2 \rightarrow 2/3\ NH_3 + 1/2\ O_2$$

$\Delta_r H°$ = -255.2 kJ mol^{-1}-H_2 (liquid water),
-211.2 kJ mol^{-1}-H_2 (water vapour)
$\Delta_r G°$ = -226.2 kJ mol^{-1}-H_2 (liquid water),
-217.7 kJ mol^{-1}-H_2 (water vapour)

These standard Gibbs energies of -226.2 kJ mol^{-1}-H_2 for liquid water and 217.7 kJ mol^{-1}-H_2 for steam can be converted to 1.17 and 1.13 V, respectively, as assumed two electron process. These are the potential differences between the anode and cathode under the standard equilibrium condition. The difference between $\Delta_r H°$ and $\Delta_r G°$ is corresponding to the heat thermal release or absorption. For liquid water, 29 kJ mol^{-1}-H_2 of heat is needed indicating an endothermic reaction. On the other hand, 6.5 kJ mol^{-1}-H_2 of heat is released for water vapour.

For the calculation of chemical equilibrium among NH_3, N_2, and H_2, specific heats at constant pressure of respective species are required in addition to $\Delta_r H°$ and $\Delta_r G°$. The specific heats at constant pressure, C_P, are as follows.

N_2: $28.9-1.57\times10^{-3}T+8.08\times10^{-6}T^2-2.87\times10^{-9}T^3$ (J mol^{-1} K^{-1}),
H_2: $29.1-1.92\times10^{-3}T+4.00\times10^{-6}T^2-8.70\times10^{-10}T^3$ (J mol^{-1} K^{-1}),
NH_3: $27.6+2.56\times10^{-2}T+9.91\times10^{-6}T^2-6.69\times10^{-9}T^3$ (J mol^{-1} K^{-1}),

The principle of calculation of NH_3 concentration for the thermodynamic equilibrium with N_2 and H_2 is explained below.

Equilibrium constant, $\boldsymbol{K}$, can be defined as:

$$\boldsymbol{K} = \frac{\boldsymbol{p}_{\mathbf{NH3}}}{\boldsymbol{p}_{\mathbf{N2}}{}^{1/2}\boldsymbol{p}_{\mathbf{H2}}{}^{3/2}} \quad ,$$

where $\boldsymbol{p}_{\mathbf{NH3}}$, $\boldsymbol{p}_{\mathbf{N2}}$, and $\boldsymbol{p}_{\mathbf{H2}}$ are partial pressures for NH_3, N_2, and H_2 against the standard pressure. At the standard condition, equilibrium constant, $\boldsymbol{K_0}$, is expressed as:

$$\ln \boldsymbol{K_0} = -\frac{\Delta_r \boldsymbol{G}°}{\boldsymbol{RT_0}} \quad ,$$

where $\Delta_r \boldsymbol{G}°$ is the standard Gibbs energy for the reaction, $\boldsymbol{R}$ and $\boldsymbol{T_0}$ are the gas constant and standard temperature. For arbitrarily temperature, $\boldsymbol{T}$, equilibrium constant, $\boldsymbol{K_T}$, is derived from above equation and Gibbs-Helmholtz equation as:

$$\ln \boldsymbol{K_T} = \frac{\mathbf{1}}{\boldsymbol{R}}\int_{\boldsymbol{T_0}}^{\boldsymbol{T}} \frac{\Delta_r \boldsymbol{H_T}}{\boldsymbol{T}^2} \boldsymbol{dT} + \boldsymbol{C} \quad ,$$

where $\Delta_r \boldsymbol{H}°_{\boldsymbol{T}}$ is the enthalpies of reaction which is a function of temperature, and $\boldsymbol{C}$ is integration constant. $\Delta_r \boldsymbol{H}°_{\boldsymbol{T}}$ at arbitrarily temperature, $\boldsymbol{T}$, can be estimated from

$$\Delta_r \boldsymbol{H}°_{\boldsymbol{T}} = \Delta_r \boldsymbol{H}° + \Delta_r \boldsymbol{C}_{\mathbf{P}} \quad ,$$

where $\Delta_r \boldsymbol{H}°$ is the standard enthalpies of reaction and $\Delta_r \boldsymbol{C}_{\mathbf{P}}$ is change of total of specific heats at constant pressure at the temperature, $\boldsymbol{T}$, for all species against the standard temperature.

The standard entropies, $\boldsymbol{S}°$ for NH_3, N_2, and H_2 are 192.8, 191.6, and 130.7 kJ mol^{-1}. The standard entropies at arbitrarily temperature is expressed as:

$$\Delta_r \boldsymbol{S}°_{\boldsymbol{T}} = \Delta_r \boldsymbol{S}° + \int_{\boldsymbol{T_0}}^{\boldsymbol{T}} \frac{\Delta_r \boldsymbol{C}_{\mathbf{P}}}{\boldsymbol{T}} \boldsymbol{dT} \quad .$$

Finally, obtained following equation is useful.

$$\ln\left(\frac{\boldsymbol{K_T}}{\boldsymbol{K_0}}\right) = \frac{\Delta_r \boldsymbol{G}°}{\boldsymbol{RT_0}} - \frac{\Delta_r \boldsymbol{G}°_{\boldsymbol{T}}}{\boldsymbol{RT}}$$

$$= \frac{\Delta_r \boldsymbol{H}° - \boldsymbol{T_0}\Delta_r \boldsymbol{S}°}{\boldsymbol{RT_0}} - \frac{\Delta_r \boldsymbol{H}°_{\boldsymbol{T}} - \boldsymbol{T}\Delta_r \boldsymbol{S}°_{\boldsymbol{T}}}{\boldsymbol{RT}} \quad .$$

The broad outline for the calculation is mentioned above. Practical calculation method is shown in many books in chemical reaction engineering.

The thermodynamic parameters and calculation of thermodynamic equilibrium are explained in the following books.

- Edit. J.R. Rumble, CRC Handbook of Chemistry and Physics 99th, CRC Press, Boca Raton, 2018.
- O. A. Hougen, K. M. Watson and R. A. Ragatz, Chemical Process Principles, Part II, John Wiley & Sons, New York, 2nd edn, 1959.
- H. Liu, Ammonia Synthesis Catalysts: Innovation and Practice, World Scientific, Singapore, 2013.