Essential role of hydride ion in ruthenium-based ammonia synthesis catalysts†

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The efficient reduction of atmospheric nitrogen to ammonia under low pressure and temperature conditions has been a challenge in meeting the rapidly increasing demand for fertilizers and hydrogen storage. Here, we report that Ca2N:e−, a two-dimensional electrode, combined with ruthenium nanoparticles (Ru/Ca2N:e−) exhibits efficient and stable catalytic activity down to 200 °C. This catalytic performance is due to [Ca2N]1+·eL−·Hx− formed by a reversible reaction of an anionic electron with hydrogen ([Ca2N]1+·eL−·Hx−) during ammonia synthesis. The simplest hydride, CaH2, with Ru also exhibits catalytic performance comparable to Ru/Ca2N:e−. The resultant electrons in these hydrides have a low work function of 2.3 eV, which facilitates the cleavage of N2 molecules. The smooth reversible exchangeability between anionic electrons and H+ ions in hydrides at low temperatures suppresses hydrogen poisoning of the Ru surfaces. The present work demonstrates the high potential of metal hydrides as efficient promoters for low-temperature ammonia synthesis.

Introduction

Catalytic ammonia synthesis is vital for the production of synthetic fertilizers and serves as an active nitrogen source for important chemicals. Dinitrogen (N2) is a typically inert molecule because of the strong N≡N bond (945 kJ mol−1). Therefore, high temperature (400–600 °C) and high pressure (20–40 MPa) are required for industrial ammonia synthesis (Haber–Bosch process), which results in high energy consumption. Recently, ammonia has also attracted much attention as a hydrogen storage material due to its high capacity for hydrogen (17.6 wt%).10a,11 Although these electronic promoters lower the energy barrier for N2 dissociation, the enthalpy of hydrogen adsorption on the Ru catalyst is also increased, leading to high surface coverage by H atoms (hydrogen poisoning).12 Accordingly, the electronic promotion effect for N2 dissociation is retarded by the competitive adsorption of H2. It is therefore highly desirable to develop a new Ru catalyst that can promote N2 dissociation and prevent hydrogen poisoning. It was demonstrated that the 12CaO·7Al2O3 electrode (Cl2A7:e−)13-supported Ru catalyst exhibits much higher activity for ammonia synthesis than alkali-promoted Ru catalysts.14,15 The intrinsically low work function (ca. 2.4 eV) of Cl2A7:e−15 in this catalyst promotes N2 dissociation on Ru, which leads to a reduction in the activation energy to half (ca. 55 kJ mol−1) of that for conventional Ru catalysts. A recent kinetic analysis revealed that the bottleneck for ammonia synthesis is shifted from N2 dissociation to the formation of N–Hx species.16 In addition, this catalyst has reversible exchangeability of electrons and hydride ions, and is almost immune to hydrogen poisoning of the Ru surface, which is a serious drawback for conventional Ru catalysts. These results imply that both electrons and hydride ions play a crucial role in effective ammonia synthesis. However, the outstanding
activity of C12A7:e− is diminished at low temperatures (<320 °C), which is strongly correlated with the weak H2 desorption properties at low temperatures. The electron–hydride ion exchange reaction in C12A7:e− is accomplished by H desorption through a cage wall composed of a rigid monolayer of Ca-Al-O; therefore, the exchange reaction in C12A7:e− requires a relatively high temperature that is sufficient to excite thermal vibration and allow H to escape from the cage. Therefore, our design concept for a highly active low-temperature ammonia synthesis catalyst is embodied by inorganic electrode materials with hydride ions exposed to the surface, i.e., metal hydrides.

Dicalcium nitride, [Ca2N]−e− (denoted as Ca2N:e−), was confirmed as a two-dimensional (2D) electride with a low work function (2.6 eV), in which anionic electrons confined between the [Ca2N]− layers as counter anions17 can be partly exposed to the surfaces. In addition, this material can be converted into Ca3NH ([Ca2N]−H−) by the reaction between an anionic electron and a hydrogen, which is analogous to that for C12A7:e−. Therefore, Ca2NH was selected as the first test bed material to verify our hypothetical design concept of metal hydrides for low-temperature ammonia synthesis.

Here we report that metal hydride materials such as Ca3NH and CaH2, which are not intrinsically low work function materials, strongly promote the cleavage of N2 to form NH3 on Ru nanoparticles under low pressure and temperature conditions. The low work function (2.3 eV) is immediately realized by the formation of hydrogen vacancies in these Ru-loaded hydride materials during ammonia synthesis, which in turn facilitates N2 dissociation and prevents hydrogen poisoning of the Ru surface.

Results and discussion

Catalytic performance of Ru-loaded Ca2N:e−

Fig. 1 shows the temperature dependence for ammonia synthesis over various Ru catalysts and Table 1 summarizes the catalytic properties of various Ru catalysts. The Ru dispersion of Ru/Ca2N:e− (3.1%) is much smaller than that of Ru(2%)-Cs/MgO (50.4%) because of its low surface area (1.5 m2 g−1), which is similar to the results for Ru/C12A7:e−. However, Ru/Ca2N:e− exhibits high catalytic activity (at 340 °C) comparable to Ru(2%)-Cs/MgO, which is one of the most active catalysts for ammonia synthesis reported to date.20,21 Accordingly, the turn-over frequency (TOF) with Ru/Ca2N:e− is higher than that with Ru–Cs/MgO by an order of magnitude. It is noteworthy that Ru/Ca2N:e− exhibits higher catalytic activity than Ru/C12A7:e− or Ru(2%)-Cs/MgO, especially below 300 °C, and ammonia formation can be distinctly observed even at 200 °C. The apparent activation energy of Ru/Ca2N:e− for ammonia synthesis is 60 kJ mol−1, which is one-half of that of Ru–Cs/MgO (120 kJ mol−1). We have previously reported20 that a change in the activation energy is observed for Ru/C12A7:e−, i.e., the activation energy at 400–320 °C is 50 kJ mol−1 but exceeds 90 kJ mol−1 at lower reaction temperatures (320–250 °C) and no reaction is observed at 200 °C. These results indicate that Ru/Ca2N:e− is superior to Ru/C12A7:e− for low-temperature ammonia synthesis. Furthermore, we note that Ru/Ca2N:e− functions as a stable catalyst for ammonia synthesis over long periods without degradation in activity. Fig. 1b shows that the initial ammonia synthesis rate was maintained even after 54 h under high pressure conditions (1.0 MPa), and the total amount of produced ammonia reached 27 mmol, which is more than 25 times the total nitrogen content in Ca2N:e− (1.06 mmol). This result indicates that the ammonia produced is not derived from the decomposition of the Ca2N:e− support.

Fig. 1c and d show the dependence of the ammonia synthesis rate on the partial pressure of N2 and H2, respectively. The reaction orders with respect to N2, H2, and NH3 over various Ru catalysts are also summarized in Table S1.† The reaction order for N2 with conventional heterogeneous catalysts is 0.8–1.0,11,20,21 where N2 dissociation is the rate-determining step for ammonia synthesis. In contrast, the reaction order for N2 with Ru/Ca2N:e− is almost one-half, which is attributed to a more dense population of N adatoms on Ru/Ca2N:e− than on the other catalysts. Two results were noted; one is that the Ru/Ca2N:e− catalyst also facilitates the N2 isotopic exchange reaction (15N2 + 14N2 = 215N14N) with a lower activation energy (59 kJ mol−1) than conventional Ru catalysts (>130 kJ mol−1)16 (Fig. S1†), indicating that the energy barrier for N2 dissociation is significantly lowered by Ru/Ca2N:e−. The other result is that Ru/Ca2N:e− has a positive reaction order with respect to H2 in contrast to the case for Ru–Cs/MgO (β < 0), which indicates that ammonia synthesis over Ru/Ca2N:e− is not inhibited by hydrogen adsorption, i.e., hydrogen poisoning.11,20 Thus, Ru/Ca2N:e− maintains the key kinetics observed with Ru/C12A7:e−, in that N2 cleavage is not the rate-determining step for ammonia synthesis16 and the reactions are free from hydrogen.

**Fig. 1** (a) Catalytic activity for ammonia synthesis over various Ru catalysts (2 wt%) as a function of reaction temperature (reaction conditions: catalyst, 0.1 g; WHSV, 3 600 mL gcat−1 h−1; reaction pressure, 0.1 MPa). (b) Reaction time profile for ammonia synthesis over Ru (5 wt%)/Ca2N at 340 °C (reaction conditions: catalyst, 0.1 g; WHSV, 3 600 mL gcat−1 h−1; reaction pressure, 1.0 MPa). (c, d) Dependence of ammonia synthesis on the partial pressure of (c) N2 and (d) H2 using various Ru catalysts (2 wt%) at 340 °C under atmospheric pressure.
poisoning on the Ru surface. Generally, the promotion effect of alkali compounds such as Cs-oxide in a Ru catalyst is a trade-off between lowering the activation barrier for N₂ dissociation and increasing the competitive adsorption of H₂. However, this serious drawback can be overcome by using Ca₂N as a support material. Furthermore, the catalytic activity of Ru/Ca₂N increased with an increase in the reaction pressure at 320 °C (Fig. S2†). On the other hand, the increment in the catalytic activity of Ru/C12A7 is moderate at this temperature, which is due to the poisoning effect of H atoms on Ru/C12A7 at low reaction temperature (≤320 °C). These results clearly indicate that Ru/Ca₂N exhibits improved performance for ammonia synthesis compared with Ru/C12A7, even at lower temperatures and elevated pressures.

### Structural properties of Ca-nitride catalysts

X-ray diffraction (XRD) and Raman spectroscopy measurements confirmed that Ca₂N, an inorganic hydride, is formed in the Ru/Ca₂N catalyst during the ammonia synthesis reaction. Fig. 2a shows that Ru/Ca₂N after ammonia synthesis has no diffraction peaks attributable to the Ca₃N phase (Fig. 2b),30,32,33 whereas new peaks due to Ca²⁺ and cubic structure (Fig. 2c) appear.35,37 There is no CaN phase (cubic structure, Fig. 2d), which consists of Ca²⁺ and NH²⁺ ions (the formal charge of hydrogen is +1), in Ru/Ca₂N after the reaction.26,28 The formation of Ca₂N in the catalyst was also elucidated from in situ Raman spectroscopy measurements (Fig. 2e). Two intense bands at 173 and 299 cm⁻¹ for Ca₂N are red-shifted to 180 and 322 cm⁻¹, respectively, under the reaction conditions. The Raman spectrum for CaN has broad bands in the range from 100 to 1000 cm⁻¹ and is completely different from that of Ca₃N (Fig. S3†). In addition, CaN has an intense band centered at 3122 cm⁻¹, which is attributed to the N-H stretching mode in imide ions.29,30 Although Ru/Ca₂N also showed weak bands in the range of 3100–3300 cm⁻¹ after the reaction, the intensity is much smaller than that for Ca₂N, which indicates that the catalyst consists mainly of Ca₂N. In addition, Ru/CaNH has much lower catalytic activity and a higher activation energy (110 kJ mol⁻¹) than Ru/Ca₂N (Fig. 1, S2† and Table 1). The kinetic analysis (Fig. 1 and Table S1†) revealed that N₂ cleavage is the rate-determining step for Ru/CaNH and the catalyst is subject to hydrogen poisoning like the conventional Ru catalysts.

To understand the reactivity of these materials with hydrogen, temperature-programmed absorption (TPA) and desorption (TPD) of H₂ on the catalysts were examined. Ru/Ca₂N can absorb hydrogen above 150 °C, which means that the hydrogen storage reaction (H² + e⁻ → H₂⁻) takes place to form Ca₂NH (Fig. 2f). In contrast, no H₂ absorption peak was observed for Ru/CaNH and a negative peak appeared at 500–600 °C, which corresponds to hydrogen desorption from the sample, i.e., decomposition. Fig. 2g shows that H₂ is released (H₂⁻ → H² + e⁻) from Ru/Ca₂N after reaction above 200 °C (the actual material is Ru/Ca₂N) and the H⁻ ion content was estimated to be 10.6 mmol g⁻¹, which is in good agreement with the theoretical amount (10.5 mmol g⁻¹) of H⁻ ions in Ca₂NH. Furthermore, the onset temperature for H₂ desorption from Ru/Ca₂N after the reaction is much lower than that for Ru/CaNH. The TPA and TPD results show that hydrogen incorporation and desorption reactions proceed above 200 °C over Ru/Ca₂N. Therefore, a nonstoichiometric phase represented by [Ca₂N]⁻ · e⁻ + H²⁻, rather than stoichiometric Ca₂NH, is formed by the reaction between anionic ions and H⁻ ions [Ca₂N⁻ + H⁻ ↔ [Ca₂N]⁻ · H⁻] during ammonia synthesis. This exchangeability is a key reaction confirmed in Ru/C12A7, but the significant difference between Ru/Ca₂N and Ru/C12A7 is the onset temperature for H₂ desorption, i.e., 200 °C for Ru/Ca₂N and 350 °C for Ru/C12A7.

### DFT calculations

To shed more light on the electronic state of Ca₂N, density functional theory (DFT) calculations were conducted (detailed conditions are described in the ESIF). Fig. 3a shows a computational model of the Ca₂N(100) surface, and Fig. 3b–d show the calculated electronic states of Ca₂N(100), Ca₂N(100), and Ru-loaded Ca₂N(100), respectively. The calculations were executed under the condition of an electrically neutral unit cell. The calculated work functions (WFs)31 for Ca₂N (3.3, 2.5 eV) and Ru (4.8 eV) are close to the measured values30,32,33 (Table 2), which indicates the reliability of the DFT calculations. The

### Table 1 Catalytic properties of various Ru catalysts

| Catalyst     | Ru loading (wt%) | S_{BET} (m² g⁻¹) | Dₚₜ (nm) | N₂/(mmol g⁻¹) | r_{NH₃} (mmol g⁻¹ h⁻¹) | TOF (×10⁴) (s⁻¹) | Eₘ (kJ mol⁻¹) |
|--------------|----------------|-----------------|---------|---------------|---------------------|------------------|--------------|
| Ru/Ca₂N⁻²   | 1.8            | 1.5             | 3.1     | 42.8          | 5.1                 | 1674             | 91.5         | 60           |
| Ru/CaNH     | 1.8            | 1.0             | 4.5     | 30.2          | 7.2                 | 53               | 2.0          | 110          |
| Ru/C12A7⁻²  | 1.8            | 1.0             | 4.7     | 28.7          | 8.3                 | 745              | 24.9         | 51 (400–320 °C) |
| Ru/CaH₂     | 1.8            | 1.0             | 4.7     | 28.7          | 8.3                 | 2174             | 14.9         | 91 (320–200 °C) |
| Ru/Ca₂N⁻²   | 2.0            | 3.8             | 12.3    | 10.9          | 22.3                | 1539             | 98.0         | 51           |
| Ru/Ca₂N⁻²   | 2.0            | 12.0            | 50.4    | 2.5           | 45.7                | 697              | 4.2          | 120          |

* Dispersion (D₀), particle size (d), and the number of surface Ru atoms (N₂) were calculated on the basis of CO chemisorption values, assuming spherical metal particles and a stoichiometry of Ru/CO = 1.²⁷⁻³⁷ NH₃ synthesis rate (r_{NH₃}); conditions: catalyst (0.1 g), synthesis gas (H₂/N₂ = 3, 60 mL min⁻¹), weight hourly space velocity (WHSV) = 36 000 mL g⁻¹ h⁻¹, pressure (0.1 MPa). † TOF was calculated from the rate of ammonia synthesis divided by N₂. ** Eₘ is the apparent activation energy calculated from Arrhenius plots for the reaction rate in the temperature range of 340–250 °C.
calculated WF for CaNH is significantly smaller than that for CaNH, which indicates the higher electron-donating ability of CaNH than CaNH. Notably, CaNH(100) with a hydrogen vacancy (VH) \( (i.e., \text{Ca}_2\text{NH}_{1-x}(100)) \) shows a much lower WF (2.3 eV) than both CaNH (2.8 eV) and Ca\( _2\text{N}^-\) (2.5 eV). When an anionic electron is confined at the VH position in CaNH (see the inset of Fig. 3c), the anionic electron state is located above the valence band maximum (VBM) of Ca2NH, as shown in Fig. 3c. The confinement of the anionic electron in Ca\( _2\text{NH}_{1-x}(100) \) is stronger than that of the 2D layered space in CaNH, and thus Ca\( _2\text{NH}(100) \) with VH has a small WF, which reflects the strong electron-donation ability of Ca\( _2\text{NH}_{1-x} \).

Ca\( _2\text{NH}_{1-x} \) can be readily formed by the combination of Ca2NH with Ru nanoparticles. Table 2 lists the calculated formation energies of VH on the surfaces of the catalysts in the presence or absence of Ru. Relatively large VH formation energies (0.88–1.02 eV) were obtained for Ru-free Ca\( _2\text{NH}(100) \), which indicates the difficulty of hydrogen vacancy formation. The density of states (DOS) for an H\(^-\) ion in Ca\( _2\text{NH}(100) \) is found at a relatively deep level, as shown in Fig. 3c and the inset of Fig. 3d (\(-6 \text{ eV below the Fermi level } (E_F) \) for bulk H\(^-\) and \(-4 \text{ eV below } E_F \) for surface H\(^-\)); therefore, the formation of anionic electrons by H desorption requires a relatively large amount of energy. However, the situation is significantly changed when a Ru cluster is loaded on the Ca\( _2\text{NH}(100) \) surface; the VH formation energy for Ru\( _x \)-loaded Ca\( _2\text{NH}(100) \) is decreased to 0.43–0.67 eV. Fig. 3d shows that the DOS for an H\(^-\) ion bonded with Ru (H\(^b\) in the inset of Fig. 3d) are energetically shifted up from a relatively deep level to a shallow level (\(-0.5 \text{ eV below } E_F \)). Thus, an H\(^-\) ion bonded with Ru is almost ready to form an anionic electron by the desorption of H\(^b\). The lift-up of the H\(^-\) states is caused by the fraction of the anti-bonding level with Ru, and thus originates from the presence of surface H\(^-\). In other words, the orbital hybridization between Ru and surface H\(^-\) leads to an electron donation from surface H\(^-\) to Ru, which makes the desorption as H\(^b\) easier. This situation is maintained even when an N\(_2\) molecule is adsorbed on Ru; the formation energy for VH on Ru\( _x \text{N}_2 \)-Ca\( _2\text{NH}(100) \) is 0.49 eV. In contrast, a large VH formation energy is observed for CaNH (1.71 eV), which corresponds well to the experimental evidence presented in Fig. 2g. These computational results support the idea that anionic electrons with a low WF are formed in non-stoichiometric hydrides, [Ca\( _2\text{N}^-\)\( \cdot \text{H}_{1-x} \)]\( \cdot \text{H}_x^- \), by Ru catalysts during the reaction, which facilitates \( \text{N}_2 \) cleavage on the hydride via electron donation from the anionic electrons to the loaded Ru nanoparticles.

**Reaction mechanism over Ru[Ca\( _2\text{N}^-\)\( \cdot \text{H}_{1-x} \)]\( \cdot \text{H}_x^- \)**

Ammonia synthesis from \( \text{N}_2 \) and \( \text{D}_2 \) was examined to elucidate the reaction mechanism over Ru[Ca\( _2\text{N}^-\)\( \cdot \text{H}_{1-x} \)]\( \cdot \text{H}_x^- \). The initial gas (reaction time = 0 h) consists mainly of \( \text{N}_2 \) (\( m/z = 28 \)) and \( \text{D}_2 \) (\( m/z = 4 \)), whereas the amounts of other species such as \( \text{H}_2 \) (\( m/z = 2 \))...
ions rather than directly react with N adatoms. TPD measurements (Fig. 4b) show that H$_2$, HD, and D$_2$ species were desorbed from the catalyst after the reaction. It is thus evident that some H$^-$ ions in Ru[[Ca$_2$N]$^-\cdot$e$_{1-x}$H$_x^-\cdot$H$_x^-$ are replaced by D$^-$ ions during the ammonia synthesis reaction. The incorporation of D$^-$ ions proceeds simultaneously with NH$_3$ formation, so that the exchange rate of H$^-$ ions in Ru[[Ca$_2$N]$^-\cdot$e$_{1-x}$H$_x^-\cdot$H$_x^-$ with D$^-$ ions can be estimated to be 1.66 mmol g$^{-1}$ h$^{-1}$ from the initial NH$_3$ formation rate (0 h). On the other hand, when Ru[[Ca$_2$N]$^-\cdot$e$_{1-x}$H$_x^-\cdot$H$_x^-$ is heated at 340 °C under a D$_2$ atmosphere without N$_2$ (Fig. S6†), the exchange rate of H$^-$ with D$^-$ ions remains at only 0.18 mmol g$^{-1}$ h$^{-1}$, which is lower by an order of magnitude than that (1.66 mmol g$^{-1}$ h$^{-1}$) shown in Fig. 4a. These results reveal that N adatoms on Ru[[Ca$_2$N]$^-\cdot$e$_{1-x}$H$_x^-\cdot$H$_x^-$ preferentially react with H atoms derived from H$^-$ ions in [Ca$_2$N]$^-\cdot$e$_{1-x}$H$_x^-\cdot$H$_x^-$ rather than H atoms produced by the dissociative adsorption of H$_2$ on Ru surfaces because H atoms on Ru are readily incorporated into the support material to form H$^-$ ions by reaction with an anionic electron.

To summarize these results, we propose the reaction mechanism illustrated in Fig. 4c. The dissociative adsorption of H$_2$ forms H adatoms on Ru surfaces under the reaction conditions, and Ca$_2$N$^-$ is readily transformed into Ca$_2$NH by the reaction of anionic electrons in Ca$_2$N$^-$ with spillover H adatoms ([Ca$_2$N]$^-\cdot$e$^-\cdot$H $\rightarrow$ [Ca$_2$N]$^-\cdot$H$^-$, reaction 1 in Fig. 4c). Ca$_2$N$^-$ and Ca$_2$NH are in an equilibrium through the reversible hydrogen storage reaction; therefore, nonstoichiometric [Ca$_2$N]$^-\cdot$e$_{1-x}$H$_x^-\cdot$H$_x^-$ rather than stoichiometric Ca$_2$NH is expected to result from the transformation (reaction 2 in Fig. 4c). [Ca$_2$N]$^-\cdot$e$_{1-x}$H$_x^-\cdot$H$_x^-$ with small work functions strongly donate electrons into Ru, which facilitates the cleavage of N$_2$ molecules on Ru surfaces. N adatoms on Ru surfaces prefer to react with H atoms derived from the hydride to form ammonia and anionic electrons (hydrogen vacancies) in [Ca$_2$N]$^-\cdot$e$_{1-x}$H$_x^-\cdot$H$_x^-$ (reaction 3 in Fig. 4c), as demonstrated in the D$_2$ experiments. This mechanism is distinct from ammonia synthesis on conventional heterogeneous catalysts, where the reaction between N and H adatoms on transition metal surfaces produces ammonia. The incorporation of hydrogen adatoms formed on Ru surfaces into the 2D layer of Ca$_2$N is driven by reaction with anionic electrons and results in the suppression of active site saturation by hydrogen, i.e., hydrogen poisoning of Ru. Thus, the reaction mechanism is very similar to that for Ru/C12A7:e$^-$, as elucidated by kinetic analyses. Therefore, the rate-determining step for ammonia synthesis over Ru/Ca$_2$N:e$^-$ is not N$_2$ cleavage, but subsequent processes, possibly the formation of NH species. However, Ru/Ca$_2$N:e$^-$ is far superior to Ru/C12A7:e$^-$ in terms of catalytic performance for ammonia synthesis below 300 °C; Ru/C12A7:e$^-$ has moderate catalytic activity and high activation energy (90 kJ mol$^{-1}$) for ammonia synthesis below 300 °C, where the reaction mechanism is analogous to that for conventional catalysts. The H$_2$ absorption–desorption characteristics of Ru/C12A7:e$^-$ are observed above ca. 350 °C, which is due mainly to the stabilization of $^+$ ions in the positively charged sub-nanometer sized cages, so that a larger thermal energy is necessary to release hydrogen through the cage wall. On the other hand, the facile hydrogen
Table 2  Calculated work functions and hydrogen vacancy (VH) formation energies$^a$

| Compound                  | Space group | Surface index | WF$^{\text{calc}}$ (eV) | WF$^{\text{exp}}$ (eV) | $\Delta E(VH)$ (eV per atom) |
|---------------------------|-------------|---------------|--------------------------|-------------------------|-------------------------------|
| Ca$_2$N:e$^-$             | $R3m$       | (111)         | 3.3                      | 3.5$^b$                | —                            |
| Ca$_2$N:e$^-$             | $R3m$       | (112)         | 2.5                      | 2.6$^b$                | —                            |
| Ca$_2$NH                  | $Fd\bar{3}m$| (100)         | 2.8$^c$                  | —                      | —                            |
| Ca$_2$NH$_{1/16}$         | $Fd\bar{3}m$| (100)         | 2.3                      | —                      | —                            |
| Ca$_2$NH$_{2/16}$         | $Fd\bar{3}m$| (100)         | 2.3                      | —                      | 0.88–1.02                    |
| Ru/Ca$_2$NH$_{1/16}$      | —           | (100)         | —                        | —                      | 0.43–0.67                    |
| Ru/N$_2$/Ca$_2$NH$_{1/16}$| —           | (100)         | —                        | —                      | 0.49–0.91                    |
| CaH$_3$                   | $Pnma$      | (010)         | 4.0                      | —                      | —                            |
| CaH$_{3-1/24}$            | $Pnma$      | (010)         | 2.3                      | —                      | 1.08–1.11                    |
| CaNH                      | $Fm\bar{3}m$| (100)         | $\geq 3.6^{c,d}$         | —                      | —                            |
| CaNH$_{1/32}$             | $Fm\bar{3}m$| (100)         | —                        | 1.71                   | —                            |

$^a$ $\Delta E(VH)$ for compound AH$_{1-x}$ is the total energy difference, defined as $[E(AH_{1-x}) + xE(H_2)/2] - E(AH)$, where $E(AH)$, $E(AH_{1-x})$, and $E(H_2)$ are, respectively, the total energies of the stoichiometric AH, H-deficient AH$_{1-x}$, and hydrogen molecule. $^b$ Ref. 13. $^c$ Ca$_2$NH and CaNH are not metallic compounds, and thus the values of WF$^{\text{calc}}$ correspond to the positions of the valence band maximum with respect to the vacuum level. $^d$ The H atoms in CaNH show partial occupation, so that determination of the hydrogen positions for DFT calculations is a difficult task; therefore, the following assumptions were adopted only for CaNH: that (1) the lattice parameters are fixed to the experimental values, (2) the positions of hydrogen were determined to maintain the local stoichiometry at the topmost layer of the CaNH surface, and (3) the ionic positions were all fixed to those in the bulk to avoid an artificial surface reconstruction caused by an ordered configuration of H atoms. If the surface structure of CaNH with the ordered configuration of hydrogen is relaxed, then the vacuum level required for the WF calculation cannot be determined. In a realistic situation of CaNH, ionic relaxations lead to a more stable electronic structure, and thereby the position of the valence band maximum becomes deeper. Therefore, the calculated value based on the above assumptions can be recognized as a lower limit.

Fig. 4  (a) Reaction time profiles for ammonia synthesis from N$_2$ and D$_2$ over Ru/Ca$_2$N:e$^-$ at 340 °C (reaction conditions: catalyst, 0.2 g; reaction gas, N$_2$ : D$_2$ = 1 : 3; reaction pressure, 60 kPa). Prior to reaction, Ru/Ca$_2$N:e$^-$ was heated under N$_2$ + H$_2$ flow (N$_2$ : H$_2$ = 1 : 3) at 340 °C for 10 h to form Ru/Ca$_2$NH. (b) TPD profiles of Ru/Ca$_2$N:e$^-$ after the reaction (a). TPD measurements were performed (10 °C min$^{-1}$) with Ar flow. (c) Schematic illustration of ammonia synthesis over Ru/Ca$_2$N:e$^-$: During ammonia synthesis over Ru/Ca$_2$N:e$^-$, H$_2$ is incorporated into Ca$_2$N:e$^-$ as H$^-$ ions to form Ca$_2$NH (reaction 1). The H$^-$ ions are released from Ca$_2$NH, which leaves electrons to form a hydrogen vacancy near the Ru-support interface (reaction 2). The cleavage of N$_2$ proceeds effectively on Ru surfaces due to electron injection from [Ca$_2$N]$^+$·e$^-$.NH$^-$ and the nitrogen adatoms react with H radicals to form ammonia (reaction 3).
exchange reaction on Ru/Ca$_2$N$\text{e}^-$ proceeds at lower temperatures (from 200 °C) than that on Ru/C12A7$\text{e}^-$ because H$^-$ ions are located in the open spaces between two cationic slabs [Ca$_2$N]. This facile hydrogen exchange at lower temperatures thus makes it possible for noticeable ammonia synthesis to occur, even at ca. 200 °C.

The experimental results described above demonstrate the validity of our proposed design concept for the Ru-support for low-temperature NH$_3$ synthesis, i.e., the reversible exchangeability between H$^-$ ions and electrons plays an important role for effective ammonia synthesis at low temperatures. The effectiveness of this idea is further demonstrated by the use of CaH$_2$, the simplest hydride, as a support for a Ru catalyst. Although CaH$_2$ itself has a WF of 4.0 eV, the WF of CaH$_2$ with VH (i.e., CaH$_2$-[H]) has a small value (2.3 eV) similar to that for nonstoichiometric Ca$_2$NH (Table 2). Ru/CaH$_2$ exhibits high catalytic activity with a low activation energy (51 kJ mol$^{-1}$), as expected from its low work function (2.3 eV), which accounts for the strong catalytic activity with a low activation energy for NH$_3$ synthesis at lower reaction temperatures.

**Conclusions**

Ru/Ca$_2$N$\text{e}^-$ exhibits much higher catalytic performance for ammonia synthesis at low temperatures than heterogeneous catalysts reported to date, including Ru/C12A7$\text{e}^-$. This is not attributed to the Ca$_2$N$\text{e}^-$ electrode, but to a hydrogen-deficient Ca$_2$NH hydride ([Ca$_2$N$\text{e}^-$]-H$_x$) formed during the ammonia synthesis reaction. Both Ru/CaH$_2$ and Ru/Ca$_2$NH hydrides exhibit high catalytic activity for ammonia synthesis. The formation of anionic electrons in these hydrides results in a small work function (2.3 eV), which accounts for the strong electron donation ability that facilitates efficient N$_2$ cleavage on Ru. N adatoms on Ru preferentially react with H atoms derived from the hydride to form NH$_3$ species. These reactions proceed even at ca. 200 °C, so that ammonia synthesis is catalyzed above 200 °C. In addition, the hydrides suppress H$_2$ poisoning of the Ru surface due to their hydrogen storage properties. The present results demonstrate that the strong electron-donating ability and the reversible exchangeability between H$^-$ ions in the lattice and anionic electrons at low temperatures are requisite for the Ru catalyst support in low-temperature ammonia synthesis.

**Acknowledgements**

The authors appreciate M. Okunaka, S. Fujimoto, E. Sano, and Y. Takasaki for technical assistance and S. Kanbara for conducting catalytic tests. This work was supported by funds from the Accelerated Innovation Research Initiative Turning Top Science and Ideas into High-Impact Values (ACCEL) program of the Japan Science and Technology Agency (JST). A portion of this work was supported by a Kakenhi Grant-in-Aid (No. 15H04183) from the Japan Society for the Promotion of Science (JSPS).

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