Regulating kinetics and thermodynamics of electrochemical nitrogen reduction with metal single-atom catalysts in a pressurized electrolyser

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Using renewable electricity to synthesize ammonia from nitrogen paves a sustainable route to making value-added chemicals but yet requires further advances in electrocatalyst development and device integration. By engineering both electrocatalyst and electrolyzer to simultaneously regulate chemical kinetics and thermodynamic driving forces of the electrocatalytic nitrogen reduction reaction (ENRR), we report herein stereoconfinement-induced densely populated metal single atoms (Rh, Ru, Co) on graphdiyne (GDY) matrix (formulated as M SA/GDY) and realized a boosted ENRR activity in a pressurized reaction system. Remarkably, under the pressurized environment, the hydrogen evolution reaction of M SA/GDY at 55 atm exhibited a record-high NH3 formation rate of 74.15 μg h⁻¹·cm⁻², a Faraday efficiency of 20.36%, and a NH3 partial current of 0.35 mA cm⁻² at −0.20 V versus reversible hydrogen electrode, which, respectively, displayed 7.3-, 4.9-, and 9.2-fold enhancements compared with those obtained under ambient conditions. Furthermore, a time-independent ammonia yield rate using purified ¹⁵N2 confirmed the concrete ammno electroproduction. Theoretical calculations reveal that the driving force for the formation of end-on N₂• on Rh SA/GDY increased by 9.62 kJ/mol under the pressurized conditions, facilitating the ENRR process. We envisage that the cooperative regulations of catalysts and electrochemical devices open up the possibilities for industrially viable electrochemical ammonia production.

Significance

The present-day industrial ammonia synthesis is overreliance on the Haber–Bosch process, yet consumes more than 1% of the global energy supply along with gigatonne greenhouse-gas emission per year. Electrochemical nitrogen reduction reaction (ENRR) offers a sustainable path to produce ammonia under mild conditions, while its efficiency achieved by far is fairly low, which requires the development of both catalysts and electrolyzers. Here, by the cooperation of densely populated metal single atoms on graphdiyne substrate with the pressurized electrocatalytic system, the kinetics and the thermodynamic driving force of ENRR are effectively regulated, leading to a record-high ammonia yield rate. This work motivates the technological and material coevolution for the ENRR toward its envisioned application.

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and thermodynamic driving forces and be the game-changer for the ENRR.

Herein, we showcase that SACs-catalyzed N\textsubscript{2} reduction in a pressurized system is an effective design principle to enhance both the chemical kinetics and thermodynamic process, leading to the amplified ENRR activity with simultaneously retarded HER. The deployed SACs contain Ru, Rh, and Co atoms featured with densely populated active sites and stabilized on graphdiyne (GDY) support (referred to as M SA/GDY; M = Rh, Ru, and Co); these electrocatalysts were prepared by a facile and mild method via stereoconfinement of metal atoms on the GDY framework. Through extensive ENRR test using adequately cleaned N\textsubscript{2}, we found that the as-prepared M SA/GDY electrocatalysts render prominently enhanced ammonia electroproduction with obvious HER inhibition at the pressurized electrocatalytic system, suggesting positive cooperation between SAC and the pressurized environment. Remarkably, a record-high ammonia yield rate of 74.15 µg h\textsuperscript{-1} cm\textsuperscript{-2}, a Faraday efficiency (FE) of 20.36\%, and a NH\textsubscript{3} partial current density of 0.35 mA cm\textsuperscript{-2} were achieved for Rh SA/GDY at 55 atm of N\textsubscript{2}, which shows 7.3-, 4.9-, and 9.2-fold enhancement in comparison with those obtained in ambient conditions, outperforming the state-of-art ENRR catalysts. Additionally, a time-independent ammonia yield rate using adequately cleaned \textsuperscript{15}N\textsubscript{2} ensured the ammonia electrosynthesis from N\textsubscript{2}.

### Results

#### Synthesis and Characterizations.

The synthetic rationale of M SA/GDY preparation was based on the well-established reductive elimination reactions for the C–C coupling, such as Suzuki, Negishi, and Sonogashira cross-coupling progress (32–34). Typically, for the reductive elimination step, substrates and a metal cation form coordination complexes, and then the metal center accepts electrons from the substrates, leading to the formation of C–C bond and the low-valent metal center. We adopted this reaction mechanism and designed an efficient, one-pot synthetic procedure (Fig. L4) for the preparation of high-loading M SA/GDY (M = Rh, Ru, and Co) materials. Metal trichloride of RhCl\textsubscript{3}, RuCl\textsubscript{3}, and CoCl\textsubscript{2} were used as metal precursors to efficiently drive the cross-coupling process thanks to their strong oxidation ability and suitable solubility in pyridine. In the presence of a base (pyridine), the GDY monomer can be deprotonated to a certain degree, forming a coordination complex with Rh\textsuperscript{3+}, Ru\textsuperscript{2+}, and Co\textsuperscript{2+}, and then, the cross-coupling of GDY monomers occurs at elevated temperature, resulting in the formation of GDY with reduced metal atoms. The reduced metal atoms were singly immobilized on the GDY framework through stereoconfinement, yielding the desired products. Significantly, our synthetic process was proceeded by one pot under a mild temperature of 60 °C, which dramatically decreases the energy consumption (SI Appendix, Experiment section).

The obtained M SA/GDY samples were primarily subjected to a close structure and morphology analysis. Raman spectra of these samples show three different bands, ascribing to the D band (1,365 cm\textsuperscript{-1}), G band (1,534 cm\textsuperscript{-1}), and conjugated diyne linkage vibration (2,167 cm\textsuperscript{-1}) (SI Appendix, Fig. SL4) (35–37). Their X-ray diffraction patterns showed a sole broad feature at ~2θ corresponding to the interlayer distance of the carbon matrix and excluding the absence of any crystalline species in the M SA/GDY (SI Appendix, Fig. S1B) (38). Further, the scanning transmission electron microscopy (STEM) images recorded with aberration-corrected high-angle annular dark-field (HAADF) detector at various regions evidenced the atomic-level dispersion of highly concentrated metal atoms (Rh, Ru, Co) by Z-contrast analysis (Fig. 1 B, C, H, I, N, and O and SI Appendix, Fig. S2). Moreover, the atomic-scale energy-dispersive X-ray spectroscopy mapping revealed the distinguishable element signals of C and isolated metal atoms (Rh, Ru, Co) across uniformly in the GDY matrix (Fig. 1 D–G, J–M, and P–S). Inductively coupled plasma optical emission spectrometry analysis confirmed the weight fraction of corresponding metals to be 13.22, 15.31, and 12.08 wt % for Rh, Ru, and Co, respectively. In principle, this simple one-pot synthetic method can be generally extended to prepare other metal single-atom catalysts by exchanging the metal precursors with proper oxidation power.

To uncover the chemical states and atomic coordination environment of M SA/GDY, X-ray photoelectron spectroscopy (XPS) and synchrotron-based X-ray absorption spectroscopy (XAS) were performed. As shown in SI Appendix, Fig. S3, representative XPS survey spectra show two major characteristic peaks of C 1s and O 1s at 284.6 and 532 eV, respectively. The core-level XPS spectra of Ru 3d and Ru 3p can be deconvoluted into spin-orbit peaks, corresponding to the Ru \textsuperscript{0} at around 307.5 and 312.2 eV, Ru\textsuperscript{0} at 461.8 and 483.7 eV (Fig. 2 A and B) (39, 40). The reduced valence state of the metal center suggests that the reductive elimination process indeed occurs as expected, providing the driving force for the GDY formation and metal deposition. It is important to point out that the high-resolution Co 2p profile mainly comprises Co\textsuperscript{2+} at around 780.5 and 796.4 eV, which arises from the easy oxidation of Co atoms (Fig. 2C) (41). Furthermore, the X-ray absorption near-edge spectroscopy (XANES, Fig. 2D) revealed that the absorption edge of Rh SA/GDY is overlapped well with that of Rh foil, in agreement with the zero valence feature of the Rh single atoms. The Fourier-transformed extended X-ray absorption fine structure (FT-EXAFS) was applied to explore the precise coordination structure. As shown in Fig. 2E, a sole and dominant peak at ~1.5 Å is ascribed to the Rh–C bond, which is shorter than the Rh–Rh bond at 2.4 Å, suggesting the salient single-atom feature. In addition, EXAFS fitting shows that the Rh coordination number is 3.92, close to 4, demonstrating the presence of Rh atoms coordinated by four surrounding carbon atoms (SI Appendix, Fig. S4 and Table S1).

#### ENRR Tests.

Nitrogen has poor solubility in water and its concentration in water at standard conditions (25 °C and 1 atm) is 6.1 × 10\textsuperscript{-4} M. Such low N\textsubscript{2} concentration, accompanied by its sluggish kinetics, induces the low N\textsubscript{2} adsorption and activation. According to Henry’s law, the dissolved N\textsubscript{2} concentration in water is in proportion to the N\textsubscript{2} partial pressure (Fig. 3A). It is logical to anticipate that more N\textsubscript{2} could be delivered to the electrode surface under high N\textsubscript{2} partial pressure. Thereby, the performance metrics of ENRR were examined in a membrane-separated three-electrode cell under ambient and pressurized conditions, respectively. Under both conditions, a high-purity N\textsubscript{2} gas (99.999%) was purged sequentially through a Cu-based impurity trap and a liquid-nitrogen-cooled trap to capture the impurities such as NO\textsubscript{x} and residual NH\textsubscript{3}. Under ambient conditions the adequately cleaned \textsuperscript{14}N\textsubscript{2}/\textsuperscript{15}N\textsubscript{2} gas was continuously circulated in the electrolyzer while under pressurized conditions the purified \textsuperscript{15}N\textsubscript{2} gas was delivered to the electrolyzer without gas circulation (Fig. 3B and SI Appendix, Figs. S5 and S6). The setups manipulated at different environments hold great promise not only to eliminate the exogenous contaminations but also to reduce the consumption of supplied gas, especially, the expensive \textsuperscript{15}N\textsubscript{2} gas, thus leading to an accurate and cost-effective electrolysis scheme (2). It should be noted that the anodic compartment in the pressurized electrolyzer contains not only a mixed solution of 0.005 M H\textsubscript{2}SO\textsubscript{4} and 0.1 M K\textsubscript{2}SO\textsubscript{4} but also additional 0.01 M ascorbic acid to prevent the oxygen evolution reaction. All of the potentials were recorded versus a Ag/AgCl electrode and converted to the reversed hydrogen electrode (RHE) scale. For a quantitative assessment of electrochemical NH\textsubscript{3} production, ion chromatography and NMR were explored while the potential by-product of hydrazine was evaluated by the Watt and Chrise approach. Their corresponding calibration curves are depicted in SI Appendix, Figs. S7–S9.
Before starting the pressurized ENRR measurements, we used an internal reference, $K_3[Fe(CN)_6]$, to test if the reference electrode could properly work under pressurized conditions. The cyclic voltammetry of the ferri/ferrocyanide redox couple was recorded on a glassy carbon electrode. As shown in SI Appendix, Fig. S10, the corresponding redox peaks situated at almost the position despite the exerted pressure changes, ensuring the reliable potentials collected in the following pressurized ENRR measurements. Taking Rh SA/GDY as a representative example, we start with systematic ENRR tests under various N$_2$ pressures (1−55 atm N$_2$). The linear sweep voltammetry (LSV) curves show an increased response for current density under the elevated N$_2$ pressures of 1, 10, 30, and 55 atm, respectively (SI Appendix, Fig. S11). Moreover, under the pressure of 55 atm, the LSV curves recorded in the electrolyte with saturated N$_2$ and Ar exhibit a more obvious enlarged current gap than those under ambient conditions, presumably contributed by the enrichment of accessible N$_2$-induced preferential ENRR (Fig. 3C). Next, we conducted pressure-dependent chronoamperometry measurements for Rh SA/GDY at controlled potentials to examine the electroproduction of NH$_3$ yield and FE. To our delight, the current densities at different potentials exhibited little degeneration in all electrocatalytic environments, suggesting the robust structure of Rh SA/GDY catalyst (SI Appendix, Figs. S12–S15B).

The posttested electrolyte was subjected to ion chromatography, in which the retention time located around 4 min was contributed by NH$_4^+$ (SI Appendix, Figs. S12–S15A). We found that the Rh SA/GDY exhibited a moderate ENRR activity under 1 atm, and the corresponding NH$_3$ yield rate and FE gradually increased as the potential is negatively shifted and reached at peak values of 10.10 μg h$^{-1}$·cm$^{-2}$ and 4.12% at −0.25 and −0.2 V, respectively (SI Appendix, Fig. S12C and Table S2). After the thresholds, the relative performance decreased due to the diffusion limitation of N$_2$ to the surface of the electrode provoked by vigorous HER. Increasing N$_2$ pressure to 10, 30, and 55 atm in the electrolyzer leads to substantially enhanced NH$_4^+$ production, and their optimized performances were achieved as follows: 16.31 μg h$^{-1}$·cm$^{-2}$ at −0.25 V and 5.56% at −0.2 V under 10 atm; 36.87 μg h$^{-1}$·cm$^{-2}$ and 12.31% at −0.2 V under 30 atm; 74.15 μg h$^{-1}$·cm$^{-2}$ and 20.36% at −0.2 V under 55 atm (Fig. 3D and SI Appendix, Figs. S13–S15C and Tables S3–S5). Fig. 3E summarizes and compares the optimum NH$_3$ yield, FE, and NH$_3$ partial current ($j_{NH_3}$) under different N$_2$ pressures. Clearly, all of the values of NH$_3$ yield rate, FE, and $j_{NH_3}$ of Rh SA/GDY increased markedly along with the increase of N$_2$ pressure. Especially, the NH$_3$ yield rate, FE, and $j_{NH_3}$ under 55 atm render 7.3-, 4.9-, and 9.2-fold enhancements, respectively, than those obtained under ambient conditions. These observations highlight the ENRR activity of Rh SA/GDY under...
pressurized environments by engaging both N₂ delivery and HER suppression. As expected, the pressurized ENRR behavior of Rh SA/GDY by far surpasses many of the previously reported state-of-art ENRR catalysts (SI Appendix, Table S10). Of note, no hydrazine was detected under the pressurized electrolysis, suggesting the excellent selectivity of the catalyst (SI Appendix, Fig. S16).

To verify the nitrogen source of the produced NH₃ by Rh SA/GDY, we carried out four control experiments and measured the NH₃ production using 1) the electrolyte pressurized with Ar at −0.2 V for 2 h, 2) the electrolyte pressurized with N₂ at open-circuit potential for 2 h, 3) the electrolyte pressurized with N₂ at −0.2 V with bare carbon cloth for 2 h, and (4) the electrolyte saturated with ¹⁵N₂ at open-circuit potential for 2 h under ambient conditions. None or a negligible amount of NH₄⁺ signals were detected in those tests, ruling out the possibility of catalyst degradation or extraneous pollution-induced NH₃ production (SI Appendix, Fig. S17).

Under 55 atm N₂, we have measured the ENRR stability of the Rh SA/GDY electrodes by carrying out six cycles of electrolysis at −0.2 V. The results showed remarkable stability with negligible attenuation in terms of NH₃ yield rate and FE. For instance, the NH₃ production activity remained 88.3% of the initial performance after six runs (Fig. 3F and SI Appendix, Fig. S18 and Table S6). The durable electrocatalytic behavior reflects the robust composition/structure of Rh SA/GDY. The morphology of densely populated single Rh atoms on GDY is well conserved without aggregation after the stability measurements (SI Appendix, Fig. S19 A and B). Additional XPS study also verified that the structure and the chemical state of Rh were maintained after electrocatalysis (SI Appendix, Fig. S19 C and D).

Isotope labeling experiments using adequately cleaned ¹⁵N₂ as feeding gas were conducted to trace the ammonia synthesis under ambient conditions due to the limited pressure of ¹⁵N₂ gas. As illustrated in Fig. 3G, the ¹H NMR spectrum of the electrolyte after electrolysis using ¹⁴N₂ as the feeding gas displayed a doublet coupling at 7.15 and 7.02 ppm, confirming the generation of ¹⁵NH₄⁺. Meanwhile, the typical triplet peaks of ¹⁴NH₄⁺, potentially from impurities of electrolyte and catalyst, were not observed. Moreover, the integration area of ¹⁵NH₄⁺ signals growth gradually with the increase of electrolysis time. The amounts of produced ¹⁵NH₄⁺ after 6- and 12-h electrolysis were quantified to be 56.4 and 108.6 μg, corresponding to the ¹⁵NH₃ yield rates of 9.4 and 9.05 μg h⁻¹ cm⁻², respectively (Fig. 3H); their FEs were calculated as 3.35 and 2.98% (SI Appendix, Fig. S20 and Table S7), respectively. These results are very close to the above-mentioned results under 1 atmosphere of ¹⁴N₂, implying that the detected NH₃ in the electrolysis experiments are indeed from the NRR.

Next, it is interesting to see if the pressurized electrolysis can be applied to regulate ENRR performances of other SACs in general. We then proceed with the pressurized ENRR experiments using Ru SA/GDY and Co SA/GDY at 55 atm. As expected, the catalysts displayed fairly high ENRR activity, among which Ru SA/GDY could drive a maximum NH₃ yield rate of 47.3 μg h⁻¹ cm⁻², an FE of 11.76%, and a j₁NH₃ of 0.22 mA cm⁻² at −0.2 V, and the Co SA/GDY gave optimal values of 33.46 μg h⁻¹ cm⁻² at −0.25 V, an FE of 8.2%, and a j₁NH₃ of 0.13 mA cm⁻² at −0.25 V (Fig. 3I and SI Appendix, Figs. S21 and S22 and Tables S8 and S9). The high performances show advantages of the SAC-based NRR and the pressurized electrolysis systems, demonstrating a general and cooperative strategy in reprogramming ENRR. Taken all together, the observations presented in this work showcase the conclusion that nanostructuring of high-
loading metal-based SACs in combination with the pressurized electrosystems could suppress the HER, enhance the N₂ adsorption, and thus improve the ammonia production efficiency of the ENRR in general.

**DFT Calculations.** We next performed first-principles calculations with density-functional theory (DFT) implanted in VASP at the spin-polarized generalized gradient approximation level for Rh SA/GDY to unravel the effects of the pressurized system in boosting ENRR activity (42, 43). The binding energy of Rh atom to GDY is calculated to be $-5.37 \text{ eV}$, which suggests that the Rh/GDY catalyst is very stable. Bader analysis shows that 0.38 electron is transferred from Rh to GDY. The projected density of states of Rh and the C atoms coordinated to Rh shows that their orbitals are greatly hybridized, consistent with the strong binding of Rh (SI Appendix, Fig. S23). The partial pressure of N₂ is 50 atm unless otherwise specified. There are potentially two adsorption fashions for N₂ on Rh SA/GDY: the end-on one and the side-on one. At 50 atm of N₂, the adsorption free energies of N₂ are calculated to be $-0.48 \text{ eV}$ for the former and $-0.06 \text{ eV}$ for the latter. The end-on N₂* is more stable than the side-on N₂*. The adsorption free energy of N₂ in the end-on fashion at 1 atm is calculated to be $-0.38 \text{ eV}$. In comparison, the driving force for the formation of end-on N₂* at 50 atm is 0.1 eV larger than that at 1 atm, corresponding to 9.62 kJ/mol energy. As a result, the high pressure of N₂ significantly promotes the adsorption of N₂, which in turn suppresses the HER. We have also investigated the activity of the alkyne C atoms coordinated to Rh. The adsorption of N₂ at these C sites is uphill by 2.29 eV at 50 atm, which is 1.39 eV lower than that on the pristine graphdiyne, but 2.77 eV.

![Graph showing the solubility of N₂ gas versus the partial pressure.](imageA)

![Graph showing the ammonia yield and its corresponding FE for Rh SA/GDY under ambient and 55-atm conditions, respectively.](imageB)

![Graph showing the cycling stability results of Rh SA/GDY at $-0.2 \text{ V}$.](imageC)

![Graph showing the 1H NMR spectra and corresponding $^{15}\text{NH}_4^+$ yield with the isotopic $^{15}\text{N}_2$ for 6- and 12-h electroreduction.](imageD)

![Graph showing the comparison of the optimum NH₃ yield, FE, and $j_{NH_3}$ for the prepared Rh, Ru, and Co SA/GDY.](imageE)
higher than that at the Rh site. Therefore, the Rh site is much more active for the adsorption and reduction of N2.

Three possible pathways for the N2 reduction were investigated, namely alternating, distal, and enzymatic pathways (44, 45). The calculated free-energy surfaces and the optimized structures are shown in Fig. 4. For both alternating and distal pathways, N2 adsorption is in the end-on fashion with the adsorption free energy of −0.48 eV. At 0.0 V vs. RHE, the first hydrogenation step (N2* → HNN*) is uphill by 0.86 eV. Following the alternating pathway, HNN* → HNNH* is still endothermic by 0.59 eV. Other hydrogenation steps in this path are all downhill (note that the desorption of NH3 is endothermic by 0.58 eV, which is surmountable at room temperature). Therefore, the potential limiting step of the alternating pathway is the first step with a limiting potential of −0.86 V.

The distal pathway shares many common intermediates with the alternating pathway, which includes the end-on adsorbed N2* and HNN*, NH2* and NH3*. Following the distal pathway, the end-on HNN* is not converted to HNNH* but to H2NN*. This step is only endothermic by 0.20 eV. With the transfer of the third (H2+ e−), H2NN* is reduced to N* with a NH3 molecule released. This step is uphill by 0.82 eV, which is slightly lower than that for N2* → HNN*. Hydrogenation of N* to NH2* is all exothermic. Therefore, the potential-limiting step for the distal pathway is still the first proton-coupled electron step with a limiting potential of −0.86 V.

For the enzymatic pathway, the N2 adsorption mode is considered as the side-on fashion with the adsorption free energy of −0.06 eV. Similar to the alternating pathway, two N atoms are also hydrogenated alternatively except that the intermediates take the side-on adsorption patterns. Interestingly, N2* and HNN* prefer the end-on adsorption, whereas H2NN* and H2NNH2* prefer the side-on adsorption (Fig. 4B). The energy of the side-on HNNH* is the same as that of end-on HNNH* but 0.39 eV higher than that of H2NN* in the distal path. Although the energy of the side-on N2* and HNN* are higher than those of the end-on N2* and HNN*, the reduction of the side-on N2* to HNN* is uphill by 0.85 eV, which is almost the same as that of the alternating pathway. The reduction of the side-on HNN* to HNNH* is slightly endothermic by 0.19 eV. Other hydrogenation steps in the enzymatic pathway are all exothermic. Therefore, the potential-limiting step of the enzymatic pathway is also the first hydrogenation step with a limiting potential of −0.85 V.

Taken all these intermediates into consideration, the N2 reduction by Rh SA/GDY would very likely follow a hybrid path via low-energy intermediates (Fig. 4B and C) (44, 46). For example, the H2NN* species in the distal pathway may shuttle to the enzymatic pathway, which avoids the high-energy intermediate N*, leads to the formation of side-on H2NNH*, and thereby reduces the barrier for the conversion of H2NNH*. But, the potential-limiting step of this hybrid pathway is still N2* → HNN* with a limiting potential of −0.86 V. However, if N2* in the enzymatic pathway shuttles to the distal pathway first and then H2NN* shuttles back to the enzymatic pathway, the limiting potential will become −0.44 V.

Conclusion

In summary, we have demonstrated positive cooperation of metal single-atom catalysts with a pressurized electrolysis system to simultaneously regulate both kinetics and thermodynamic process, leading to a significant boost in the ENRR activity by delivering more N2 to the electrode surface and thus impeding the HER. The applied catalysts were nanostructured by stereoconfinement-induced single-metal-atoms (Rh, Ru and Co) on graphdiyne, and these catalysts feature ultrahigh loading amounts of isolated metal centers. The pressurized ENRR measurements showcased significantly enhanced ammonia electroproduction with simultaneously reduced HER. Under pressurized conditions of 55 atm of N2, the Rh SA/GDY displayed a NH3 yield rate of 74.15 μg h−1 cm−2, an FE of 20.36%, and a j/NH3 of 0.35 mA at −0.2 V, which values are 7.3-, 4.9-, and 9.2-fold higher than those obtained at the ambient conditions. The proposed strategy and findings provide a valuable electrocatalysis scheme that cooperatively integrates both efficient catalysts and the pressurized reaction system, which is a step forward to the electrochemical ammonia production.

Materials and Methods

The synthetic strategy and experimental sections of this work are provided in SI Appendix. These methods contain the synthesis of Rh SA/GDY, Ru SA/GDY, and Co SA/GDY catalysts, structure characterization. Detailed electrochemical measurements under ambient and pressurized conditions are also included. The calculation method for NH3 yield rate and FE and the computation theory are elaborated in SI Appendix.

Data Availability. All study data are included in the article and SI Appendix.

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