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−·e−L−x·Hx− formed by a reversible reaction of an anionic electron with hydrogen ([Ca2N]·e− + xH ↔ [Ca2N]1−·e−L−x·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%) and facile liquefaction under mild conditions. Ammonia synthesis at low temperature is thermodynamically favorable but still presents a major challenge. Extensive studies on N2 activation with organometallic complexes have been conducted over the last decade. Although NH3 has been successfully produced under ambient conditions, the rate of formation is still far from appropriate for practical application, and strong reducing agents and extra proton sources are required to afford NH3.

In heterogeneous catalysts, it is widely recognized that ruthenium (Ru) catalysts work under milder conditions than iron-based catalysts for the Haber–Bosch process. The activity of Ru catalysts is substantially enhanced by electron injection from alkali or alkali earth metal oxide promoters. 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). 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 (C12A7·e−)33-supported Ru catalyst exhibits much higher activity for ammonia synthesis than alkali-promoted Ru catalysts. The intrinsically low work function (ca. 2.4 eV) of C12A7·e− 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−H4 species. 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\textsuperscript{−} is diminished at low temperatures (<320 °C), which is strongly correlated with the weak H\textsubscript{2} desorption properties at low temperatures. The electron–hydride ion exchange reaction in C12A7:e\textsuperscript{−} is accomplished by H desorption through a cage wall composed of a rigid monolayer of Ca-Al\textsubscript{2}O\textsubscript{3}; therefore, the exchange reaction in C12A7:e\textsuperscript{−} 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 electride materials with hydride ions exposed to the surface, i.e., metal hydrides.

Dicalcium nitride, \([\text{Ca}_2\text{N}]\text{e}^-\) (denoted as Ca\textsubscript{2}N\textsubscript{e}\textsuperscript{−}), was confirmed as a two-dimensional (2D) electride with a low work function (2.6 eV), in which anionic electrons confined between the \([\text{Ca}_2\text{N}]^-\) layers as counter anions\textsuperscript{17–19} can be partly exposed to the surfaces. In addition, this material can be converted into Ca\textsubscript{2}NH \(([\text{Ca}_2\text{N}]^-\text{H}^-)\) by the reaction between an anionic electron and a hydrogen, which is analogous to that for C12A7:e\textsuperscript{−}. Therefore, Ca\textsubscript{2}NH 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 Ca\textsubscript{2}NH and CaH\textsubscript{2}, which are not intrinsically low work function materials, strongly promote the cleavage of N\textsubscript{2} to form NH\textsubscript{3} 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 N\textsubscript{2} dissociation and prevents hydrogen poisoning of the Ru surface.

Results and discussion

Catalytic performance of Ru-loaded Ca\textsubscript{2}N\textsubscript{e}\textsuperscript{−}

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/Ca\textsubscript{2}N\textsubscript{e}\textsuperscript{−} (3.1%) is much smaller than that of Ru(2%)-Cs/MgO (50.4%) because of its low surface area (1.5 m\textsuperscript{2}g\textsuperscript{−1}), which is similar to the results for Ru/C12A7:e\textsuperscript{−}. However, Ru/Ca\textsubscript{2}N\textsubscript{e}\textsuperscript{−} 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.\textsuperscript{20,21} Accordingly, the turn-over frequency (TOF) with Ru/Ca\textsubscript{2}N\textsubscript{e}\textsuperscript{−} is higher than that with Ru–Cs/MgO by an order of magnitude. It is noteworthy that Ru/Ca\textsubscript{2}N\textsubscript{e}\textsuperscript{−} exhibits higher catalytic activity than Ru/C12A7:e\textsuperscript{−} 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/Ca\textsubscript{2}N\textsubscript{e}\textsuperscript{−} for ammonia synthesis is 60 kJ mol\textsuperscript{−1}, which is one-half that of Ru–Cs/MgO (120 kJ mol\textsuperscript{−1}). We have previously reported\textsuperscript{9} that a change in the activation energy is observed for Ru/C12A7:e\textsuperscript{−}, i.e., the activation energy at 400–320 °C is 50 kJ mol\textsuperscript{−1} but exceeds 90 kJ mol\textsuperscript{−1} at lower reaction temperatures (320–250 °C) and no reaction is observed at 200 °C. These results indicate that Ru/Ca\textsubscript{2}N\textsubscript{e}\textsuperscript{−} is superior to Ru/C12A7:e\textsuperscript{−} for low-temperature ammonia synthesis. Furthermore, we note that Ru/Ca\textsubscript{2}N\textsubscript{e}\textsuperscript{−} 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 Ca\textsubscript{2}N\textsubscript{e}\textsuperscript{−} (1.06 mmol). This result indicates that the ammonia produced is not derived from the decomposition of the Ca\textsubscript{2}N\textsubscript{e}\textsuperscript{−} support.

Fig. 1c and d show the dependence of the ammonia synthesis rate on the partial pressure of N\textsubscript{2} and H\textsubscript{2}, respectively. The reaction orders with respect to N\textsubscript{2} and H\textsubscript{2} over various Ru catalysts are also summarized in Table S1.\textsuperscript{†} The reaction order for N\textsubscript{2} with conventional heterogeneous catalysts is 0.8–1.0,\textsuperscript{11,22,23} where N\textsubscript{2} dissociation is the rate-determining step for ammonia synthesis. In contrast, the reaction order for N\textsubscript{2} with Ru/Ca\textsubscript{2}N\textsubscript{e}\textsuperscript{−} is almost one-half, which is attributed to a more dense population of N atoms on Ru/Ca\textsubscript{2}N\textsubscript{e}\textsuperscript{−} than on the other catalysts. Two results were noted; one is that the Ru/Ca\textsubscript{2}N\textsubscript{e}\textsuperscript{−} catalyst also facilitates the N\textsubscript{2} isotopic exchange reaction (\textsuperscript{15}N\textsubscript{2} + \textsuperscript{14}N\textsubscript{2} = \textsuperscript{21}N\textsubscript{14}N) with a lower activation energy (59 kJ mol\textsuperscript{−1}) than conventional Ru catalysts (>130 kJ mol\textsuperscript{−1}) (Fig. S1†), indicating that the energy barrier for N\textsubscript{2} dissociation is significantly lowered by Ru/Ca\textsubscript{2}N\textsubscript{e}\textsuperscript{−}. The other result is that Ru/Ca\textsubscript{2}N\textsubscript{e}\textsuperscript{−} has a positive reaction order with respect to H\textsubscript{2} in contrast to the case for Ru–Cs/MgO (β < 0), which indicates that ammonia synthesis over Ru/Ca\textsubscript{2}N\textsubscript{e}\textsuperscript{−} is not inhibited by hydrogen adsorption, i.e., hydrogen poisoning.\textsuperscript{11,20} Thus, Ru/Ca\textsubscript{2}N\textsubscript{e}\textsuperscript{−} maintains the key kinetics observed with Ru/C12A7:e\textsuperscript{−}, in that N\textsubscript{2} cleavage is not the rate-determining step for ammonia synthesis\textsuperscript{9} and the reactions are free from hydrogen.
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:e⁻ as a support material. Furthermore, the catalytic activity of Ru/Ca₂N:e⁻ 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:e⁻ is moderate at this temperature, which is due to the poisoning effect of H atoms on Ru/C₁₂A₇:e⁻ at low reaction temperature (≤320 °C). These results clearly indicate that Ru/Ca₂N:e⁻ exhibits improved performance for ammonia synthesis compared with Ru/C₁₂A₇:e⁻, even at lower temperatures and elevated pressures.

**Structural properties of Ca-nitride catalysts**

X-ray diffraction (XRD) and Raman spectroscopy measurements confirmed that Ca₂NH, 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 Ca₂N phase (Fig. 2b), whereas new peaks due to Ca₂NH with cubic structure (Fig. 2c) appear. There is no CaNH 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. The formation of Ca₂NH 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 CaNH has broad bands in the range from 100 to 1000 cm⁻¹ and is completely different from that of Ca₂NH (Fig. S3†). In addition, CaNH has an intense band centered at 3122 cm⁻¹, which is attributed to the N-H stretching mode in imide ions. 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 Ca₂NH, which indicates that the catalyst consists mainly of Ca₂NH. 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 (H⁰ + e⁻ → H⁻) 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 (H⁻ → H⁰ + e⁻) from Ru/Ca₂N⁻ after reaction above 200 °C (the actual material is Ru/Ca₂NH) 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⁻⁺]²⁻·H⁻, rather than stoichiometric Ca₂NH, is formed by the reaction between anionic electrons and H⁻ ions [Ca₂N⁻⁺ + H⁻ → [Ca₂N⁻⁺]²⁻·H⁻] during ammonia synthesis. This exchangeability is a key reaction confirmed in Ru/C₁₂A₇:e⁻, but the significant difference between Ru/Ca₂N⁻ and Ru/C₁₂A₇:e⁻ is the onset temperature for H₂ desorption, i.e., 200 °C for Ru/Ca₂N⁻ and 350 °C for Ru/C₁₂A₇:e⁻.

**DFT calculations**

To shed more light on the electronic state of Ca₂NH, density functional theory (DFT) calculations were conducted (detailed conditions are described in the ESI†). Fig. 3a shows a computational model of the Ca₂NH(100) surface, and Fig. 3b–d show the calculated electronic states of Ca₂NH(100), Ca₂NH₁₋ₓ(100), and Ru-loaded Ca₂NH(100), respectively. The calculations were executed under the condition of an electrically neutral unit cell. The calculated work functions (WFs) for Ca₂N (3.3, 2.5 eV) and Ru (4.8 eV) are close to the measured values (19,22,23) (Table 2), which indicates the reliability of the DFT calculations. The
calculated WF for Ca$_2$NH is significantly smaller than that for CaNH, which indicates the higher electron-donating ability of Ca$_2$NH than CaNH. Notably, Ca$_2$NH(100) with a hydrogen vacancy (VH, i.e., Ca$_2$NH$_{1-x}$) shows a much lower WF (2.3 eV) than both Ca$_2$NH (2.8 eV) and Ca$_2$N$\text{e}^-$ (2.5 eV). When an anionic electron is confined at the VH position in Ca$_2$NH (see the inset of Fig. 3c), the anionic electron state is located above the valence band maximum (VBM) of Ca$_2$NH, as shown in Fig. 3c. The confinement of the anionic electron in Ca$_2$NH$_{1-x}$ is stronger than that of the 2D layered space in Ca$_2$N$_x$ and thus Ca$_2$NH(100) with VH has a small WF, which reflects the strong electron-donation ability of Ca$_2$NH$_{1-x}$.

Ca$_2$NH$_{1-x}$ can be readily formed by the combination of Ca$_2$N$_x$ 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$_2$NH(100), which indicates the difficulty of hydrogen vacancy formation. The density of states (DOS) for an H$^-$ ion in Ca$_2$NH(100) is found at a relatively deep level, as shown in Fig. 3c and the inset of Fig. 3d (–6 eV below the Fermi level ($E_F$) for bulk H$^-$ and –4 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$_2$NH(100) surface; the VH formation energy for Ru$_x$-loaded Ca$_2$NH(100) is decreased to 0.43–0.67 eV. Fig. 3d shows that the DOS for an H$^-$ ion bonded with Ru (H$^0$ in the inset of Fig. 3d) are energetically shifted up from a relatively deep level to a shallow level (–0.5 eV below $E_F$). Thus, an H$^-$ ion bonded with Ru is almost ready to form an anionic electron by the desorption of H$^0$. 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$^0$ easier. This situation is maintained even when an N$_2$ molecule is adsorbed on Ru; the formation energy for VH on Ru$_x$N$_2$–Ca$_2$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$_2$N$^-$]$_x$e$_{1-x}$H$_{y^+}$, by Ru catalysts during the reaction, which facilitates N$_2$ cleavage on the hydride via electron donation from the anionic electrons to the loaded Ru nanoparticles.

**Reaction mechanism over Ru[Ca$_2$N$^-$]$_x$e$_{1-x}$H$_{y^+}$**

Ammonia synthesis from N$_2$ and D$_2$ was examined to elucidate the reaction mechanism over Ru[Ca$_2$N$^-$]$_x$e$_{1-x}$H$_{y^+}$. The initial gas (reaction time = 0 h) consists mainly of N$_2$ (m/z = 28) and D$_2$ (m/z = 4), whereas the amounts of other species such as H$_2$ (m/z = 2}
ions rather than directly react with N adatoms. TPD measurements (Fig. 4b) show that H2, HD, and D2 species were desorbed from the catalyst after the reaction. It is thus evident that some H− ions in Ru/[Ca2N]−·e1−·H+ are replaced by D− ions during the ammonia synthesis reaction. The incorporation of D− ions proceeds simultaneously with NH3 formation, so that the exchange rate of H− ions in Ru/[Ca2N]−·e1−·H+ with D− ions can be estimated to be 1.66 mmol g−1 h−1 from the initial NH3 formation rate (0–3 h). On the other hand, when Ru/[Ca2N]−·e1−·H+ is heated at 340 °C under a D2 atmosphere without N2 (Fig. S6†), the exchange rate of H− ions 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/[Ca2N]−·e1−·H+ preferentially react with H atoms derived from H− ions in [Ca2N]−·e1−·H+ rather than H atoms produced by the dissociative adsorption of H2 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 H2 forms H adatoms on Ru surfaces under the reaction conditions, and Ca2N− is readily transformed into Ca2NH by the reaction of anionic electrons in Ca2N− with spillover H adatoms ([Ca2N]−·e− + H → [Ca2N]−·H+, reaction 1 in Fig. 4c). Ca2Ne− and Ca2NH are in an equilibrium through the reversible hydrogen storage reaction; therefore, nonstoichiometric [Ca2N]−·e1−·H+ rather than stoichiometric Ca2NH is expected to result from the transformation (reaction 2 in Fig. 4c). [Ca2N]−·e1−·H+ with small work functions strongly donate electrons into Ru, which facilitates the cleavage of N2 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 [Ca2N]−·e1−·H+, rather than stoichiometric Ca2NH as demonstrated in the D2 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.14 The incorporation of hydrogen adatoms formed on Ru surfaces into the 2D layer of Ca2N 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.16 Therefore, the rate-determining step for ammonia synthesis over Ru/Ca2N:e− is not N2 cleavage, but subsequent processes, possibly the formation of NH species. However, Ru/Ca2N: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 H2 absorption-desorption characteristics of Ru/C12A7:e− are observed above ca. 350 °C,16 which is due mainly to the stabilization of H− ions in the positively charged sub-nanometer sized cages, so that a larger thermal energy is necessary to release hydrogen through the cage wall.15 On the other hand, the facile hydrogen
Table 2  Calculated work functions and hydrogen vacancy (VH) formation energies\textsuperscript{a}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space group</th>
<th>Surface index</th>
<th>WF\textsuperscript{calc} (eV)</th>
<th>WF\textsuperscript{exp} (eV)</th>
<th>(\Delta E (VH)) (eV per atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ca}_2\text{N}:e)</td>
<td>(R\bar{3}m)</td>
<td>(111)</td>
<td>3.3</td>
<td>3.5\textsuperscript{b}</td>
<td>—</td>
</tr>
<tr>
<td>(\text{Ca}_2\text{N}:e)</td>
<td>(R\bar{3}m)</td>
<td>(112)</td>
<td>2.5</td>
<td>2.6\textsuperscript{b}</td>
<td>—</td>
</tr>
<tr>
<td>(\text{Ca}_2\text{NH})</td>
<td>(F\bar{d}\bar{3}m)</td>
<td>(100)</td>
<td>2.8\textsuperscript{c}</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(\text{Ca}<em>2\text{NH}</em>{1/16})</td>
<td>(F\bar{d}\bar{3}m)</td>
<td>(100)</td>
<td>2.3</td>
<td>—</td>
<td>1.00</td>
</tr>
<tr>
<td>(\text{Ru/\text{Ca}<em>2\text{NH}</em>{1/16}})</td>
<td>—</td>
<td>(100)</td>
<td>—</td>
<td>0.88–1.02</td>
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<tr>
<td>(\text{Ru/\text{Ca}<em>2\text{NH}</em>{1/16}})</td>
<td>—</td>
<td>(100)</td>
<td>—</td>
<td>0.43–0.67</td>
<td>—</td>
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<tr>
<td>(\text{CaH}_2)</td>
<td>(Pnma)</td>
<td>(010)</td>
<td>4.0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(\text{CaNH})</td>
<td>(Fm\bar{3}m)</td>
<td>(100)</td>
<td>2.3</td>
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<tr>
<td>(\text{CaNH}_{1/32})</td>
<td>(Fm\bar{3}m)</td>
<td>(100)</td>
<td>3.6\textsuperscript{c,d}</td>
<td>—</td>
<td>1.71</td>
</tr>
</tbody>
</table>

\textsuperscript{a} \(\Delta E(VH)\) for compound \(\text{AH}_{1-x}\) is the total energy difference, defined as \([E(\text{AH}_{1-x}) + xE(H_2)/2] - E(\text{AH})\), where \(E(\text{AH}), E(\text{AH}_{1-x}),\) and \(E(H_2)\) are, respectively, the total energies of the stoichiometric \(\text{AH}, H\)-deficient \(\text{AH}_{1-x},\) and hydrogen molecule. \textsuperscript{b} Ref. 13. \textsuperscript{c} \(\text{Ca}_2\text{NH}\) and \(\text{CaNH}\) are not metallic compounds, and thus the values of WF\textsuperscript{calc} correspond to the positions of the valence band maximum with respect to the vacuum level. \textsuperscript{d} The \(H\) atoms in \(\text{CaNH}\) 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 \(\text{CaNH}\): 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 \(\text{CaNH}\) 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 \(\text{CaNH}\) 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 \(\text{CaNH}\), 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 \(\text{Ru/\text{Ca}_2\text{N}:e}\) at 340 °C (reaction conditions: catalyst, 0.2 g; reaction gas, \(N_2:D_2 = 1:3\); reaction pressure, 60 kPa). Prior to reaction, \(\text{Ru/\text{Ca}_2\text{N}:e}\) was heated under \(N_2:H_2\) flow (\(N_2:H_2 = 1:3\)) at 340 °C for 10 h to form \(\text{Ru/\text{Ca}_2\text{NH}}\). (b) TPD profiles of \(\text{Ru/\text{Ca}_2\text{N}:e}\) after the reaction (a). TPD measurements were performed (10 °C min\textsuperscript{−1}) with \(Ar\) flow. (c) Schematic illustration of ammonia synthesis over \(\text{Ru/\text{Ca}_2\text{N}:e}\). During ammonia synthesis over \(\text{Ru/\text{Ca}_2\text{N}:e}\), \(H_2\) is incorporated into \(\text{Ca}_2\text{N}:e\) as \(H^{-}\) ions to form \(\text{Ca}_2\text{NH}\) (reaction 1). The \(H^{-}\) ions are released from \(\text{Ca}_2\text{NH}\), 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 \(\text{[Ca}_2\text{N]}^{-}\cdot e_{1-x}\cdot H_x^{-}\) 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 exchange-ability 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$_2$ (i.e., CaH$_2$-$\text{e}^-$) 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 (Table 1), and has reaction orders for N$_2$ and H$_2$ similar to those for Ru/Ca$_2$N$\text{e}^-$ (Table S1). The formation of hydrogen vacancies in CaH$_2$ is difficult because hydrogen desorption from CaH$_2$ occurs above 600 °C.$^{36}$ However, hydrogen can easily desorb from the surface of CaH$_2$ above 200 °C in the presence of a Ru catalyst (Fig. S7†). Thus, anionic electrons are formed in Ru/CaH$_2$ during the reaction, which results in efficient ammonia 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]$^-$·e$^-$·H$_2$) formed during the ammonia synthesis reaction. Both Ru/CaH$_2$ and Ru/Ca$_2$N 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 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.

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Notes and references