Low-temperature ammonia synthesis on electron-rich [RuH₆] catalytic centers

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Ammonia is a central vector in sustainable global growth, but the usage of fossil feedstocks and centralized Haber-Bosch synthesis conditions causes >1.4% of the global anthropogenic CO₂ emissions. While nitrogenase enzymes convert atmospheric N₂ to ammonia at ambient conditions, even the most active manmade inorganic catalysts fail due to low activity and parasitic hydrogen evolution at low temperatures. Here, we show the [RuH₆] catalytic center in ternary ruthenium complex hydrides (Li₂RuH₆ and Ba₂RuH₆) activate N₂ preferentially and avoid hydrogen over-saturation at low temperatures and near ambient pressure by delicately balancing H₂ chemisorption and N₂ activation. The active [RuH₆] catalytic center is capable of achieving an unprecedented yield at low temperatures via a shift in the rate-determining reaction intermediates and transition states, where the reaction orders in hydrogen and ammonia change dramatically. Temperature-dependent atomic-scale understanding of this unique mechanism is obtained with synchronized experimental and density functional theory investigations.

Introduction

Ammonia is critical to our food production ecosystem¹,² and the single most produced polluting chemical (~170 million tons per year)³,⁴, while also holding the potential to become one of the most promising carbon-free and low-cost long term energy carriers⁵,⁶. The industrial Haber-Bosch (H-B) process employs a Fe-based catalyst, fossil-fuel sourced H₂, and requires harsh operating conditions (typically 673-723 K and 100-300 bar of pressure). The large-scale and centralized H-B process accounts for nearly 2% of the world’s consumption of fossil fuels⁷, and consequently 1.44% of the global anthropogenic CO₂ emissions⁸. The development of small-scale processes that rely on renewable electricity as an energy source to sustainably produce the H₂ feedstock would thus be transformative in several ways. It would provide critical technological support towards the audacious goal of carbon-free growth and ensuring the green transition. Two indispensable targets would be reached simultaneously, where renewable energy penetration is arduous – food production and clean mobility⁹,⁰. A decentralized, low CAPEX NH₃ synthesis process targeted at emerging markets with significant future population growth needs would also support the core U.N. sustainability goals.

While direct electrochemical ammonia production represents the Holy Grail, the documented yields remain very far from any kind of commercialization¹¹. The discovery of efficient heterogeneous or homogeneous catalysts that exhibit high activity under mild conditions would thus be a key enabler for the decentralized production of green ammonia. For industrial ammonia synthesis, it is widely recognized that Ru-based catalysts work better than Fe-based catalysts under milder reaction conditions¹²,¹³. However, the high activation energy for direct N₂ dissociation and the severe poisoning effect of hydrogen on conventional Ru metal catalyst renders efficient NH₃ synthesis under lower temperatures (< 623 K) and lower pressures (< 50 bar) unattainable¹⁴. Therefore, many attempts to develop new catalysts for efficiently catalyzing N₂+H₂ to NH₃ under mild conditions¹⁵–¹⁷. Recently discovered, a new class of ammonia catalysts – the ternary ruthenium complex hydrides¹⁸ is a breakthrough in this endeavor. The ternary ruthenium hydride’s ability to efficiently synthesize NH₃ at <10 bar and < 573 K conditions lies in the unique chemistry of the coordination complex and the alkali (alkaline earth) metal framework, facilitating a catalytic mechanism bridging homogeneous and heterogeneous concepts, which are clearly distinct from the Ru metal catalyst. For ternary Ru complex hydride catalysts, Ru is in an ionic state, and N₂ undergoes non-dissociative hydrogenolysis over the hydride[H⁺]-rich and electron-rich [RuH₆]⁺ complex with the aid of the surrounding Li or Ba cations. The dynamic and synergistic engagement of all the components of the ternary hydrides creates a reaction path with a narrow energy span and leads to ammonia production with superior activities.

In this paper, we present the reaction mechanism facilitating ternary ruthenium complex hydrides to successfully produce NH₃ at low temperature (448 K ≤ T ≤ 573 K) by selective N₂ activation and escaping H₂ over-saturation. This work shows the unique ability of the [RuH₆]⁺ catalytic center in the ternary ruthenium hydride to shift its rate-determining intermediate states and transition states of the N₂+H₂ to NH₃ reaction path in response to the lowering of the reaction temperature, which brings a significant change in reaction order of hydrogen and ammonia. This variation in the kinetics as a function of operating conditions (temperature, reactant partial pressures, etc.) is not a common phenomenon in catalysis but is observed in some cases¹⁹–²³. Nonetheless, the mechanistic details
behind it are seldom investigated, especially at an atomic level. Here, we achieve this via seamless integration of experimental and computational techniques to reveal the temperature-dependent catalytic process. Our finding discloses that an electron-rich active center with a comparable affinity towards $N_2$ and $H_2$ are critical for mild-condition ammonia catalysis. The thorough fundamental understanding developed in this study can be further used to design new low-temperature ammonia catalysts with better performance and has the potential to drive the green ammonia technology into a new direction.

Results and discussion
Figure 1 shows that the [RuH$_2$] catalytic center in Ru complex hydride catalysts ($Li_xRuH_6$ and $Ba_yRuH_6$) not only outperforms the BS site of Ru metal catalysts under the same working conditions but also produces $NH_3$ at low temperatures. As discussed below, two inherent properties of the [RuH$_2$] catalytic center are critical towards the observed outstanding activity at low temperatures: (a) its selectivity for chemisorbing $N_2$ over $H_2$ and (b) a self-adjusting mechanism of avoiding hydrogen over-saturation sustaining the $N_2$ to $NH_3$ conversion cycle.

The catalytically active ternary hydride surface with excess Li and hydrogen (consists of two additional LiH for every six [RuH$_2$] centers, i.e., $4[RuH_3]+2[LiH]+2Li$) is energetically moderately selective towards $N_2$ on $H_2$ chemisorption. The model considered (110) plane of $Li_xRuH_6$, which is the most stable crystal face for this material (Figure 2A). The details of the $Li_xRuH_6$ active surface used for this study are in Figures 2B and 2C. The presence of additional two Li and two $H$ (from two LiH) on the surface breaks its local symmetry. As a result, one of the [RuH$_2$] polyhedral turns into a pentagonal based pyramidal instead of standard octahedral. This [RuH$_2$] site (denoted as [RuH$_2$]) with pentagonal based pyramidal polyhedral is the preferred site for $N_2/H_2$ adsorption compared to other [RuH$_2$] sites with the octahedral coordination due to lower steric hindrance (Figure S1). In contrast, [RuH$_2$] sites on the $Li_xRuH_6$ active surface can not adsorb further any $N_2/H_2$. The extra two Li (from additional LiH) on the surface also create hindrances for $N_2/H_2$ adsorption on other neighbouring [RuH$_2$] sites and cause partial deactivation. However, other [RuH$_2$]/[RuH$_2$] sites and extra Li on the surface are vital for the $N_2+H_2$ to $NH_3$ conversion process.

![Figure 1](image1.png)  
**Figure 1** Comparison of $NH_3$ synthesis rate and active site structure of ternary Ru complex hydride catalysts and Ru metal catalysts. Reaction conditions: 1 bar of syngas, $N_2/H_2=1:3$, and a weight hourly space velocity (WHSV) of 60000 ml g$^{-1}$ h$^{-1}$.

![Figure 2A](image2A.png)  
**Figure 2A** The XRD pattern of the as-prepared $Li_xRuH_6$ sample demonstrating (110) plane as its most stable façade. The Miller indexes are marked above the corresponding peaks. B and C are respectively the side, and top view of the catalytic active ternary hydride surface, i.e., $Li_xRuH_6$ surface with two extra LiH dissociatively adsorbed on it. Plot B shows the four-layered $Li_xRuH_6$ slab’s side view with two Li ions from the additional two LiH on the surface. Plot C is the top view of the surface, highlighting four [RuH$_2$] and two [RuH$_2$] (accommodating two $H$s from the two LiH complexes. The dissociative addition of two LiH on the surface breaks the surface symmetry locally, and one of the [RuH$_2$] complex transformed into a pentagonal based pyramidal polyhedral (marked by the circular encoder) from an octahedral polyhedral. Color code: Li-light gray, Ru-red, and H-yellow.
The chemisorption $H_2$ on the Li$_x$Ru$_6$ active surface here can be expressed as:

$$[\text{RuH}_6]^* + H_2 \rightarrow [\text{RuH}_6]H_2$$

(1)

For simplicity, we are representing the Li$_x$Ru$_6$ active surface (which has four [RuH$_6$] complex, two [RuH$_2$] complex, and two extra Li) only by the active catalytic site [RuH$_6$]*. Here, the lattice hydrogens of Ru are inside the square brackets ([RuH$_6$]/[RuH$_2$]). The chemisorbed H$_2$ remains molecular ([RuH$_6$]H$_2$) till the H-H bond breaks (one of the hydrogens goes to the neighboring Ru ([RuH$_6$]) and becomes part of the lattice and creates two [RuH$_2$] in the process (Figure S2). The transformation of the chemisorbed H$_2$ to lattice H can be written as:

$$[\text{RuH}_6]H_2 + [\text{RuH}_6] \rightarrow 2[\text{RuH}_2]$$

(2)

Meanwhile, the competitive chemisorption of N$_2$ on the Li$_x$Ru$_6$ active surface is:

$$[\text{RuH}_6]^* + N_2 \rightarrow [\text{RuH}_6]N_2$$

(3)

The calculated binding free energies show that the preferential adsorption of N$_2$ over H$_2$ at the [RuH$_6$]* active center is further enhanced at lower temperatures (Figure 3A). This feature is critical for the understanding of the catalytic mechanism, particularly when combined with the kinetics of dissociative hydrogen chemisorption and hydrogen transfer over the [RuH$_6$] centers. Figure 3B displays the free energy landscape for dissociation of chemisorbed H$_2$ (state-I) on the [RuH$_6$] active center (eqn.(2)). Although the dissociative chemisorption of H$_2$ into two lattice H$_2$ is facile, the subsequent transfer of lattice H$_2$ as [RuH$_2$] (state-II), via a transition state (TS$_{II}$), is prohibited by a high activation energy of 1.1 eV (Figure S2) as estimated with nudged elastic band simulations. The transfer of the chemisorbed H$_2$ to lattice H is Li-mediated and encounters repulsive force from neighboring H$_2$, making the activation barrier high. Instead, at low temperature, the active center retains the hydrogen atoms to form a [RuH$_6$]H$_2$ complex (state-II), which is not a very stable state and can easily desorb H$_2$ at temperatures above 300 K to release the [RuH$_6$] catalytic site for N$_2$ activation (see Figure 3B). The mechanism of H$_2$ chemisorption/desorption ensures not all [RuH$_6$] centers are converted to [RuH$_2$] complexes, even in an H$_2$-rich environment. Thus, the catalyst surface is not hydrogen oversaturated by lattice H that bonds firmly to the respective Ru blocking the active sites. This contrasts with Ru and other late transition metal catalysts, where H-poisoning, due to favorable thermodynamics, effectively prevents N$_2$ adsorption. The opposing behavior between Ru metal and Li$_x$Ru$_6$ catalysts is elegantly captured in the NH$_3$ formation rate under varying pressure (Figure S3). The lack of hydrogen poisoning effect allows enhanced ammonia production at a higher hydrogen partial pressure on Li$_x$Ru$_6$.

The chemisorption of H$_2$ on the ternary hydride active surface has unique fingerprints (Figure 3B). The chemisorption of H$_2$ happens through a physisorbed transition state TS$_{III}$, with a negligible barrier of 0.07 eV (Figure S4). The H from the chemisorbed H$_2$ participates in on-site scrambling with the lattice H on the [RuH$_6$] active center. The on-site scrambling of the hydrogen has an insignificant activation energy of 0.04 eV (Figure S5). Experimentally, we observe a minor reversible adsorption/desorption of H$_2$ in the temperature range of 373 K to 473 K in the temperature programmed desorption (TPD) profile with no trace of net LiH, Ru powder, or a mixture of LiH and Ru (Figure S6), which reinforces the observation of the chemisorbed nature of the H$_2$ adsorption on the Li$_x$Ru$_6$ active surface. After charging with D$_2$, the detection of the mixed HD signal in the TPD profile strengthens the conclusion of the on-site scrambling of D from chemisorbed D$_2$ with lattice H (inserted plot of Figure 3B). A more robust signal of H$_2$/HD than D$_2$ in the TPD profile points out the magnitude of the on-site scrambling of the chemisorbed D$_2$ with the lattice H.

Our study shows that the N$_2$+H$_2$ to NH$_3$ conversion cycle on the Li$_x$Ru$_6$ catalyst surface happens through 13 different surface states (states 0-12). Visualization of the NH$_3$ formation mechanism on the Li$_x$Ru$_6$ catalyst surface with intermediate states is provided in Figure 4.

Here, the state-0 and state-1 are the Li$_x$Ru$_6$ catalyst surface with active [RuH$_6$] center and the chemisorbed N$_2$ on it ([RuH$_6$]NN), respectively, as presented by the eqn.(3). The state-2 is ([RuH$_6$]NHN), where the adsorbed N$_2$ is hydrogenated by one of the hydrides from the same Ru site where N$_2$ is activated (i.e., H from [RuH$_6$]-NN):

$$[\text{RuH}_6]N_2 \rightarrow [\text{RuH}_6]NHN$$

(4)
Figure 4 Visualization of the $N_2$ to NH conversion path on the Li$_2$Ru$_6$ catalyst surface. The catalytic conversion cycle went through 13 different surface states (marked by 0-12). The hydrogenation of the activated nitrogen by the lattice hydrogen is marked as "[H] transfer". Color code: Li-light gray, Ru-red, H-yellow, and N-blue.

State-3 is $([\text{RuH}_3]_{\text{NNH}})$, in which the activated $N_2$ is further hydrogenated by one hydride from neighboring $[\text{RuH}_2]$:

$$[\text{RuH}_3]_{\text{NNH}} + [\text{RuH}_2] \rightarrow [\text{RuH}_2]_{\text{NNH}} + [\text{RuH}_6]$$

(5)

In state-4 $([\text{RuH}_3]_{\text{NNH}}+2[\text{RuH}_2])$, one $H_2(g)$ gaseous molecule chemisorbs and then dissociates into two lattice hydrogens on the surface:

$$[\text{RuH}_3]_{\text{NNH}} + 2[\text{RuH}_2] + H_2g \rightarrow [\text{RuH}_2]_{\text{NNH}} + 2[\text{RuH}_7]$$

(6)

State-5 is $([\text{RuH}_3]_{\text{NNH}})_{\text{H}_2}$, where the activated $N_2$ is further hydrogenated from one hydride of an adjacent $[\text{RuH}_2]$ site:

$$[\text{RuH}_3]_{\text{NNH}} + [\text{RuH}_7] \rightarrow [\text{RuH}_7]_{\text{NNH}} + [\text{RuH}_6]$$

(7)

In state-6 $([\text{RuH}_2]_{\text{NNH}}+2[\text{RuH}_6])$, the N-N bond fully dissociates:

$$[\text{RuH}_3]_{\text{NNH}} + [\text{RuH}_6] \rightarrow [\text{RuH}_2]_{\text{NN}} + [\text{RuH}_6]_{\text{H}_2}$$

(8)

In state-7 $([\text{RuH}_2]_{\text{NNH}}+2[\text{RuH}_6])$, the first molecule of NH$_3$ is formed, which then desorbs from the surface and creates state-8 $([\text{RuH}_3]_{\text{NNH}})$:

$$[\text{RuH}_3]_{\text{NH}} + [\text{RuH}_6]_{\text{H}_2} \rightarrow [\text{RuH}_3]_{\text{NH}} + [\text{RuH}_5]_{\text{NH}_3}$$

(9)

$$[\text{RuH}_3]_{\text{NH}} + [\text{RuH}_5]_{\text{NH}_3} \rightarrow [\text{RuH}_3]_{\text{NH}} + [\text{RuH}_5]_{\text{NH}_3}$$

(10)

In state-9 $([\text{RuH}_3]_{\text{NH}}+2[\text{RuH}_6])$, the remaining $N$ is hydrogenated further from the hydrides of an adjacent $[\text{RuH}_3]$ site:

$$[\text{RuH}_3]_{\text{NH}} + [\text{RuH}_5] + [\text{RuH}_7] \rightarrow [\text{RuH}_3]_{\text{NH}} + [\text{RuH}_6]$$

(11)

The 2nd molecule of NH$_3$ is formed in state-10 $([\text{RuH}_2]_{\text{NH}}+2[\text{RuH}_6])$, which then desorbs from the surface and results in state-11 $2[\text{RuH}_3]::$

$$[\text{RuH}_3]_{\text{NH}_2} + [\text{RuH}_5] + [\text{RuH}_7] \rightarrow [\text{RuH}_3]_{\text{NH}} + [\text{RuH}_5] + [\text{RuH}_6]$$

(12)

$$[\text{RuH}_3]_{\text{NH}} + [\text{RuH}_3]_{\text{NH}} + [\text{RuH}_6] + [\text{RuH}_6]$$

(13)

Two consecutive direct adsorptions of $H_2(g)$ molecule replenish the two hydride-deficient $[\text{RuH}_3]$ sites on the state-11, result in state-12 $([\text{RuH}_3])$ and then finally back to state-0:

$$2[\text{RuH}_3] + H_2g \rightarrow [\text{RuH}_3] + [\text{RuH}_7]$$

(14)

$$[\text{RuH}_3] + H_2g \rightarrow \text{renewed surface}$$

(15)

The overall chemical reaction in one catalytic cycle on Li$_2$Ru$_6$ catalyst surface is:

$$N_{2g} + 3H_{2g} \rightarrow NH_{3g}$$

(16)

The path shows a series of well-balanced and moderate activation energies – all with $E_a \leq 0.82$ eV (see Table S1).

For better understanding the low temperature reaction pathway, the variations of reaction energetics as a function of temperature are explored and then analyzed by applying the energetic span model, in which the turnover frequency (TOF) determining transition state (TDTs) and TOF determining intermediate state (TDI) that maximize the energy span determine the rates and kinetics of the catalytic cycle$^{24,25}$. The energetic span approximation$^{25}$ of the exothermal catalytic cycle to calculate turn over frequency (TOF) from the energetic span ($\delta E$) of the free energy path:

$$TOF = \frac{k_B T}{h} e^{-\delta E/k_B T}$$

(17)

In this model, the free energy of TOF-determining transition state ($\Delta G_{TDTs}$), TOF-determining intermediate state ($\Delta G_{TDI}$) and the free energy of reaction ($\Delta G_r$) defines $\delta E$:

$$\delta E = \left\{ \begin{array}{ll} \Delta G_{TDTs} - \Delta G_{TDI}, & \text{if TDTs appears after TDI} \\ \Delta G_{TDI} - \Delta G_{TDTs} + \Delta G_r, & \text{if TDTs appears before TDI} \end{array} \right. $$

(18)

The activation enthalpy ($\Delta H_\alpha$) for the catalytic path is back-calculated from the $\delta E$ and the entropy correction ($T \Delta S$):

$$\Delta H_\alpha = \delta E + T \Delta S$$

(19)

Figure 5 (and Figure S7) shows the development of the free energy path of the catalytic cycle of $N_2+H_2$ to $NH_3$ on the Li$_2$Ru$_6$ catalyst surface with a lowering of reaction temperature (448 K $\leq T \leq 573$ K).
The change in temperature shifts the TDI and TDTS of the catalytic cycle, with an inflection temperature being at 498 K. Experimentally, the Arrhenius plot for ammonia synthesis (Figure 6A) locates this inflection point around 523 K. In addition, all measured kinetic parameters for ternary hydride catalyst (Li4RuH6/MgO) are temperature-dependent (Figure 6), indicating the complex temperature-dependent switching of rate-determining states (i.e. TDI and TDTS).

As shown in Figure 5, the TDTS moves from the transition state 4-5 (TS4,5) to TS5,6 as the temperature goes lower than the inflection point 498 K. Meanwhile, the TDI shifts from state 12 to state 0. For clarity, the inserted plot in Figure 5 presents a schematic view of the shift in TDI/TDTS with temperature. There might be one inflection for each change in TDI/TDTS, which we can not resolve due to their proximity. Another essential feature in the catalytic path is the energy difference between state 12 and state 9. At 573 K, the free energies of states 9 and 12 are similar, and they are both likely candidates for the TDI. The energy difference between state 12 and state 9 increases with decreasing temperature, and the state 12 is TDI in the range 498 K < T < 573 K. The theoretically derived activation enthalpy (ΔH₀) and TOF, and experimentally derived apparent activation energy (E_app) and TOF are listed in Table S2. The value of ΔH₀ at 448 K is 98.2 kJ mol⁻¹. While at 573 K, with state 9 as TDI, the ΔH₀ is calculated to be 72.4 kJ mol⁻¹. An increase in temperature lowers the activation enthalpy and increases the TOF, agreeing well with the trends observed experimentally. The apparent activation energy for Li4RuH6 catalyst determined by Arrhenius plot is E_app = 71.2 kJ/mol at temperatures higher than 523 K, and significantly increased value of 102.8 kJ/mol at temperatures below 523 K (Figure 6A). In contrast, there is no change in E_app and other kinetic parameters for conventional Ru metal catalyst (Ru/MgO) in a wide temperature range (498-648 K).
Figure 6 Experimentally derived kinetic parameters. A: Arrhenius plots of supported Li$_{2}\text{RuH}_6$/MgO and Ru/MgO catalysts. B to D: dependence of ammonia synthesis rates on the partial pressures of NH$_3$ and H$_2$, respectively, under a total pressure of 1 bar at 573 K (filled symbols) and 498 K (open symbols) over supported Li$_{2}\text{RuH}_6$/MgO and Ru/MgO catalysts. The reaction order of NH$_3$, N$_2$, and H$_2$ is represented by α, β, and γ, respectively.

For Li$_2$RuH$_6$ catalyst, the energetic span and the TOF vary continuously with temperature. The temperature dependent TDI and TDTS modifications follow the entropy of intermediates and transition states. The entropy of a state is strongly affected by the adsorption/desorption of gas molecules. Such changes in the TDI or TDTS will tend to affect both $\Delta H_2$ and the reaction order in gas molecules. This is beautifully captured by the analysis of the reaction order of NH$_3$, N$_2$, and H$_2$ for Li$_2$RuH$_6$ (Figure 6B-D). The reaction orders changed from $+0.3$ to $-0.47$, $0.91$ to $0.82$, and $-0.59$ to $-0.18$ respectively for H$_2$, N$_2$, and NH$_3$ with the decrease of temperature. These changes are in stark contrast to the constant values for Ru metal catalyst (Ru/MgO), i.e., $-0.23$, $1.12$, and $-0.85$, respectively for H$_2$, N$_2$, and NH$_3$. It is worth noting that, although the H$_2$ reaction orders of ternary Ru hydride catalysts decrease with the decrease of temperature, they are still higher than that of the Ru metal catalyst. Moreover, NH$_3$ poisoning effects on the [RuH$_6$] center lessens at lower temperatures, providing a favorable scenario for effective catalysis.

Conclusions

The present study highlights the dynamic nature of the [RuH$_6$] catalytic center in enabling mild condition ammonia synthesis. The presence of [RuH$_2$] complex facilitates the hydrogenation of the activated nitrogen from the surplus lattice hydrides. On the contrary, a too high concentration of [RuH$_2$] complex on the surface can deactivate the catalyst from dinitrogen adsorption. The high activation energy for lattice $H$ transfer of the chemisorbed H$_2$ observed in this unique class of material maintains a delicate balance between the availability of lattice hydrogen and active sites. The preferential N$_2$ chemisorption over H$_2$ and kinetic blockage of hydrogen over-saturation are key elements to the success of ternary Ru complex hydride systems for catalyzing NH$_3$ synthesis at low temperatures. Furthermore, a unique temperature-dependent tuning of the reaction kinetics is observed for [RuH$_6$] catalytic center, resulting from a shift in the TDI and TDTS along the reaction pathway.

We have been able to achieve a precise temperature resolved atomic-scale understanding of the reaction mechanism at the [RuH$_6$] catalytic center, its unique thermodynamics, and kinetic aspects that enable exceptional low-temperature activity. These scientific insights need to be exploited towards optimizing complex transition metal hydrides as ammonia catalysts as well as exploring a newer class of materials that can replicate the behavior of [RuH$_6$] catalytic center in the pursuit of renewables powered decentralized room temperature/pressure ammonia synthesis.

Conflicts of interest

The authors declare no competing financial interest

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