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Publication date:
2020

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Pan, J. (2020). Computational design of catalysts for the sustainable reduction of nitrogen into ammonia. Technical University of Denmark.

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Computational design of catalysts for the sustainable reduction of nitrogen into ammonia

PhD thesis
Jaysree Pan
July 2020

Department of Energy Conversion and Storage
Technical University of Denmark
Computational design of catalysts for the reduction of nitrogen into ammonia

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Preface

This thesis is submitted in candidacy for a Ph.D. degree from the Technical University of Denmark (DTU). The work has been conducted between August 2016 and July 2020 at the section of Atomistic Scale Modelling and Materials, at the Department of Energy Conversion and Storage supervised by Prof. Tejs Vegge and Dr. Heine Anton Hansen.

Velux Foundations financially supported the Ph.D. study through research center V-Sustain (#9455) from August 2016 to May 2020. For June 2020 to July 2020, the Ph.D. study is financed by the EU project ARENHA (#862482).

Jaysree Pan
July 2020
Lyngby
Acknowledgments

For me, this Ph.D. was an incredible journey full of excitement, joy, and memorable moments. I am truly blessed with beautiful peoples around me, both at work and home, without whom this journey could have been incomplete.

I am lucky to work under two very best supervisors Tejs and Heine. Tejs guided me closely throughout the Ph.D. but also encouraged my intellectual freedom and space to grow. Heine, on the other hand, was always there for any technical discussion with his in-depth theoretical knowledge and experience in theoretical catalysis. I am lucky to have the best possible working environment, thanks to all my ASC group members and ASC group secretary Karina. Ole is expertly maintaining the Niflheim, which has provided a stable computing environment for Ph.D. work. I was fortunate to find experimental collaboration with Prof. Chen's group from Dalian, China. I thank all of them from the bottom of my heart.

I wanted to thank the Velux Foundations through research center V-Sustain (#9455) and EU project ARENHA (#862482) for financially supporting this PhD study.

I am also blessed with loving parents who still treat me as their "little girl." They are my "Neverland," where I am always loved and cared like a child. I am a proud mother of the most beautiful daughter Tilu, who has completed my existence. And there is Arghya, who is my classmate, my best friend, my office colleague, my husband and the father of my daughter. I can not think of a life without Arghya and Tilu.
Abstract

Nitrogen fixation into ammonia supports the food supply we rely on, along with other industries, and it can become the vector to an inexpensive renewable energy storage system. However, the usage of fossil feedstock and centralized Haber-Bosch synthesis conditions causes >2% of the global anthropogenic CO₂ emissions. The demand for sustainable ammonia production drives immense research interest in developing catalysts that can work under mild conditions as it can potentially replace the existing centralized fossil fuel-based Haber-Bosch process with small, decentralized units. Even the most active bulk inorganic catalysts fail due to low activity and parasitic hydrogen evolution at low temperatures.

A completely new class of catalysts, ternary ruthenium hydrides (Li₄RuH₆ and Ba₂RuH₆) composed of the electron- and H-rich [RuH₆] anionic centers is shown to follow non-dissociative dinitrogen reduction, where hydridic H transports electron and proton between the centers, and the Li(Ba) cations stabilize NₓHᵧ (x: 0 to 2, y: 0 to 3) intermediates. The synergistic effect facilitates a very complex reaction mechanism with a narrow energy span and small kinetic barriers leading to functional ammonia production kinetics under mild conditions. It also observed that the [RuH₆] catalytic center activate N₂ preferentially and avoid hydrogen over-saturation at low temperatures and near ambient pressure, by delicately balancing H₂ chemisorption and N₂ activation. The unprecedented yield at low temperatures occurs due to a shift in the rate-determining reaction intermediates and transition states, where the reaction orders in hydrogen and ammonia change dramatically.

Vanadium oxynitride, a member of the unexplored class of catalysts for ammonia evolution containing multi anionic species, is also studied thoroughly with computational studies. For the first time, the nitrogen reduction pathway in oxynitrides and the role of the mixed anions is established. The coexistence of oxygen and nitrogen leads to improved stability of the active surface-states, activity, and selectivity over hydrogen evolution. Moderate to low oxygen concentration is suggested to best impact catalytic properties due to optimal balance between consecutive protonation preference at N-sites over V-sites, low onset potential (0.4V-RHE), and facile N₂ adsorption at N-vacancy sites. The critical N-vacancy active sites that support a Mars van Krevelen mechanism for ammonia evolution are protected from self-annihilation by the mixed-valence anions, large kinetic barriers, and site blocking by O*/OH*/H* due to highly favorable N₂ absorption.
Resume

Kvælstoffiksering i ammoniak understøtter fødevareforsyningen, vi er afhængige af sammen med andre industrier, og det kan blive vekturen til et billig lagringssystem med vedvarende energi. Imidlertid forårsager brugen af fossilt råmateriale og centraliserede Haber-Bosch-syntesebetingelser > 2% af de globale menneskeskabte CO₂-emissioner. Efterspørgslen efter bæredygtig ammoniakproduktion driver enorm forskningsinteresse for at udvikle katalysator, der kan arbejde under milde forhold, da den potentielt kan erstatte den eksisterende centraliserede fossile brændstofbaserede Haber-Bosch-proces med små, decentrale enheder. Selv de mest aktive uorganiske katalysatorer i bulk mislykkes på grund af lav aktivitet og parasitisk brintudvikling ved lav temperatur.

En helt ny klasse af katalysatorer, ternære rutheniumhydrid (Li₃RuH₆ og Ba₂RuH₆) sammensat af de elektroniske og H-lyge [RuH₆] anioniske centre viser sig at følge ikke-dissociativ dinitrogenreduktion, hvor hydridisk H transporterer elektron og proton mellem centrene, og Li (Ba) -kationerne stabiliserer NₓHᵧ (x: 0 til 2, y: 0 til 3) mellemprodukter. Den synergistiske virkning letter en meget kompleks reaktionsmekanisme med et snævert energispænd og små kinetiske barrierer, der fører til god ammoniakproduktionskinetik under milde forhold. Det observerede også, at [RuH₆] -katalytisk center aktiverer N₂ fortrinsvis og undgår hydrogenovermætning ved lave temperaturer og nær omdøvelsestryk ved forsigtigt at afbalancere H₂-kemisorption og N₂-aktivering. Det hidtil uskabte udbytte ved lave temperaturer forekommer på grund af en forskydning i de hastighedsbestemmende reaktionsmellemprodukter og overgangstilstande, hvor reaktionsordrerne i brint og ammoniak ændrer sig dramatisk.

List of papers

I. Ternary ruthenium complex hydrides for ammonia synthesis
   Qianru Wang*, Jaysree Pan*, Jianping Guo, Heine Anton Hansen, Hua Xie, Ling Jiang,
   Lei Hua, Haiyang Li, Yeqin Gua, Peikun Wang, Wenbo Gao, Lin Liu, Hujun Cao, Zhitao
   Xiong, Tejs Vegge, Ping Chen

   Under review in Nature (* joint 1st author)

II. A low-temperature reaction mechanism for ammonia synthesis on electron-rich [RuH₆]
catalytic centers
    Jaysree Pan*, Qianru Wang*, Jianping Guo, Heine Anton Hansen, Ping Chen, Tejs Vegge

    Under review in ACS Energy Letters (* joint 1st author)

III. Vanadium oxynitrides as stable catalysts for electrochemical reduction of nitrogen to
    ammonia: the role of oxygen
    Jaysree Pan, Heine Anton Hansen, Tejs Vegge

    Being submitted in Journal of Materials Chemistry A
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1. Introduction

Scientific and technological knowledge is the keystone for continued innovation, and in applied forms, the essential component of our complex economy. It can be argued as the main force behind all dramatic changes in human history, including those currently underway. Developments like the steam engine changed how we work or travel. So too did electricity and atomic energy. Currently, the Internet is redefining human life as a whole – both individually and collectively. Technology affects the highly developed and the developing countries alike and each, in its own context. Although primarily positive, on rare occasions, humanity has been negatively impacted by scientific advancements when utilized by rogue forces. As technologies take more profound control or our everyday life as well as our future in unnoticeable manners, it is more crucial than ever to think of responsible research and innovation to identify and invest in research areas that are meant for the greater good.

1.1. Technology and sustainability

Starting from the summer of 2018, Swedish school kid Greta Thunberg decided to protest against the supposedly malevolent actions of global political and economic leaders towards abandoning the wellbeing of future generations for short term personal wealth gains or analogs. Without agreeing or disagreeing with her strong, forthright opinion on the complicit nature of our leaders, we as researchers can definitely commit to developing technologies that are sustainable in the long term and are inclusive in nature such that they cater to the broader population – so-called the forgotten billions.

The current general push towards sustainability if simply interpreted as any further expansion of pollution causing activities like personal transport or consumption of meat, it will mean forcing 70% of the world population to have a life that is utterly unacceptable by 1st world standards. On the other hand, if we help everyone reach a desirable quality of life that we are used to employing current means of production and industry, we will burn through all resources at five times the current rate – a situation straight out of Greta’s nightmare. Being able to afford a comfortable life is a fundamental human right, but we must achieve that without wreaking havoc on the planet we call home. Meeting fundamental human life needs while preserving nature is the essence of sustainable development. This might seem to be an impossible goal, but not if we can harness the power of accelerated scientific advancements, especially if done with the help of virtue.
signaling leaders as a coordinated global effort focused on developing technology that can enable ‘sustainable economic growth’ – an oxymoron as of now.

The United Nations 2030 Agenda for Sustainable Development includes 17 interconnected Sustainable Development Goals (SDG) towards a global plan of action for people, planet, and prosperity\(^1\). Trade-offs exist between the domains of higher welfare and wellbeing, infrastructures for development; and achieving sustainable usage of the natural environment. Unless aided by radical new innovation, this agenda is bound to fail or remain incomplete. For example, one of the underlying welfare notion connecting SDG one (no poverty), two (zero hunger), and three (good health) is high-quality nutrition for all. To provide 7.5 billion people high-quality food that is nutritionally equivalent to food typically available to Danes, we have to expand our food production significantly. We have to use more chemical fertilizer and emit more pollutants. That would negatively climate, land and the sea – clear reversal of other SDGs of the agenda.

Japanese energy economist Yoichi Kaya proposed the correlation between environmental impact and economy via the identity\(^2\)

\[ C = P \times \frac{\text{GDP}}{P} \times \frac{E}{\text{GDP}} \times \frac{C}{E} \]

which relates carbon emissions, \(C\), to population (\(P\)); per capita gross domestic product (\(\frac{\text{GDP}}{P}\)); energy intensity of the economy (\(\frac{E}{\text{GDP}}\)); and emissions per unit of energy (\(\frac{C}{E}\)). The Kaya identity tells us that attempting to reduce emissions sharply without significant changes in industrial and agricultural practices, would substantially shrink the economy. Policymakers typically ignore the impact of population and GDP growth, as lowering them can not be regarded as viable. However, form a global perspective, those are the most significant driver of environmental impact growth. The most impoverished contrived have the highest population growth rate and need a fast-growing economy to provide its citizens with an acceptable quality of life.

It has been proposed that long term commitment to a technology-led approach can minimize the environmental impact with higher probability and much lower cost\(^3\) than the emissions-target enforcing approach whose success is sensitive to the political climate. This approach works by replacing emissions targets with credible long-term global commitments to invest in R&D that makes sustainable alternatives more economical. Breakthrough technologies, thus arising, will automatically incentivize the deployment of new or improved low-carbon technologies as they become scalable and cost-effective. This approach is also attractive to developing countries such as China, India, Brazil and Indonesia as they can participate in an energy-technology race empowered by a young, highly educated STEM workforce. China has already shown its prowess in this matter. This is also appealing to the younger generations as they can take up the challenge of sustainability with their scientific and creative capabilities rather than by sacrificing their future.
### 1.2. Catalysis and human development

Catalysis has profoundly impacted human life for thousands of years, starting from when more than ten thousand years ago, we learn to utilize enzymatic catalysis to make food and drink like bread and wine. In the recent past, among most impactful cases include - making petroleum-based fuels less polluting with nickel-based catalysts, the invention of Haber Bosch process of ammonia production, Fischer Tropsch process, Ziegler Natta polymerization, automotive exhaust catalytic reactor among many others. It is hard to imagine civilized society today without the role of catalysis in the fundamental aspects of life, namely energy, food, and water. It touches every aspect of human life now. The modern industrialized world would be inconceivable without catalysts. The impact can of catalysis in the modern economy is perceived from the fact that of all industrially made products, 95% by volume, 70% by processes are synthesized by means of catalysis, and 80% of the added value in the chemical industry is based on catalysis. The total commercial value of all catalysts worldwide is over US$ 17.2 billion in 2014, and catalysis contributes to more than 35% of the world’s GDP.

Innovation in catalysis is core to meeting many of the critical challenges that society faces as a whole today. For sustainability centered solutions as well, commercial success and scaling can only be obtained through an innovation-driven approach that is grounded in the fundamental science of new catalyst development. Especially heterogeneous catalysis is becoming an essential tool to achieve sustainability in the production of energy and chemicals by minimizing energy demand and waste production, improving energy/chemical conversion ratio, and treatment for pollutants in air and water. For example, significant breakthroughs have been achieved recently in sustainably recycling CO$_2$ into useful fuels and chemicals with renewable electricity. The commercialization of such technologies has already started.

Even for the legacy chemical industries, which are the largest consumer of fossil fuel energy and feedstocks, improvement in sustainability can be achieved by replacing the energy source (e.g., going from carbonaceous fuel to renewable electricity) and replacing the feedstock chemical with renewably sourced chemical (e.g., replacing hydrogen from natural gas with hydrogen produced by photo or electrocatalytic method from water). Such modification in large scale chemical processes needs in-depth scientific and engineering research.
1.3. Importance of ammonia production

78% of the atmosphere is composed of nitrogen that exists in chemically and biologically inactive gaseous form. The conversion of nitrogen gas into nitrates and nitrites through atmospheric, industrial, and biological processes is called nitrogen fixation. The nitrogen cycle—the redox chemistry of nitrogen in the atmosphere, in soil, and water—is at the core of how life sustains on earth. All of the body protein in plants and animals are part of this cycle. Other than a tiny amount of nitrogen activation happening through lightning strikes, there are primarily two mechanisms by which almost inert N\textsubscript{2} becomes part of the ecological and biological cycle of the planet. One is biological – symbiotic bacteria, diazotrophs use nitrogenase enzyme to reduce dinitrogen. This process is as old as our ecosystem. On the other hand, an almost equal amount of nitrogen fixation happens through a man-made industrial process that is barely a hundred years old. Fritz Haber discovered how ammonia could be synthesized by reacting atmospheric dinitrogen with hydrogen in the presence of iron at high pressures and temperatures (Nobel prize 2018). Carl Bosch subsequently developed it on an industrial scale (Nobel prize 1931). Today, this reaction is known as the Haber–Bosch process. The importance of this discovery will not be overestimated if we say it has impacted human life more than even telecommunication or computers. Without this discovery of this process, limitation in world food production would mean six billion of us would not exist today\textsuperscript{9}. In his Nobel lecture, Haber explained that his primary motivation for synthesizing ammonia from nitrogen was the growing demand for food - “it was clear that the demand for fixed nitrogen, which at the beginning of this century could be satisfied with a few hundred thousand tons a year, must increase to millions of tons”\textsuperscript{10}. Currently, we produce 170 million tons of ammonia with primary utilization in fertilizer production using the same Haber Bosch process. Unfortunately, along with bringing food for billions of people, it also created a cascade of negative environmental changes - increase in water and air pollution, high greenhouse-gas levels, and a loss of biodiversity resulting from dense agriculture supported by fertilizers\textsuperscript{11}.

Ammonia is used not just for fertilizer production but a range of other essential products like synthetic chemicals, medicaments, dyes, explosives, and resins. At 170 million tons per year, it is the world’s most produced chemical. A significant amount of energy is consumed to speed up the slow rate of conversion by high temperature (>500°C) and high pressure (>200 atm). Methane, a natural gas, is used as the hydrogen source. The prevalent energy source is the combustion of natural gas or coal. About 600 kg of natural gas is consumed to produce a ton of ammonia in the most efficient facilities – amounting to a total of about 5% of global natural gas
supply. The total fossil CO$_2$ emissions from NH$_3$ synthesis with the current basket of energy sources can be estimated to be more than 670 million tonnes per year$^{12}$. This amounts to about 2.5% of all anthropogenic CO$_2$ emissions worldwide. To achieve the economy of scale in cost and energy consumption given the specific conditions required for this reaction, typical ammonia plants are of humongous size. Plants recently developed by Casale and Haldor Topsoe can deliver up to 6,000 tons of ammonia every day. A century of optimization has improved the energy requirement so much that it is now much lower than the biological process of nitrogen fixation that requires 5 eV (15 ATP) per nitrogen molecules$^{13}$. While centralized facilities bring high efficiency, the opposite is true for the downstream use of fertilizers by farmers. The distribution of large, centrally produced supplies of fertilizer requires efficient transportation and shipping to the last mile, which is nonexistent in developing countries – where we will see the highest population growth and thus growth in food demand. These are also the communities where uncertainties of supply and high unit cost of fertilizer from expensive transport and middleman based supply chain causes the most pain for poverty stricken farmers. Merely lowering the pressure of the Haber-Bosch process and thus the compression infrastructure can reduce 50% capital cost – making such plants accessible to poorer countries. Even better, enabling ambient condition ammonia synthesis can bring it to the doorstep of the farmers. The significance of this process is highlighted when we consider the fact that ten of seventeen UN SDG is linked with this (Figure 1.1). As explained previously, they are often in conflict with each other but can be met in unison if we are successful in the groundbreaking innovation of ambient pressure and temperature distributed ammonia production process.
1.4. Synthetic routes to ammonia

Along with solid-gas interface heterogeneous thermal catalysis (like Haber Bosch process) and biological enzymatic fixation, ammonia can also be produced by electrochemical nitrogen reduction or plasma synthesis (Figure 1.2). Thermo- and electrocatalytic processes are well understood and studied widely in search of optimal catalyst design for ammonia synthesis. This thesis covers these two processes.
1.5. **Thermo-catalytic ammonia synthesis**

Ammonia synthesis from $\text{N}_2$ and $\text{H}_2$ is an exothermic entropy decreasing reaction, where lower temperature and higher pressure should favor the yield. However, this reaction is kinetically restricted by the very stable $\text{N}≡\text{N}$ bond. Metallic catalysts have been very extensively studied for this reaction. Alkali promoted Ru is the best elemental metal catalyst for this process, but Fe based catalysts are used industrially, albeit those are slightly less active because of their significantly lower price. Ru-based catalysts suffer from high cost and severe hydrogen poisoning\(^\text{16}\). On metallic catalysts, Stepped surfaces are the most active in $\text{N}_2$ activation\(^\text{17}\). The reaction intermediates (adsorbed $\text{N}^*$, $\text{NH}^*$, and $\text{NH}_2^*$) bind too strongly to the surface making active sites unavailable. At higher temperatures, active sites are available, but reaction becomes uphill in energy, which is mitigated by increasing the pressure (Figure 1.3).

Scaling law between the activation energy for $\text{N}_2$ dissociation and $\text{N}^*$ adsorption on metals explains the difficulty of finding metallic catalysts for an ambient thermocatalytic process. Alternative classes of catalysts, as well as usage of secondary effects, from promoter\(^\text{18}\), and support\(^\text{19,20}\), have been studied to break this scaling law. Possibly if the mechanism is different, this particular limitation might be invalid, leading to new catalyst optimization opportunities. Plasma enhanced catalysis has been touted as a possible alternative to the Haber–Bosch route.
process for allowing ammonia production at ambient pressure and temperature\textsuperscript{21}. It has been tried out in ammonia synthesis to break the kinetic and thermodynamic limiting factors\textsuperscript{22}.

Figure 1.3. Theoretically calculated free energy diagrams for ammonia synthesis using density functional theory simulations for a stepped Ru surface (a) at different temperatures for a fixed reactant pressure of 1 bar, and (b) at different reactant pressures at a fixed temperature of 700K. The numbers in (a) and (b) refer to the elementary reaction steps of a dissociative mechanism shown in (c).\textsuperscript{13}

1.6. Electro-catalytic ammonia synthesis

Ambient condition electrochemical ammonia synthesis can be the holy grail of nitrogen fixation. It can be done at the point of usage and utilize intermittent renewable electricity when there is excess generation over baseload. Such an approach can not only support a sustainable food and chemical industry but also provide means for long term inexpensive energy storage option to a renewable heavy electricity grid. Experimental studies using solid electrodes in aqueous electrolytes have been plagued by slow kinetics and a large required overpotentials as well as poor faradaic efficiencies of less than 1% for ammonia\textsuperscript{23}. Hydrogen evolution is the much faster and main competing reaction. This can be explained form the theoretically derived limiting potential volcano plots based on reaction intermediate scaling relations for both hydrogen and ammonia evolution (Figure 1.4). Hydrogen evolution is always thermodynamically preferred over ammonia irrespective of which metal is taken. The fast kinetics of proton transfer compared to nitrogen further improve on the kinetics of hydrogen evolution. Both the dissociative and associative path (Figure 1.5) of ammonia evolution can be limited by hydrogen evolution. A
research direction can be focused on finding catalysts that break the limiting scaling relationship\textsuperscript{24}. Solving the low selectivity challenge is the most important research theme in electrocatalytic ammonia production. A nitrogen vacancy mediated Mars van Krevelen mechanism has been proposed for transition metal nitrides\textsuperscript{25}. Better selectivity toward has been obtained using molecular catalysts and enzymes\textsuperscript{26–28}. These catalysts are not scalable and stable, tend to get deactivated within a short time period. Oxides have also been tried out without significant improvement in faradic efficiency\textsuperscript{29,30}. Usage of non-aqueous electrolytes to hinder access to protons is a strategy for restraining hydrogen evolution for better ammonia selectivity\textsuperscript{31}. For example, a hydrophobic fluorinated ionic liquid with low water content and high N\textsubscript{2} solubility has been shown to minimize the hydrogen evolution, but it suffers from slow kinetics due to slow mass transfer in the viscous electrolyte\textsuperscript{32}. Reliable detection of a small quantity of ammonia produced by laboratory setups is a challenge and results that not properly qualified can misguide the research direction.\textsuperscript{33}

\textbf{Figure 1.4}. Electrochemical ammonia evolution (black) and hydrogen evolution (red) limiting potential ($U_L$) as a function of nitrogen binding energy ($\Delta G_N$) plotted for close-packed transition metal terraces and. The solid lines refer to the limiting potential volcano obtained using scaling relationships between adsorbed surface intermediates while each individual point is explicitly computed.\textsuperscript{23}
1.7. Computational catalysis design

Insilico design of materials with specific properties has now become mainstream research methods along with experimental techniques of synthesis and test. As far as catalysis design is concerned, improvement in speed, accuracy, and treatable system size with density functional theory (DFT) made it now possible to describe catalytic reactions at surfaces with the detail and accuracy required for computational results to compare favorably with experiments. DFT simulations can estimate the interaction energies of molecules and atoms with metal surfaces with sufficient accuracy to describe trends in reactivity across catalyst families. The kinetics of a catalytic reaction can now be evaluated only with DFT simulation of reaction barriers, reaction energies, and the associated entropies. The agreement between DFT based modeling and experiment\textsuperscript{35,36} illustrate the accuracy and value of computational estimation of catalytic properties (Figure 1.6).
Figure 1.6. Comparison of simulation and experimental results for ammonia synthesis productivity over ruthenium catalyst.\textsuperscript{37}

The complete kinetic description of a given system takes significant time and expertise to establish and thus nonoptimal to do so for each candidate while searching for better catalysts. Establishment of atomic scale electronic structure based descriptors that determine the macroscopic kinetics has been a breakthrough in the field of computational catalysis. The number of parameters that govern the overall process might be too many to perform combined optimization. The fact that activation energies for elementary surface reactions are strongly correlated with adsorption energies. Furthermore, the adsorption energy of similar adsorbates is also correlated (scaling relations), enabling us to perform a dimensionality reduction of the overall optimization problem.\textsuperscript{38} Additionally, elementary reactions and barriers across catalysts surfaces show a linear Brønsted–Evans–Polanyi relation and reactions belonging to the same class even follow the same relation.\textsuperscript{39} Such correlations lead directly to a volcano relationship between the rate and adsorbate binding energy descriptor, allowing us to optimize catalysts for a given reaction very quickly with a handful of DFT simulations.\textsuperscript{37,40,41} Electronic property based descriptors even let us link bulk properties to catalytic properties, making the screening task even easier.

The electrochemical reactions on catalyst surfaces are more complicated than solid-gas heterogeneous catalysis due to the liquid phase in direct contact with the catalyst's surface and due to the charging of the surface.\textsuperscript{42,43} The recent development of simplified models has made
quantum mechanical simulations of electrochemical reaction feasible. The computational hydrogen electrode model\textsuperscript{44} especially helped translate many of the core concepts of computational catalyst design area directly from thermocatalytic to electrocatalytic systems\textsuperscript{45,46}. It has been extensively used for simulation of electrocatalysts for ammonia evolution\textsuperscript{24,25}.

Using DFT simulations, we can approximately evaluate high catalytic activity or selectivity, but it is difficult to do so for long-term stability and other important factors that originate from a long time and length scale phenomena and thus can not be captured. Thus DFT based computational catalyst design must be performed hand in hand with experimental studies under realistic conditions. Experimental validation and optimization, followed by computational screening, will always be central to creating new scalable stable catalysts.

### 1.8. Thesis outline

This PhD project focus on DFT based simulation catalysts in mainly two directions for the discovery of selective ammonia evolution catalysts that are highly active at ambient pressure and temperature. For the thermocatalytic process, we have explored ternary ruthenium hydrides – Li$_4$RuH$_6$ and Ba$_2$RuH$_6$, and for the electrocatalytic process, we have explored the vanadium oxynitride system. The outline of the thesis is as follows:

- **Chapter 1: Introduction**
  The importance of catalysis, ammonia, and innovation needed for ambient ammonia processes are discussed with the view of the united nations sustainable development goals. I also explain how computational modeling is an excellent tool for that.

- **Chapter 2: Theory and methodology**
  Basic concepts in computational catalysis are explained along with density functional theory based total energy simulations that are used in this project extensively.

- **Chapter 3: Ternary ruthenium hydrides as thermocatalyst**
  A brief introduction to the project and how the content of the first two included articles complement each other

- **Chapter 4: Vanadium oxynitrides as electrocatalyst**
  A brief introduction to an article to be submitted soon

- **Chapter 5: Conclusion and outlook**
2. Theory and methodology

The computational models used for this PhD project encompass both quantum mechanical simulations for total energy based on DFT, but also numerical models that utilize DFT derived energetics numbers to reaction parameters at the atomic scale. Basic concepts in density functional theory and computational catalysis are briefly discussed here.

2.1. Electronic structure

Material properties are in principle determined by the electronic structure and thus can be obtained by solving the time-dependent Schrödinger equation\textsuperscript{47} for the electronic wavefunction of the system:

\[ \hat{H}\psi = i\frac{\partial}{\partial t}\psi \]  

(2.1-1)

Where \( \hat{H} \) is the Hamiltonian operator and \( \psi \) is the electronic wavefunction which is dependent on nuclear and electronic coordinates and time. For systems consisting of two or more electron, no closed-form analytical exact solution exists. Therefore, we need to take necessary approximations and use numerical techniques to obtain solutions for practical material simulations. The absence of optical excitation means simulations for thermo- or electrocatalysis do not require time dependency. Assuming time-invariant orbitals, the N-electron time-independent Schrödinger equation is

\[ \hat{H}\psi = E\psi \]  

(2.1-2)

Now \( \psi \) is the N electron wavefunction without time variation and \( E \) is the total energy of the system.

As the nuclei are three or more orders of magnitude heavier than the electrons, the adiabatic approximation (also called Born-Oppenheimer approximation\textsuperscript{48}) can be applied to treat the motion of nuclei and electrons separately. It is assumed that electrons follow nuclear motion instantaneously. The Hamiltonian can be written as

\[ \hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V_{ext}(r_i) + \frac{1}{2} \sum_{i<j}^{N} \frac{1}{|r_i - r_j|} \]  

(2.1-3)
The first term is the kinetic energy operator for the electrons ($\hat{T}$). The 2nd term is the external potential from the nuclei ($\hat{V}_{\text{ext}}$) acting on electrons. The 3rd term is the electron-electron Coulomb interaction ($\hat{V}_{\text{int}}$). Terms from nuclear-nuclear interaction can be calculated easily, and the nuclear kinetic energy operator is ignored based on adiabatic approximation. So the Hamiltonian looks like

$$\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{int}}$$

2.1-4

### 2.2. Density functional theory

The success of density functional theory originates from the translation of 3N variable wavefunction problem to an electronic charge density optimization problem, which is a three spatial coordinate based variable. This makes simulations with many atoms feasible. In DFT, Hamiltonian operators are a function of spatial charge density ($\rho(r)$) distribution. The Hohenberg Kohn theorems\(^{49}\) provide a connection between the charge density distribution and the electronic wavefunction. 1st Hohenberg and Kohn theorem proves that unique ground state density $\rho(r)$ comes from unique external potential and the total energy of the ground state wave function is also unique. The energy of the system becomes

$$E[\rho] = T[\rho] + V_{\text{ext}}[\rho] + \int d^3 r \, V_{\text{ext}}(r) \rho(r)$$

2.2-1

The 2nd Hohenberg Kohn theorem states that the ground state energy can be obtained variationally i.e., the ground state density leads to minima in the total energy. Kohn and Sham\(^{50}\) proposed a scheme to map an interacting particle (under the influence of an external potential) problem to non-interacting particles (in an effective potential $V_{\text{eff}}$, well) problem such that the ground state density remains the same. The same ground-state density implies (2nd Hohenberg Kohn theorem) that the total energy of these two systems are the same. Thus we can write

$$E[\rho(r)] = T_s[\rho(r)] + V_H[\rho(r)] + E_{\text{xc}}[\rho(r)] + V_{\text{ext}}[\rho(r)]$$

2.2-2
\[ T_s \text{ is the kinetic energy of the non-interacting electron gas, } V_H \text{ is the Hartree energy. } E_{xc} \text{ portrays electron exchange and correlation, which is basically an unknown term that needs to be approximated.} \]

\[ \left\{ -\frac{1}{2} \nabla^2 + V_{\text{eff}}(r) \right\} \psi_i = \epsilon \psi_i \quad \rho(r) = \sum_{i \in \text{occupied}} |\psi_i|^2 \quad \text{while} \]

\[ V_{\text{eff}}(r) = V_{\text{ext}} + \int \frac{\rho(r')}{|r-r'|} dr' + \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)} \]

The T_s part is obtained by iterative solution of Kohn Sham equations (2-7 and 2-8). Iteration is done between the charge density and effective potential (which is basically the nuclear positions i.e. atomic structure) starting from an approximate charge density until convergence is reached (figure 2.1).

**Figure 2.1.** Iterative minimization technique for DFT total energy calculations\textsuperscript{51}
2.3. Exchange correlation functional

Electron exchange energy comes from the Pauli exclusion principle, and the correlation term portrays dependency of electron-electron interaction on the presence of other electrons. DFT calculated ground state energy is dependent on exchange-correlation functional. In the simplest approximation, it is assumed that \( E_{xc} \) is only dependent on local charge density \( \rho \) (LDA).

\[
E_{xc}^{\text{LDA}}[\rho] = \int \varepsilon_{xc}^{\text{LDA}}[\rho(r)] dr
\]

2.3-1

Where \( \varepsilon_{xc} \) is the functional. Catalyst surfaces show a large variation in charge density, especially near the surface and due to reaction intermediate and surface interaction. The next level of approximations includes gradient of charge density (generalized gradient approximation (GGA)) in the model \(^{53}\) without increasing computational cost significantly.

\[
E_{xc}^{\text{GGA}}[\rho] = \int \varepsilon_{xc}^{\text{GGA}}[\rho(r), \nabla \rho(r)] dr
\]

2.3-2

Based on the type of system simulations, parameters of the exchange correlation functional are often optimized to match experimentally observed high-level quantum simulation data. One of the most popular types of GGA functional that has been optimized for catalyst surface DFT simulations is like RPBE \(^{54}\). This functional has been used for all simulations done in this project.

2.4. Practical simulations with VASP

Simulations done in this PhD project used the Vienna Ab initio Simulation Package, which implements the iterative scheme with a plane wave basis set for wavefunction representation. The simulation cells are periodic boundary condition boxes, which are suitable for bulk crystal structures. By considering vacuum regions along with the crystalline region, surfaces can also be calculated. The actual simulated system along the normal to surface direction is basically
consecutive layers of catalyst slab punctuated with a large vacuum. Molecules can be calculated by considering vacuum in all three dimensions such that periodic images to not interact. Among the parameters to be supplied to VASP code, $E_{\text{cut}}$ determines how high accuracy the plane wave representation is. In addition, the reciprocal space (first Brillouin zone) is sampled with a Monkhorst-Pack grid\textsuperscript{55}. VASP uses Projector Augmented Method (PAW), where the tightly bound core electrons are frozen and outer electrons are represented by soft projector functions.

### 2.5. Adsorbate binding energy

The binding energy of an adsorbate on a catalyst surface can be calculated from total energy calculation of the surface without the adsorbate, that of the surface with the adsorbate and free energy of reference molecules. For example, the binding energy of H* ($\Delta E_{H^*}$) will be

\[
\Delta E_{H^*} = E_{H^*} - E_{\cdot} - \frac{1}{2} E_{H_2}
\]

where, $E_{H^*}$ is the free energy of the surface with the H* adsorbate, $E_{\cdot}$ is that of the surface only, $E_{H_2}$ is the energy of CO$_2$ and H$_2$ molecules. $^*$ denotes an empty active site, and $A^*$ denotes an adsorbate A bound to that active site.

### 2.6. Temperature correction methods

Finite temperature free energy contributions come from heat capacity ($C_p$), entropy (TS) and zero-point energy ($E_{ZPE}$). Evaluation of vibrational degrees of freedom is needed to evaluate these for molecules and adsorbates. The contributions from the solid catalyst surface are negligible comparatively. Vibrational calculations using a two-point finite difference approximation with small displacements of 0.01 Å along all three axes for each atom in the adsorbate and spectator species are done. Vibrational modes and their free energy contributions are calculated and analyzed using the Atomistic Simulation Environment (ASE)\textsuperscript{56}. The free energies of molecules are calculated within the ideal gas approximation\textsuperscript{57} assuming vibrational, rotational and translational modes are decoupled. For adsorbates that are strongly bound to the active site of the catalyst and rotational modes are restricted, temperature corrections were evaluated by treating the adsorbate degrees of freedom as independent quantum mechanical harmonic oscillators within the harmonic
approximation. However, some time the behavior is in between gas (free translator / free rotor) and strongly bound adsorbate (harmonic oscillator). So a hindered translator/hindered rotor model is taken to account for this behavior. In this model, for an adsorbate containing N atoms, two degrees of freedom are treated as hindered translations in the two directions parallel to the surface, one degree of freedom perpendicular to the surface is treated as a hindered rotation and the remaining 3N-3 degrees of freedom are treated as vibrations.

2.7. **Nudged elastic band method**

The nudged elastic band method (NEB) is used to define the minimum energy path, and the corresponding saddle point between two stable states called initial and final states. In this method, numbers of equidistant images along the path optimize themselves to minimize the energy of every image while maintaining equal distances from its immediate neighbors. During this optimization, spring forces act along the band between the images controlled the image distribution. Simultaneously, the perpendicular part of the true force moves the images down in energy to achieve the minimum energy path. Better convergence to a minimum energy path with sufficient resolution through NEB depends on the good initial guess of the path and enough number of intermediated images in the path. The minimum energy path and the transition state results reported in this thesis are produced by NEB as implemented in VASP.

2.8. **Energy span method**

The energetic span model is used to calculate turn over frequency (TOF) from the free energy path of N2 to NH3 catalytic cycle from the energetic span (δE):

\[
\text{TOF} = \frac{k_B T}{h} e^{-\frac{\delta E}{k_B T}}
\]

2.8-12

In this model, δE defined by the free energy of TOF-determining transition state (ΔG_{TDTS}), TOF-determining intermediate state (ΔG_{TDI}) and the free energy of reaction (ΔG_r < 0).
\[ \delta E = \begin{cases} 
\Delta G_{TDTS} - \Delta G_{TDI}, & \text{if TDTS appears after TDI} \\
\Delta G_{TDTS} - \Delta G_{TDI} + \Delta G_r, & \text{if TDTS appears before TDI} 
\end{cases} \]

In the free energy path, TDTS and TDI are the transition state and the intermediate state that maximizes the \( \delta E \) within that catalytic cycle.

The activation enthalpy \( (\Delta H_a) \) for the catalytic cycle can be back-calculated from the \( \delta E \) and the entropy correction \( (T\Delta S) \):

\[ \Delta H_a = \delta E + T\Delta S \]

Apart from the intrinsic errors of the DFT energy calculations, a primary source of error in the TOF calculation from the energetic span approximation is the \( T\Delta S \) corrections applied to generate \( \delta E \).

In the energetic span model, reactant and products in between TDTS and TDI govern the rate and order of the reaction.

### 2.9. Computational hydrogen electrode model

At the electro-catalytic solid-liquid interface, effects from electrolyte molecules and electric field makes accurate estimation of free energy of adsorption very difficult. One has to systematically simulate a large number of adsorbate/catalyst surface configurations with the full details of the electrified electrolyte-catalyst interface to estimate average adsorption energy – which is not computationally feasible. The computational hydrogen electrode (CHE) approximates the reaction free energy of an electrochemical reaction at a certain applied potential using calculations done without considering electrolyte molecules. The reaction free energy of each coupled electron-proton transfer \( (\Delta G_{\text{step}}) \) is simply added to the applied potential \( (U) \) to get the modified free energy change under the application of potential.

\[ \Delta G_{\text{step}}(U) = \Delta G_{\text{step}}(U = 0) + eU \]

Where \( e \) is the charge of an electron. If the potential is chosen to be on a reversible hydrogen electrode (RHE) scale, where the following reaction is reversible at 0 V vs RHE (V-RHE)
\[ \frac{1}{2} H_2 = H^+ + e^- \]  2.9-16

Once the calculation is done for 0 V-RHE, positive or negative potential is calculated that can turn all reaction steps free energy change at least zero to enable the reaction to go forward. This potential is called onset potential.
3. Ternary ruthenium hydrides as thermocatalysts

This portion of the PhD project focused on building a basic scientific understanding of the catalytic process and novel catalytic phenomenon in ternary ruthenium hydride compounds. We proved the discovery of these catalysts is a quantum leap in ambient ammonia production. Although I led the scientific expedition through theoretical modeling once the collaborating group stumbled upon the initial positive results, the project running for the last three years was done in close collaboration between theoretical and experimental groups with weekly scientific discussion. This PhD candidate did all the computational work. As the theoretical work proposed novel scientific findings, the group at Dalian performed the required experimental validation and verification in unison. While the theoretical work forms the major component of this thesis, the experimental work forms the main component of a PhD thesis of the lead author from the experimental group. Both the articles are shared 1st author between these two PhD students.

The very strong nitrogen triple bond hinders good turnover frequency in heterogeneous ammonia synthesis. In biological nitrogenase based nitrogen fixation this barrier is overcome by hydrogen associative conversion where the reduction of the triple bond takes place synchronously with the formation of N-H bonds via successive or concerted proton and electron transfer steps. Mimicking this approach to ammonia production with a stable inorganic catalyst can lead us to the holy grail of ambient ammonia production. We discovered that the ternary ruthenium hydrides Li4RuH6 and Ba2RuH6 represent an entirely new class of compound catalysts composed of the electron- and H-rich [RuH6] anionic centers that allow non-dissociative dinitrogen reduction by hydride route. This is a completely different approach from using hydrides as catalyst support with a limited role in the catalytic process.

Among the critical theoretical results obtained in this project, the 1st article covers the extremely complex reaction mechanism involving thirteen intermediate states and multiple adsorption/dissociation and lattice H transfer processes – that has been mapped out from exhaustive reaction and lattice distortion path search. Especially it simulations show how crucial is the flexible structure dynamics of the catalyst itself that plays a role in keeping the energy span small while the Li/Ba cations for stabilizing NxHy (x: 0 to 2, y: 0 to 3) intermediates. The theoretical study also shows that the hydrogenation of the adsorbed N2 happens preferentially from the lattice hydride due to its lower kinetic barrier.

For contribution coming from this PhD project, the 2nd article focus on the chemical phenomenon pertaining to the catalytic effect of the electron- and hydrogen-rich [RuH6] centers that enable
record ammonia yield at temperatures as low as 448 K. DFT simulations are used to show that unparalleled low-temperature activity is due to essentially barrier-free hydrogen adsorption and scrambling on the Ru-complexes. It is further supported by a kinetically prohibited transfer of lattice hydrogen (activation energies >1 eV) to neighboring Ru-complexes. The catalyst thereby balances hydrogen over-saturation and preferential dinitrogen adsorption. These findings also explain the drastic changes in the reaction order of hydrogen and ammonia, when going from 573 K to 448 K, as resulting from substantial shifts in the rate determining transition state (TDTS) and intermediate (TDI) at temperatures below 498 K. The mechanistics of this novel class of low-temperature catalysts relies on a combination of steps and processes from both homogeneous and heterogeneous catalysis, which layout a new path in the pursuit of near-ambient ammonia catalysts.
Paper I
Ternary ruthenium hydrides for mild-condition ammonia synthesis

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Ammonia is the feedstock for nitrogen fertilizers and a potential carbon-free energy carrier, but the current production emits more CO₂ than any other chemical producing reaction in the World. The demand for decarbonizing the ammonia industry by using renewable energy has renewed research interests into catalyst development for effective N₂ reduction under mild conditions - a grand scientific challenge1-3. Conventional heterogeneous catalysts based on metallic Fe or Ru mediate dinitrogen dissociation and hydrogenation through a relatively energy-costing pathway. The ternary ruthenium hydrides Li₄RuH₆ and Ba₂RuH₆ reported in this work, on the other hand, represent an entirely new class of compound catalysts, which are composed of the electron- and H-rich [RuH₆] anionic centers for non-dissociative dinitrogen reduction, where hydridic H transports electron and
proton between the centers, and the Li(Ba) cations for stabilizing NₓHᵧ (x: 0 to 2, y: 0 to 3) intermediates. The dynamic and synergistic involvement of all the components of the ternary hydrides facilitates an entirely novel reaction mechanism with a narrow energy span and perfectly balanced activation energies for the multi-step process, leading to ammonia production with superior kinetics under mild conditions.

The energetics and mechanism of a catalytic process depend explicitly on the interaction between the reacting species and the active center, which is exemplified in the activation and conversion of N₂ to NH₃ over natural and man-made catalysts. In biological ⁴,⁵ or organometallic N₂ fixation ⁶-⁸ catalyzed by FeMo(V) cofactor or soluble transition metal (TM) complexes, N₂ coordinates to the ionic TM center in a mild exothermic manner and undergoes a hydrogen associative conversion, i.e., the reduction of the N≡N bond takes place synchronously with the formation of N-H bonds via successive or concerted proton and electron transfer steps. Simultaneous formation of the side product dihydrogen is indeed a major concern in these systems. When the catalysis is carried out on an extended Fe or Ru metal surface, N₂ adsorbs on the active center composed of multiple TM atoms (C₇ or B₅ site of Fe or Ru, respectively) and dissociates exothermically into chemisorbed N atoms followed by a stepwise hydrogenation to NH₃ ⁹-¹². The relatively high kinetic barrier for N₂ dissociation and/or strong adsorption of intermediate species on Fe or Ru metal surface render NH₃ synthesis under near-ambient conditions unattainable ¹³. Creating an active center with suitable electronic structure and reacting environment for effective “hydrogenolysis” of N₂ by H₂ would synergize the energy input and output in breaking and establishing chemical bonding, and thus endow the catalysis of narrow energy span ¹⁴. Encouraging attempts have been made via creating catalytic center of isolated or clustered TM on an oxide support ¹⁵,¹⁶ or defect-borne Co₃Mo₃N surface ¹⁷, while catalytic ammonia formation under mild conditions has yet to be demonstrated.

There is increasing interests in exploring hydrides as functional supports of Ru nanoparticles or additives of 3d metals or their nitrides to catalyze ammonia synthesis ¹⁸-²⁰. Interestingly, our previous investigation reveals that laser-generated gaseous clusters such as [Li₄FeH₆]⁻ and [Li₅FeH₇]⁻ etc. can react with dinitrogen stoichiometrically forming
NH₂-containing clusters ²¹. This finding inspired us to investigate whether the ternary hydrides of alkali (or alkaline earth) and transition metals would have the potential to catalyze ammonia formation from N₂ and H₂. The synthesis of Li₄FeH₆ requires extremely high pressure of 6.1 GPa ²², but its Ru analogues are stable entities and can be facilely prepared under normal condition ²³. We therefore investigated ternary Ru hydrides, a class of mixed ionic-covalent compounds having a general chemical formula of Aₓ[RuH₆] (A = Li, Na, Mg, Ca or Ba etc., x= 4 or 2) ²³,²⁴, for ammonia synthesis. Of particular interests are Li₄RuH₆ and Ba₂RuH₆, which can be synthesized via reacting Ru metal with LiH or BaH₂, respectively. Ru in Li₄RuH₆ has a low valence state as indicated by charge state analysis ²⁴. Our Bader charge calculations also reveal that Li donates electronic charge to [RuH₆]; H, on the contrary, is negatively charged (Extended Data Fig. 1). The H- and electron-rich [RuH₆]⁺ anions sit inside the K₄CdCl₆-type framework of Li (or Ba) cations with a Ru-Ru distance of 5.09 (5.78) Å (Extended Data Fig. 2). These ternary ruthenium hydrides differ distinctly from the closed packed Ru metal surface and the isolated molecular Ru complexes in electronic, compositional and structural properties as illustrated in Figs. 1a, 1b and 1c.
**Fig. 1. Properties of Li₄RuH₆.** a, Li₄RuH₆ surface with the unit cell of Li₄RuH₆ shown on the right side (Ru-red, H-yellow, Li-white). b, Ru (0001) surface (the B₅ site is highlighted in bright red). c, the model of molecular Ru complex (L-ligand). d, The pressure-composition isotherms of the dehydrogenation of Li₄RuH₆ and the corresponding van’t Hoff plot, the lines are guide to eye. e, *in situ* SR-PXD characterization of Li₄RuH₆ sample under atmospheric N₂-3H₂ and elevated temperatures (from 473K to 773 K).

Our pressure-composition-isotherm and temperature-programmed reaction measurements reveal that Li₄RuH₆ has a large enthalpy change of 93.1 kJ mol⁻¹-H₂ in hydrogen desorption (the equilibrium H₂ desorption pressure is below 0.2 bar at 773 K), and only at high temperatures would Li₄RuH₆ decompose to Ru and LiH (Fig. 1d). Li₄RuH₆ is also resistant to diluted NH₃, i.e., upon feeding a mixture of NH₃ and H₂, the ternary hydride remains intact until ca. 673 K (Extended Data Fig. 3a). The *in situ* SR-PXD characterization also reveals that the hydride remains the dominant phase until ca. 651 or 738 K under N₂ or N₂+3H₂ of atmospheric pressure, respectively (Fig. 1e and Extended Data Fig. 3b). Ba₂RuH₆ is found to be even more stable than Li₄RuH₆ (Extended Data Table 1 and Figs. 3c-d)²⁵. These experimental results show that the bulk Li₄RuH₆ and Ba₂RuH₆ phases will remain stable under the ammonia synthesis conditions applied in
this study (H$_2$ partial pressure from 0.25 to 7.5 bar, operation temperature from 323 K to 573 K).

**Fig. 2. Catalytic performances.**

*a*, Activities of Li$_4$RuH$_6$-based catalysts at 573 K and the corresponding activation energies (Reaction conditions: catalyst loading 30 mg, H$_2$:N$_2$=3:1, flow rate 30 ml min$^{-1}$, and 1 bar).

*b*, Temperature-dependent NH$_3$ synthesis rates of different catalysts (Reaction conditions: H$_2$:N$_2$=3:1 (filled symbols) or H$_2$:N$_2$=2:3 (open symbols), others are the same as *a*). Error bars represent the standard deviation from three independent measurements.

*c*, Time dependence of the activities of Li$_4$RuH$_6$/MgO and Ba$_2$RuH$_6$/MgO catalysts (Reaction conditions: H$_2$:N$_2$=2:3, 10 bar, others are the same as *a*).

*d*, Time course of effluent NH$_3$ concentration in the outlet gas (Ba$_2$RuH$_6$/MgO catalyst, 200 mg, H$_2$:N$_2$=1:3, flow rate 36 ml min$^{-1}$, 1 bar). The inset shows the activities of Ba$_2$RuH$_6$/MgO catalyst in the temperature range of 373-473 K determined by $^1$H NMR measurements of NH$_3$ concentration in the outlet gas under a flow of $^{15}$N$_2$-H$_2$ or $^{14}$N$_2$-H$_2$. The activity at 473 K was also measured by conductivity meter for comparison (30 mg, H$_2$:N$_2$=2:3, flow rate 10 ml min$^{-1}$, 1 bar).
The as-prepared bulk-phase Li$_4$RuH$_6$ and Ba$_2$RuH$_6$ samples exhibit activities of ca. 150 and 120 $\mu$mol g$_{\text{cat}}^{-1}$ h$^{-1}$ at 1 bar and 573 K, respectively (Extended Data Fig. 4a). We then reduced the particle sizes of the samples to increase their surface areas. Our experimental results show that ball milling the as-prepared Li$_4$RuH$_6$ sample with inert dispersers, such as BN and MgO, can effectively reduce its crystalline size from ca. 50 nm to ca. 20 nm (Li$_4$RuH$_6$-BN(BM)) and 9 nm (Li$_4$RuH$_6$-MgO(BM)), and enhance the reaction rate by ca. 45 and 125 times, respectively (Fig. 2a). We thus employed MgO as support and synthesized Li$_4$RuH$_6$/MgO and Ba$_2$RuH$_6$/MgO catalysts by introducing Li and Ba to the parent Ru/MgO catalyst. These supported catalysts (their TEM images and HAADF-STEM characterizations are given in Extended Data Figs. 5-6) possess the characteristic features (Ru-H stretch and surface composition) of the bulk-phase hydrides (Extended Data Fig. 7). The Li$_4$RuH$_6$/MgO catalyst shows ca. 400-fold increase in activity from the bulk-phase Li$_4$RuH$_6$, but has a similar apparent activation energy of ca. 71 kJ mol$^{-1}$ (0.74 eV) to other Li$_4$RuH$_6$-based catalysts (Fig. 2a and Extended Data Fig. 8a), manifesting an effective exposure of active sites in the supported catalyst. The supported ternary hydride catalysts perform extraordinarily well under mild conditions and show constant activities for 100 hours (Figs. 2b and c). In particular, the Ba$_2$RuH$_6$/MgO significantly outperforms the most active Ru catalysts reported to date, and its activity at 523 K is over one order of magnitude higher than the benchmark Cs-promoted Ru/MgO catalyst (Table 1 and Extended Data Table 3). It is important to note that if the Li$_4$RuH$_6$/MgO and Ba$_2$RuH$_6$/MgO samples are exposed to air, their activities drop significantly to the level of the Ru/MgO sample. Similarly, the direct introduction of Li$_2$O to Ru/MgO does not bring notable changes in activity (Extended Data Fig. 4b). This result demonstrates that the ternary hydride form is of critical importance for the efficient catalysis.
Table 1. Catalytic Properties of Ru-based catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ru content (wt %)</th>
<th>r\textsubscript{NH\textsubscript{3}}\textsuperscript{a}</th>
<th>TOF\textsuperscript{b}</th>
<th>Reaction order</th>
<th>E\textsubscript{a} (kJ mol\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>573 K</td>
<td>523 K</td>
<td>573 K</td>
<td>523 K</td>
<td>α(NH\textsubscript{3})</td>
</tr>
<tr>
<td>Li\textsubscript{4}RuH\textsubscript{6}/MgO</td>
<td>8.0</td>
<td>22.0</td>
<td>4.4</td>
<td>20.9</td>
<td>-0.59</td>
</tr>
<tr>
<td>Ba\textsubscript{2}RuH\textsubscript{6}/MgO</td>
<td>5.0</td>
<td>34.0</td>
<td>8.7</td>
<td>59.7</td>
<td>-0.63</td>
</tr>
<tr>
<td>Ru/MgO</td>
<td>8.7</td>
<td>1.7</td>
<td>0.25</td>
<td>1.3</td>
<td>-0.24</td>
</tr>
<tr>
<td>Cs-Ru/MgO</td>
<td>7.3</td>
<td>5.7</td>
<td>0.60</td>
<td>9.9</td>
<td>-0.09</td>
</tr>
</tbody>
</table>

\textsuperscript{a}NH\textsubscript{3} synthesis rate (mmol g\textsubscript{cat}^{-1} h\textsuperscript{-1}); catalyst loading 30 mg, H\textsubscript{2}:N\textsubscript{2} =2:3, flow rate 30 ml min\textsuperscript{-1}, and 10 bar.

\textsuperscript{b} TOF (\times10\textsuperscript{-3} s\textsuperscript{-1}) was calculated based on the surface Ru content derived from the average particle size observed by TEM and spherical assumption of the particle morphology (Extended Data Table 2). Conventional chemisorption measurement is not applicable to the ternary hydrides because they react with CO.

The most prominent kinetic features of this new class of ternary hydride catalysts are the smaller apparent activation energies and the positive reaction orders of H\textsubscript{2} (Table 1 and Extended Data Figs. 8b-e), which are distinctly different from other conventional Ru metal-based catalysts that suffer from severe hydrogen poisoning and thus exhibit strong temperature-activity dependence\textsuperscript{12,26}. These features enable the ternary hydride catalysts particularly effective at low temperatures, i.e., their operation temperatures are substantially down shifted by ca. 100 K from the pristine Ru/MgO (Fig. 2b). The Li\textsubscript{4}RuH\textsubscript{6}/MgO and Ba\textsubscript{2}RuH\textsubscript{6}/MgO catalysts present constant increases of turn-over-number (TON) at 448 K and 423 K, respectively, and the turn-on and turn-off NH\textsubscript{3} signals under an alternative feeding of N\textsubscript{2} + H\textsubscript{2} and H\textsubscript{2}. Noted that no ammonia was detectable upon feeding N\textsubscript{2} only to Li\textsubscript{4}RuH\textsubscript{6} showing lattice H cannot work alone for ammonia (Extended Data Fig. 9). We subsequently probed the function limit of the hydride catalysts by adopting the charge-transfer ionization time-of-flight mass spectroscopy (CTI-TOFMS) with low NH\textsubscript{3} detection limit\textsuperscript{27}. Both the CTI-TOFMS and the conductivity meter (the conventional ammonia detection method) gave similar effluent NH\textsubscript{3} concentrations of ca.
70 ppm at 398 K and 20 ppm at 373 K from the Ba$_2$RuH$_6$/MgO catalyzed system (Extended Data Fig. 10). The CTI-TOFMS further detected a constant effluent ammonia concentration of ca. 5 ppm at 348 K and 2 ppm at 323 K, respectively (Fig. 2d). In order to assert the origin of the nitrogen in the produced ammonia, we also performed a series of isotopic labeled control experiments and employed $^1$H NMR for the quantitative measurements (Extended Data Fig. 11). As shown in Fig. 2d inset, feeding the Ba$_2$RuH$_6$/MgO catalyst with $^{15}$N$_2$-H$_2$ or $^{14}$N$_2$-H$_2$ results in nearly identical ammonia production rates, respectively, providing a conclusive evidence that the ammonia formed originates from the feeding gas.

Hydridic H is a combined source of electron and proton and was found to exert profound effects on nitrogen fixation $^{28}$. In enzymatic ammonia synthesis catalyzed by FeMo- or FeV-cofactor, the key intermediate was suggested to be a bridging hydride species, which undergoes reductive elimination of dihydrogen to create an electron-enriched Fe center capable of catalyzing N$_2$ reduction $^{4,5}$. Various manmade TM hydride complexes behave similarly and can serve as a platform for forming N$_2$ complexes $^{8,29}$. Some early TM hydrides such as multinuclear Ti hydride complex can further execute reductive protonation of N forming imido units $^{30,31}$. Except that the highly reduced silyl functionalized Fe(N$_2$)(H)$_n$ complex undergoes unusual intramolecular hydride migration to N $^{32}$, no N-H bond formation was observed, however, over the reaction of N$_2$ and late TM hydride complexes owning to the insufficient activation of N$_2$ by electron-deficient TM center $^{8}$. As a matter of fact, the Ru hydride complex [PPh$_3$]$_3$Ru(H$_2$)H$_2$ reacts with N$_2$ forming the dinitrogen complex [PPh$_3$]$_3$Ru(N$_2$)H$_2$ and H$_2$ $^{33}$. As for heterogeneous Ru metal catalysts, the surface hydrides would exert a severe poisoning effect that defers low-temperature N$_2$ activation and conversion $^{26}$ and the H-associative mechanism is suppressed relative to the dissociative mechanism $^{34,35}$. The H-rich ternary Ru hydrides, on the contrary, effectively catalyze N$_2$ and H$_2$ to NH$_3$ under mild conditions, reflecting a distinct electronic configuration and function mechanism of the active center.

We thus investigated the mechanism of ammonia formation over Li$_4$RuH$_6$ experimentally and theoretically (Fig. 3). The as-prepared Li$_4$RuH$_6$ sample was bombarded with laser to generate gaseous clusters for mass spectroscopy (MS) analysis. The composition and structure of the clusters would hint at or correlate with the surface
of Li₄RuH₆²¹,³⁶. Taking into the consideration of the isotopes of Ru, the clusters with relatively intensive peaks include [Li₄RuH₆]⁻ and its complexes with LiH. Bombarding Li₄RuH₆ in N₂ atmosphere, interestingly, highlights the production of a set of NH₂-containing clusters (Fig. 3b).

Our DFT calculations show that the [RuH₆] terminated (110) surface is the most stable low Miller index surface under operational conditions, and that the surface has an intriguing flexibility in accommodating excess lithium and hydrogen. As shown in Extended Data Fig. 12, the addition of excess LiH to the surface composed of six Li₄RuH₆ units is exothermic and results in the formation of [RuH₇] complexes at the low-to-moderate temperatures and pressures investigated here. These data correlate with the observation of LiH affinity to [Li₄RuH₆]⁻ in the cluster experiment (Fig. 3b). It is important to note that certain over-stoichiometry in surface hydrogen and lithium (two extra LiH) actually induces a preference for N₂ over H₂ adsorption at the active pentagonal base pyramidal polyhedral [RuH₆] site. The competitive adsorption of N₂ and H₂ is not pronounced over Ba₂RuH₆, however, the addition of excess BaH₂ enhances N₂ adsorption, which may account for its higher TOF (see Extended Data Fig. 13 and Table 1). Based on the experimental observation and the theoretical calculations, a model Li₄RuH₆ (110) surface composed of six Li₄RuH₆ units and stabilized by two extra LiH was adopted to simulate NH₃ formation at 573 K and 1 bar.

The full reaction pathway has been mapped out using DFT calculations and found to be highly complex, involving no less than 13 intermediate states and multiple adsorption/dissociation and lattice H transfer processes. Given the complexity and dynamic nature of the surface, a large number of possible pathways were investigated (a few are shown in Extended Data Fig. 14), where the one shown in Fig. 3a was found to display the minimum energy span, i.e., the smallest free energy distance between the intermediate state and the transition state with the highest degree of rate control¹⁴. The energy span is as low as 1.75 eV under the mild experimental conditions imposed here, which is substantially lower by >1.0 eV than that observed on Ru (211)¹³, and in good agreement with the enhanced TOF observed relative to Ru/MgO (Table 1). Further, it is important to stress that although the path involves many activated processes, all of the kinetic barriers are found to below 79 kJ/mol (0.82 eV).
Here, N₂ chemisorbs on the [RuH₆] site (0-1) in an end-on mode with an elongated N-N bond length of 1.14 Å manifesting a moderate activation, which correlates with our DRIFT observation of a N-N stretching of adsorbed N₂ at 2116 cm⁻¹ (confirmed by ¹⁵N₂ adsorption at 2047 cm⁻¹) (Fig. 3c). The DFT calculations show that the direct dissociation of dinitrogen over the surface is strongly kinetically inhibited, which is understandable since Ru in Li₄RuH₆ is electron-deficient and the Ru-Ru distance (5.09 Å) is much longer compared with that in Ru metal (2.71 Å), which is unfavorable for the direct dissociation of dinitrogen. The non-dissociative N₂ activation is also supported by the of kinetic ¹⁵N₂-¹⁴N₂ exchange experiments over Ru/MgO and Li₄RuH₆/MgO samples, i.e., on the degassed Ru/MgO sample, the formation of ²⁹N₂ with appropriate rate at 473 K was observed evidencing effective homolytic N₂ splitting on a Ru metal surface. However, such a phenomenon is not pronounced over the Li₄RuH₆/MgO sample, i.e., the initial ²⁹N₂ formation rate is ca. 1/4 of that of Ru/MgO, in reverse order to their ammonia synthesis rates (Fig. 3d and Extended Data Fig. 15). A non-dissociative pathway is thus expected to prevail over Li₄RuH₆.

Our theoretical study shows that the hydrogenation of the adsorbed N₂ can happen both from the gaseous dihydrogen and from the lattice H, where the latter is preferred due to its lower kinetic barrier. In the full path presented by Fig. 3a, all the hydrogenation steps of the activated dinitrogen to form NH₃ take place only by lattice Hs, evidencing the role of lattice H in transporting electron and proton. While the gaseous dihydrogen molecule adsorption replenishes lattice H deficiency of the surface during the process. Such a mechanistic feature can be at least partially supported by the H/D isotope experiments, i.e., the H-rich ammonia and its fragments with m/z = 17 and 16 first increase and then decrease (Fig. 3e) when feeding the Li₄RuH₆ catalyst with N₂ and D₂.

As shown in Fig. 3, the first hydrogenation of the adsorbed N₂ (1-2) happens from the intra-site H (H from [RuH₆]-NN) and is endergonic by ca. 0.66 eV without kinetic barrier. The hydridic H is transferred to the polarized N-N antenna and undergoes reductive protonation forming activated [RuH₅]-NHN species, where both N atoms gain electrons from the hydridic H and bond with neighboring Li (Li-N bond length is 1.90 Å) (The Bader charge analyses are given in Extended Data Fig. 16). The second ([RuH₅]-NHNH) and the third ([RuH₅]-NHNH₂) hydrogenation steps (2-3 and 4-5) occur by the reductive
protonation of the lattice Hs transferred from the neighboring [RuH$\text{7}$] sites and assist by surface Li (Extended Data Fig. 17a). The N-N bond dissociates via a Li-assisted multi-step path with a kinetic barrier of 0.64 eV creating a [RuH$\text{5}$]-NH and a [RuH$\text{6}$]-NH$_\text{2}$ species (5-6) (Extended Data Fig. 17b). The first NH$_\text{3}$ ([RuH$\text{5}$]-NH$_\text{3}$) formed from the intra-site H transfer (6-7) desorbs from the surface without kinetic barrier (7-8). The remaining [RuH$\text{5}$]-NH species then consumes two lattice Hs from two neighboring [RuH$\text{7}$] sites and forms [RuH$\text{5}$]-NH$_\text{2}$ (8-9) and the second NH$_\text{3}$ species (9-10), respectively (Extended Data Fig. 17c). The second NH$_\text{3}$ species leaves Ru and hangs loosely on the neighboring Li (as [Li]-NH$_\text{3}$) and then desorbs from the surface (10-11). The surface is then replenished by the second and the third dihydrogen adsorption and restores the initial state (11-12 and 12-0).

![Diagram](image)

Fig. 3. Mechanistic investigations on N$_\text{2}$ activation and hydrogenation over Li$_\text{4}$RuH$_\text{6}$ surface. a, The calculated free energy pathway for the 13-step reaction mechanism with an energy span of only 1.75 eV, the kinetic barriers are enclosed in brackets. The images
of the 13 states are simplified, [H] represents lattice hydrogen transfer. b, Mass spectra of clusters generated from Li$_4$RuH$_6$ sample under a pure He (blue line) and a mixture of N$_2$-He (red line) atmosphere. c, DRIFT spectra of the fresh, post-tested, and post-$^{14}$N$_2$ and -$^{15}$N$_2$ adsorbed Li$_4$RuH$_6$/MgO samples. d, The initial $^{28}$N$_2$-$^{30}$N$_2$ exchange rates (red bar) and catalytic NH$_3$ synthesis rates (blue bar) of Li$_4$RuH$_6$/MgO and Ru/MgO catalysts at 473 K (in μmol g$_{cat}^{-1}$ h$^{-1}$). e, Reaction time profiles for ammonia synthesis from N$_2$ and D$_2$ over Li$_4$RuH$_6$ at 598 K.

It is important to note that every N$_x$H$_y$ species formed as well as the transition state between every step during the process shows strong interaction with the neighboring Li ions on the surface (Li-N bond length in-between 1.90-2.00 Å), i.e., Li cation stabilizes the N$_x$H$_y$ species and helps reducing the kinetic barriers, which shares some common features with that of N-K bond formation in molecular Fe and U nitride complexes during nitrogen reduction and functionalization, and that of Li-N bond formation in the Li-mediated electrochemical ammonia synthesis. Also noted is that the most stable intermediate predicted is the Li-stabilized [RuH$_5$]-NH$_2$, which correlates well with the DRIFT observation of a pair of broad N-H stretches centered at ca. 3300 and 3250 cm$^{-1}$ of the catalyst sample quenched from reaction (Fig. 3c) and the identification of NH$_2$-containing clusters in the cluster reaction (Fig. 3b). This mechanism results in positive reaction orders with respect to H$_2$ and N$_2$ and negative order of NH$_3$, agreeing well with our experimental findings and clearly distinguishing it from existing metallic ruthenium-based catalysts (Table 1).

The ternary ruthenium hydride may serve as the very first example of TM complex compound that can catalyze ammonia formation from dihydrogen and dinitrogen. The non-dissociative N$_2$ reduction is realized effectively by the cooperation of multiple electron-rich [RuH$_5$/6/7] sites, the involvement of lattice hydridic H as proton and electron carrier, and the role of alkali/alkaline earth metal cation in stabilizing N$_x$H$_y$ intermediate species. The dynamic and synergistic engagement of all the active components of ternary hydride in the catalysis demonstrates the increased freedom and power in manipulating the energetics of the elementary steps and thus opens an avenue for the design and development of efficient catalyst tackling the conversion of kinetically stable molecules.
References


**Acknowledgments** The authors acknowledge the beam time of Shanghai Synchrotron Radiation Facility and Deutsches Elektronen-Synchrotron and the help of Jo-Chi Tseng and Jozef Bednarck for in situ SR-PXD. P.C. and J.G. thank the financial support from National Natural Science Foundation of China (Grant Nos. 21988101, 21633011 and 21922205), Dalian Institute of Chemical Physics (DCLS201702), K. C. Wong Education Foundation (GJTD-2018-06) and 2011-iChEM; J.P, H.H and T.V. thank the Velux Foundations for financial support through the research center V-Sustain (#9455).

**Author contributions** P.C. conceived the idea. P.C. and T.V. supervised the research and wrote the paper. Q.W. conducted most of the experimental work and prepared SI. J.P. conducted DFT calculations and co-prepared SI. J.G. supervised the experimental work. H.H. supervised the theory work. H.X. and L.J. for GOS-MS. L.H. and H.L. for CTI-TOFMS. All authors participated the discussion and data analyses.

**Competing interests** Authors declare no competing interests.
Methods

All the materials handlings were performed in a glove box filled with purified argon to keep a low water vapor concentration (< 0.1 ppm) and a low oxygen concentration (< 1 ppm). N\textsubscript{2} (99.999\%), H\textsubscript{2} (99.9999\%), D\textsubscript{2} (99.999\%), Ar (99.999\%), N\textsubscript{2}/H\textsubscript{2} mixture with different molar ratios (99.9999\%) were purchased from Dalian Special Gases Co., LTD.

Preparation of Li\textsubscript{4}RuH\textsubscript{6} (Li\textsubscript{4}RuD\textsubscript{6}) and Ba\textsubscript{2}RuH\textsubscript{6} samples. Both Li\textsubscript{4}RuH\textsubscript{6} (Li\textsubscript{4}RuD\textsubscript{6}) and Ba\textsubscript{2}RuH\textsubscript{6} were synthesized by the calcination of ball-milled mixtures of LiH (LiD) (LiH: Alfa, 99.4\% metal basis; LiD: Aldrich, 98 atom\% D) or BaH\textsubscript{2} with Ru powder (Aladdin, 99.9\% metal basis) in hydrogen (deuterium) at elevated temperatures and pressures, as has been described in earlier reports \textsuperscript{40,41}. BaH\textsubscript{2} was obtained following the procedure described previously \textsuperscript{42}. The crystalline sizes of the as-prepared Li\textsubscript{4}RuH\textsubscript{6} and Ba\textsubscript{2}RuH\textsubscript{6} were estimated to be ca. 50 and 65 nm, respectively, by using the Scherrer equation based on the collected PXRD patterns.

Preparation of ball milled catalyst samples. Li\textsubscript{4}RuH\textsubscript{6} was ball milled in a H\textsubscript{2}-filled vessel on a Retsch planetary ball mill (PM 400, Germany) at 150 r.p.m for 3h, and was denoted as Li\textsubscript{4}RuH\textsubscript{6} (BM). Li\textsubscript{4}RuH\textsubscript{6}-BN (BM) or Li\textsubscript{4}RuH\textsubscript{6}-MgO (BM) was prepared via ball milling Li\textsubscript{4}RuH\textsubscript{6} and BN (Aladdin, 99.9\% metal basis, 1~2 μm) or MgO powder under the same conditions as that of Li\textsubscript{4}RuH\textsubscript{6} (BM), in which the Ru content is ca. 8 wt %. The MgO sample has a high specific surface area of ca. 534 m\textsuperscript{2} g\textsuperscript{-1}, which was synthesized according to the literature report \textsuperscript{43}. The crystalline sizes of Li\textsubscript{4}RuH\textsubscript{6}-BN (BM) and Li\textsubscript{4}RuH\textsubscript{6}-MgO (BM) were estimated to be ca. 20 and 9 nm, respectively, by using the Scherrer equation based on the collected PXRD patterns.

Preparation of Ru/MgO catalyst. Ru metal was deposited on the MgO support according to a urea-based decomposition precipitation (DP) method as reported in literature \textsuperscript{44,45}. The sample was further reduced in pure H\textsubscript{2} at 673 K for 5 h and was denoted as the Ru/MgO. The Ru content of as-prepared Ru/MgO catalyst was determined to be 8.7 wt \% by inductively coupled plasma mass spectrometry (ICP-AES, PerkinElmer
ICP-AES 7300DV). The average Ru particle size of as-prepared Ru/MgO is ca. 3.09 nm (Extended Data Fig. 5).

**Preparation of Li\textsubscript{4}RuH\textsubscript{6}/MgO and Ba\textsubscript{2}RuH\textsubscript{6}/MgO catalysts.** Li\textsubscript{4}RuH\textsubscript{6}/MgO catalyst with a Ru loading of ca. 8.0 wt % was prepared as follows. The reduced Ru/MgO was impregnated in a lithium-ammonia solution with a molar ratio of Li:Ru=4:1, where Li metal (Macklin, 99.9% metal basis) can be easily converted to LiNH\textsubscript{2} in the presence of Ru. After evacuating the excess NH\textsubscript{3}, the obtained sample was subsequently treated under 1 bar of H\textsubscript{2} at 573 K until no ammonia is detectable by the conductivity meter (Mettler Toledo SevenMulti), thus enabling *in situ* formation of Li\textsubscript{4}RuH\textsubscript{6} on MgO support according to the following reaction:

\[
4\text{LiNH}_2 + \text{Ru} + 5\text{H}_2 \rightarrow \text{Li}_4\text{RuH}_6 + 4\text{NH}_3
\]

The Ba\textsubscript{2}RuH\textsubscript{6}/MgO catalyst with a Ru content of 5.0 wt % was prepared in a similar way, except impregnating the Ru/MgO in a barium-ammonia solution.

**Preparation of Li\textsubscript{4}RuH\textsubscript{6}/MgO-air and Ba\textsubscript{2}RuH\textsubscript{6}/MgO-air catalysts.** The obtained supported ternary Ru hydrides were exposed to air for 2 days for sufficient oxidation, then underwent *in situ* reduction by H\textsubscript{2}–N\textsubscript{2} before catalytic testing. The obtained samples were referred as Li\textsubscript{4}RuH\textsubscript{6}/MgO-air and Ba\textsubscript{2}RuH\textsubscript{6}/MgO-air, respectively.

**Preparation of Li\textsubscript{2}O-Ru/MgO and Cs-Ru/MgO catalysts.** The Li\textsubscript{2}O-Ru/MgO and Cs-Ru/MgO catalysts were obtained by impregnating Ru/MgO with solutions of LiNO\textsubscript{3} (Kermel, ≥ 99.0%) and CsNO\textsubscript{3} (Guangfu, ≥99.0%) followed by H\textsubscript{2} reduction at 673 K for 5 h. The Li or Cs to Ru molar ratio is 4:1 or 1:1, respectively. The Ru content of Cs-Ru/MgO catalyst was determined to be 7.3 wt %.

**Catalytic reaction tests.** Ammonia synthesis was conducted in a stainless steel fixed-bed reactor with a quartz liner that operated with the supply of continuous-flow of extra pure N\textsubscript{2}–H\textsubscript{2} mixture gas (>99.9999%). Typically, 30 mg of catalyst was loaded in the liner tube on a bed of quartz wool and subsequently heated at a ramping rate of 5 K min\textsuperscript{-1} under the given pressure and flow rate. The ammonia produced was trapped in a diluted
sulfuric acid solution and the proton conductivity was recorded with time by a conductivity meter. The principle of the \( \text{NH}_3 \) quantification method has been described previously \(^{46}\). The activity data at each temperature was monitored when the catalytic performance reached a steady-state value. Blank test using the same setup did not give any measurable activity at temperatures below 673 K and 10 bar.

**TEM and STEM-EDS measurement.** Transmission electron microscopy (TEM) images were recorded on a JEM-2100 microscope, operating at an accelerating voltage of 200 kV. More than 100 particles were measured from TEM images to determine the average particle size and particle size distributions. The compositions of the catalyst, including spectral imaging to produce elemental maps were captured using high angle annular dark field scanning transmission electron microscopy (HAADF-STEM, JEM-2100F) equipped with an energy dispersive X-ray spectroscopy (EDS) detector.

**FTIR measurement.** Fourier transform infrared measurements were conducted on a Brucker Tensor II unit in the diffuse reflection (DRIFT) mode with a scan resolution of 4 cm\(^{-1}\) and an accumulation of 32 scans each time.

**\( \text{N}_2 \) physisorption.** The Brunauer-Emmet-Teller (BET) specific surface areas of the samples were determined from nitrogen adsorption-desorption isotherms measured at 77 K using an automatic gas adsorption instrument (QUADRASORB SI).

**Powder X-ray diffraction (PXRD) measurement.** PXRD patterns were collected on a PANalytical X’pert diffractometer equipped with Cu K\( \alpha \) radiation (40 KV, 40 mA) for phase identification. The test samples were loaded in a homemade sample cell that was covered with KAPTON film to avoid air or moisture contamination.

**In situ synchrotron radiation powder X-ray diffraction (SR-PXD) measurement.** *In situ* SR-PXD experiments were performed at the diffraction beamline P.02.1, DESY (Hamburg, Germany). The *in situ* cell and the procedure used were described elsewhere \(^{47}\). The wavelength was fixed at ca. 0.207 Å and a PerkinElmer XRD1621 plate image
detector (2048*2048 pixel, each of size 200*200 microns) was used to acquire the patterns, with a sample-to-detector distance of about 1400 mm. The sample was loaded in a sapphire capillary tube (0.8 mm ID) and placed in a home-made sample holder. The Li$_4$RuH$_6$ sample was heated from 298 to 773 K with a ramping rate of 1 K min$^{-1}$ in a stream of flow gas (10 ml min$^{-1}$). The Ba$_2$RuH$_6$ sample was heated from 298 to 923 K with a ramping rate of 6 K min$^{-1}$ in a steam of flow gas (5 ml min$^{-1}$). The 2D images were then integrated using FIT2D software.

**Temperature programmed techniques.** Temperature-programmed desorption (TPD) measurements were conducted in a quartz-lined stainless steel reactor and the exhaust gases were monitored with an on-line mass spectrometer (MS, Hiden HPR20). Samples (30 mg) were heated in a stream of Ar (30 ml min$^{-1}$) from room temperature to desired temperatures at a ramping rate of 5 K min$^{-1}$. Temperature-programmed reaction (TPR) with specific gas was performed with the same apparatus and similar procedures as used in TPD, except the change of carrier gas.

**Pressure-composition-temperature (PCT) measurement.** PCT dehydrogenation experiments were carried out on a gas reaction controller (Advanced Materials Corporation, USA) loaded with 800 mg of Li$_4$RuH$_6$ sample. Static P-C isotherms were determined at temperatures of 763 K, 773 K, 783 K and 793 K, respectively. The control precision of the sample temperature was ±1 K. The initial pressure in the sample chamber for hydrogen desorption was ca. 1 bar.

**Monitoring of catalytic synthesis of NH$_3$ by vacuum ultraviolet (VUV)-lamp-based charge-transfer ionization time-of-flight mass spectroscopy (CTI-TOFMS).** Real-time monitoring of ammonia synthesis at low temperatures was realized by building an integrated apparatus that consists of the home-built NH$_3$ synthesis setup (described above) and the time-of-flight mass spectroscopy equipped with VUV-lamp-based CTI-TOFMS. Full details of the VUV-lamp-based CTI-TOFMS were described in previous reports$^{27,48}$. To calibrate the instrument response (i.e., peak area) with respect to analyte concentration, ammonia standard gas mixture with concentration of 100 ppmv in syngas
(H₂:N₂=1:3) was diluted with NH₃-free syngas (H₂:N₂=1:3) to a series of lower concentrations. Extended Data Fig. 10a shows the calibration curve of the NH₃⁺ ions, and the dynamic range was obtained from 2 ppm to 100 ppm with a good linear correlation coefficient (R²=0.996). 200 mg of catalyst was loaded and tested under a flow of syngas (H₂:N₂=1:3, 36 ml min⁻¹). The reaction temperature was varied from 398 K to 323 K and the pressure was kept at 1 bar. The signals of NH₃⁺ (17 amu), H₂O⁺ (18 amu), H₃O⁺ (19 amu) and O₂⁺ (32 amu) ions were recorded during the catalytic process. The background signal of NH₃⁺ ion, determined in the same setup but without catalyst loading, was also detected as the baseline.

**Gas-phase optical spectroscopy coupled with mass spectroscopy (GOS-MS) experiment.** GOS-MS experiment was carried out using a homemade instrument with a laser vaporization source and a dual-channel time-of-flight mass spectrometer (D-TOFMS). Details of the apparatus has been described elsewhere ⁴⁹, and only a brief outline of the experiment is given below. The species were generated via pulsed laser vaporization cluster source using the second harmonic of a Nd:YAG laser (Continuum Minilite II). The sample was ablated in the presence of a supersonic beam of carrier gas. The typical stagnation pressure of carrier gas was about 3-5 bar. Under the efficient cooling by supersonic expansion of pulsed carrier gas, the clusters were cooled to ~200 K in the vacuum chamber and reacted with the pulsed gaseous reactants. The cluster ions were analyzed by the TOF mass spectrometer. Bombarding the surface of Li₄RuH₆ sample in pure He atmosphere gives a series of mass peaks. Taking account the contribution of various Ru isotopes ⁵⁰, the relatively intense peaks at m/z=134, 136, 150, 152, 166 and 168 amu can be assigned to [Li₄RuH₄]⁺, [Li₄RuH₆]⁺, [Li₄RuH₄·(LiH)₂]⁺, [Li₄RuH₆·(LiH)₂]⁺, [Li₄RuH₄·(LiH)₄]⁺ and [Li₄RuH₆·(LiH)₄]⁺ clusters, respectively. A set of LiNH₂-containing clusters were observed from the Li₄RuH₆ sample bombarded in a mixture of N₂-He (1:9), which are assigned to the [Li₄RuH₄·(LiH)₂·LiNH₂]⁺ (m/z=173 amu) and [Li₄RuH₆·(LiH)₂·LiNH₂]⁺ (m/z=175 amu) clusters, respectively.

**N₂ isotope labeling experiment.** The identification and quantification of small amount of produced NH₃ at lower temperatures should be careful. ⁵¹ To verify the origin of NH₃ from
N₂ at lower temperatures, isotopic labeling experiment was carried out using a mixture of ¹⁵N₂ (≥98%, Cambridge Isotope Laboratories, Inc.) and H₂ as the feeding gas (H₂:¹⁵N₂=2:3). We employed ¹H NMR to measure ammonia production rates from ¹⁴N₂-H₂ and ¹⁵N₂-H₂ following the procedure described in literature ⁵²,⁵³, where ¹⁴NH₄⁺ and ¹⁵NH₄⁺ can be distinguished by the ¹H spectra in which coupling to ¹⁴N is a triplet and coupling to ¹⁵N is a doublet. The ¹⁵NH₃ or ¹⁴NH₃ produced was trapped in a diluted sulfuric acid solution (pH≈3) and quantified by using ¹H NMR spectroscopy. For the NMR studies, the pH of the solutions to be tested was adjusted to 2 using concentrated hydrochloric acid aqueous solution. 5 vol% DMSO-d₆ (99.9 atom % D, 0.03% (v/v) TMS) was added for deuterium locking and referencing. All NMR experiments were performed at 298 K on a Bruker Advance III spectrometer operating at a ¹H frequency of 500 MHz. A total of 1000 transient scans were accumulated for each sample. Calibration samples were prepared with varying concentrations of ¹⁴NH₄Cl (Aladdin, 99.999%) and ¹⁵NH₄Cl (Aladdin, 99 atom%).

**H/D isotope experiment.** Ammonia synthesis from N₂ and D₂ over the Li₄RuH₆ sample was conducted using a quartz-lined stainless steel reactor connected to a home-made device that can switch instantly between two gas streams under the same temperature and pressure. Prior to isotopic reaction, the sample (ca. 30 mg) was heated to 598 K and kept for a while under atmospheric Ar flow (30 ml min⁻¹). The mixture of N₂-D₂ (1:3, 30 ml min⁻¹) was subsequently switched to the sample and the effluent gas was analyzed with a mass spectrometer (MS, Hiden HPR20). The m/z=2, 3, 4, 15, 16, 17, 18, 19 and 20 masses were recorded as a function of time to follow the reaction. ND₃ (m/z=20 amu) was hardly differentiated due to an overlap with the fragment of Ar (m/z=20 amu).

**N₂ isotopic exchange experiment.** N₂ isotopic exchange reactions were performed using a home-made stainless steel reactor connected with vacuum-pumping system. The sample was loaded into the reactor in an Ar-filled glovebox and the loading amount is 30 mg for Ru/MgO or Li₄RuH₆/MgO and 225 mg for the bulk-phase Li₄RuH₆. Prior to the exchange reactions, the Ru/MgO sample was degassed at 673 K and held for 2 h under vacuum. Li₄RuH₆/MgO and bulk-phase Li₄RuH₆ samples were treated in vacuum at 473K.
A mixture of $^{15}\text{N}_2$ and $^{14}\text{N}_2$ ($^{15}\text{N}_2:^{14}\text{N}_2=1:4.4$, total pressure: ca. 0.55 bar) was then introduced to the samples at 473 K for the exchange reaction. The m/z=28, 29, 30 masses were monitored as a function of time to follow the reaction by using a mass spectrometer.

**Kinetic studies.** The measurements of reaction order of N$_2$ or H$_2$ were carried out with a flow of mixed gas (N$_2$, H$_2$ and Ar) under conditions (573 K, 1 bar, WHSV=60000 ml g$^{-1}$ h$^{-1}$), where the effluent NH$_3$ concentration was kept constant. Our measurement conditions were far from equilibrium considering that the thermodynamic limit is ca. 2.1% under these conditions. The loading amount is 30 mg for Li$_4$RuH$_6$/MgO, Ba$_2$RuH$_6$/MgO and Cs-Ru/MgO, and 50 mg for Ru/MgO. The gas compositions of N$_2$:H$_2$:Ar were 5:50:45, 15:50:35, 25:50:25, 35:50:15, 45:50:5 for determining the N$_2$ order, and 20:40:40, 20:50:30, 20:60:20, 20:70:10, 20:80 for determining the H$_2$ order, respectively. The NH$_3$ order was determined by changing the flow rate of syngas while keeping a constant N$_2$ to H$_2$ partial pressure. Apparent activation energies were measured under atmospheric syngas (H$_2$:N$_2$=3) with a flow rate of 30 ml min$^{-1}$. The temperature range is 523-598 K for Li$_4$RuH$_6$/MgO (30 mg), 523-573 K for Ba$_2$RuH$_6$/MgO (30 mg), 573-648 K for Ru/MgO (30 mg) and 573-623 K for Cs-Ru/MgO (30 mg), respectively.

**Theoretical calculations.** For all theoretical calculations in this report we used density functional theory (DFT) with generalized gradient approximation (GGA) for the exchange-correlation potential, a plane-wave basis set and the projector augmented wave (PAW) method$^{54,55}$ as implemented in the Vienna ab-initio simulation package (VASP)$^{56}$. In this study, we set a 500 eV energy cut-off for the plane-wave basis. The free energies were calculated with ideal gas limit approximation$^{57}$ and harmonic limit/hindered harmonic limit approximation$^{58-60}$ for the gaseous molecules and for the absorbates respectively. For simulating hydrogen gas in vacuum, we used a negligible partial pressure of $10^{-9}$ Pa. The kinetic pathways and their corresponding barriers presented here were determined by the nudge elastic band method (NEB)$^{61}$ implemented in VASP. To study the Li$_4$RuH$_6$ surface, we created slabs containing four layers of the material in the (110) direction (with regards to the primitive Li$_4$RuH$_6$ cell) and with six Ru-sites on the surface. We imposed 18 Å vacuum above the top layer of the slabs to avoid the interaction between the periodic
images. During every simulation, the ions in the bottom two layers of these slabs remained fixed.

References


68. Ogura, Y. *et al.* Efficient ammonia synthesis over a Ru/La0.5Ce0.5O1.75 catalyst pre-reduced at high temperature. *Chem. Sci.* **9**, 2230-2237 (2018).


Extended Data Fig. 1. Electronic properties of stoichiometric Li$_4$RuH$_6$ surface. The charge density plot of Li$_4$RuH$_6$ surface with Bader charge analyses on Ru (red), Li (white) and H (yellow).
### (a) Li₄RuH₆

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<td>Experiment⁴⁰,⁶²</td>
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### (b) Ba₂RuH₆

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<td>a(Å)</td>
<td>b(Å)</td>
</tr>
<tr>
<td>Theor</td>
<td>This work</td>
</tr>
<tr>
<td>Refs</td>
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<tr>
<td>Experiment⁴¹</td>
<td>8.028</td>
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</table>

Extended Data Fig. 2. The crystal structures and related parameters of Li₄RuH₆ (a) and Ba₂RuH₆ (b). The Ru, Li, Ba and H atoms are presented by red, white, steel grey and yellow balls.
Extended Data Fig. 3. The stability of bulk Li₄RuH₆ and Ba₂RuH₆ under different conditions. a, TPR profile of Li₄RuH₆ in a mixture gas of NH₃-Ar (NH₃:Ar=0.5:99.5) and a mixture gas of NH₃-H₂-Ar (NH₃:H₂:Ar=0.5:75:24.5). b, In situ SR-PXD characterization of Li₄RuH₆ sample under atmospheric N₂ and elevated temperatures (from 473 K to 773 K). c, In situ SR-PXD characterization of Ba₂RuH₆ sample under atmospheric N₂-3H₂ mixture and elevated temperatures (from 637 K to 923 K). d, TPR profile of Ba₂RuH₆ in a mixture gas of NH₃-Ar (NH₃:Ar=0.5:99.5) and a mixture gas of NH₃-H₂-Ar (NH₃:H₂:Ar=0.5:75:24.5).

The above results show that the Li₄RuH₆ phase is stable up to ca. 651 K under N₂ atmosphere. While upon co-feeding H₂, it survives until 738 K (Fig. 1e). Li₄RuH₆ is also resistant to diluted NH₃ at temperature up to 500 K. While upon co-feeding with H₂, the temperature pulls ahead to 673 K. Ba₂RuH₆ phase is stable up to 923 K under
atmospheric N$_2$-3H$_2$ mixture. Ba$_2$RuH$_6$ is also resistant to diluted NH$_3$ at temperatures up to 550 K. While upon co-feeding with H$_2$, the temperature pulls ahead to 673 K.

Extended Data Fig. 4. NH$_3$ synthesis rates at 573 and 598 K. a, bulk Li$_4$RuH$_6$ and Ba$_2$RuH$_6$ catalysts. b, Li$_4$RuH$_6$/MgO, Ru/MgO, Li$_4$RuH$_6$/MgO-air, Ba$_2$RuH$_6$/MgO-air and Li$_2$O-Ru/MgO catalysts (Reaction conditions: catalyst loading 30 mg, H$_2$:N$_2$=3:1, flow rate 30 ml min$^{-1}$, and 1 bar).

After exposed to air, the hydrides were oxidized and deactivated. The activities of Li$_4$RuH$_6$/MgO-air and Ba$_2$RuH$_6$/MgO-air samples are thus much lower and are similar to that of Ru/MgO.
Extended Data Fig. 5. TEM observations. a, Ru/MgO. b, Li₄RuH₆/MgO. c, Ba₂RuH₆/MgO. The inset picture of each image shows the corresponding particle size distribution. The number of particles for each image surveyed was more than 100.

From the results of particle size distribution analyses, we can see that, after introducing Li and Ba to the parent Ru/MgO catalyst, there is a certain increase in the size of dark particles.
Extended Data Fig. 6. HAADF-STEM characterizations of the Ba$_2$RuH$_6$/MgO sample. STEM-EDS maps of Mg-K, O-K, Ba-L and Ru-L, and overlayed Mg, O, Ba and Ru are shown.

From the mapping results, we can see that Ba and Ru are in proximity and dispersed evenly over the MgO support. Li$_4$RuH$_6$/MgO sample was not characterized because Li is out of the analysis scope of EDS.
Extended Data Fig. 7. Characterization of the bulk and supported ternary hydride catalysts. a, DRIFT spectra of the as-prepared Li$_4$RuH(D)$_6$, Li$_4$RuH$_6$/MgO and Ru/MgO catalysts.  

b, Mass spectra of the species produced by pulsed laser vaporization of the Li$_4$RuH$_6$ and Li$_4$RuH$_6$/MgO targets in the presence of a He carrier gas.

Li$_4$RuH$_6$ surface has Ru-H stretching vibration in the range of 1200 to 1800 cm$^{-1}$, which is confirmed by Ru-D stretch in the deuterated sample. The Li$_4$RuH$_6$/MgO sample has a similar Ru-H stretching range as the bulk sample but somehow with red shift, which might be due to the elongated Ru-H bond after the particle size reduction to nanoscale. While for the reference sample Ru/MgO, there was no infrared absorption peak in the range of 1800-1200 cm$^{-1}$. The mass spectrum of Li$_4$RuH$_6$/MgO is similar to that of bulk phase Li$_4$RuH$_6$. These characterizations show that the supported catalyst resembles essentially to the bulk-phase Li$_4$RuH$_6$. 
Extended Data Fig. 8. Measurements of kinetic parameters. a and b Arrhenius plots of the Li₄RuH₆, ball-milled Li₄RuH₆ (Li₄RuH₆ (BM)), ball-milled mixture of Li₄RuH₆ and BN (Li₄RuH₆-BN (BM)), ball-milled mixture of Li₄RuH₆ and MgO (Li₄RuH₆-MgO (BM)), Li₄RuH₆/MgO, Ba₂RuH₆/MgO, Ru/MgO and Cs-Ru/MgO catalysts. c to e Dependence of ammonia synthesis rates on the partial pressures of NH₃, N₂ and H₂, respectively, under a total pressure of 1 bar at 573 K over Li₄RuH₆/MgO, Ba₂RuH₆/MgO, Ru/MgO and Cs-Ru/MgO catalysts.
Extended Data Fig. 9. Low-temperature catalytic activity and stability. a, Time dependence of NH₃ synthesis TON (based on the amount of surface Ru estimated from the particle size observed by TEM) over Li₄RuH₆/MgO and Ba₂RuH₆/MgO catalysts at 448 K and 423 K, respectively (Reaction conditions: catalyst loading 30 mg, H₂:N₂=2:3, flow rate 30 ml min⁻¹, and 1 bar). These data evidence the catalytic formation of NH₃. b, Time course of ammonia synthesis rate of Li₄RuH₆/MgO at 448 K and Ba₂RuH₆/MgO at 423 K under an alternative feeding of N₂-H₂ (H₂:N₂=2:3) and pure H₂ streams (Reaction conditions: catalyst loading 30 mg, flow rate 30 ml min⁻¹, and 1 bar). Upon switching from N₂-H₂ steam to pure H₂ steam, there is a rapid increase in the NH₃ production rate because the sudden increase of H₂ content (from 40% to 100%) speeds up the release rate of NH₃. c, MS spectrum of the temperature-programmed reaction of N₂ with Li₄RuH₆. No ammonia was detectable showing lattice H cannot work alone for ammonia formation.
Extended Data Fig. 10. Low-temperature catalytic performance characterized by CTI-TOFMS. a, Linear calibration curve for NH$_3^+$ in the concentration range of 2 to 100 ppm of the CTI-TOFMS. b, Activities of Ba$_2$RuH$_6$/MgO catalyst measured by conductivity meter and CTI-TOFMS at 373 and 398 K, respectively (Reaction conditions: catalyst loading 200 mg, H$_2$:N$_2$=1:3, flow rate 36 ml min$^{-1}$, and 1 bar).
Extended Data Fig. 11. Quantification of low-temperature NH₃ synthesis rates using ¹H-NMR spectroscopy. a, ¹H NMR spectra of a series of ¹⁴NH₄Cl and ¹⁵NH₄Cl solutions (with equimolar concentrations of ¹⁴NH₄⁺ and ¹⁵NH₄⁺) with different concentrations. b, Linear calibration curves for both ¹⁴NH₄⁺ and ¹⁵NH₄⁺ in the concentration range of 30 to 1000 μM. After absorbing outlet gas at 373K, 423 K and 473 K, respectively, the sulfuric acid solutions were collected for ¹H-NMR measurements, showing in c and d are the ¹H-NMR spectra of ¹⁴NH₄⁺ and ¹⁵NH₄⁺ signals, e and f are the corresponding ¹⁴NH₃ and ¹⁵NH₃ synthesis rates derived from ¹H-NMR. Conditions: Ba₂RuH₆/MgO catalyst 30mg,
H$_2$ : $^{14}$N$_2$(15N$_2$) = 2 : 3, flow rate 10 ml min$^{-1}$, 1 bar. 4 mL diluted sulfuric acid solution was used to absorb the produced NH$_3$. The absorption time is 10 min at 473 K, 30 min at 423 K and 120 min at 373 K, respectively. Blank experiment (without catalyst loading) was performed at 298 K for 120 min, where NH$_3$ concentration is below the detection limit.
Extended Data Fig. 12. The free energy plots of LiH adsorption on the stoichiometric Li₄RuH₆ surface under different conditions. LiH dissociates exothermically into surface Li and the H goes to one of the neighboring RuH₆ site creating a [RuH₇]. Adding two extra LiH to the surface results in the composition of 4RuH₆ + 2RuH₇ + 2LiH that is thermodynamically stable under the reaction condition applied in this study (373 K to 573 K, ≥ 1 bar). However, further adding LiH will block the surface from N₂ adsorption.
Extended Data Fig. 13. Competitive H₂(g) and N₂(g) adsorption on ternary hydride surface. a, Li₄RuH₆ surface with and without extra LiH. b, Ba₂RuH₆ surface with and without extra BaH₂. Our free energy calculations show that H₂ adsorption is strongly favored over N₂ adsorption on the stoichiometric Li₄RuH₆ surface; while on the over-stoichiometric surface especially on the Li₄RuH₆ surface with two extra LiH, N₂ adsorption is preferred to H₂ adsorption. The competitive adsorption of N₂ and H₂ is not pronounced over the stoichiometric Ba₂RuH₆, however, the addition of excess BaH₂ enhances N₂ adsorption, which may account for its higher TOF.
Extended Data Fig. 14. A few possible pathways for N₂ activation and hydrogenation on Li₄RuH₆ surface. The free energy profiles of a and b are based on a model of Li₄RuH₆ (110) surface composed of four Li₄RuH₆ units and stabilized by one extra LiH. The calculated energy span for these two paths are 3.50 eV and 3.72 eV, respectively. The free energy profiles of c and d (without kinetic barriers) are based on a model of (110) surface with six Li₄RuH₆ units and stabilized by two extra LiH. All free energy pathways are calculated at 573 K and 1 bar (H₂:N₂ ratio is fixed at 3, and the concentration of NH₃ is 0.27% that is consistent with the experimental condition.)
Extended Data Fig. 15. **N₂ exchange reactions.** Time course of $^{14}$N$^{15}$N formation over Li₄RuH₆/MgO, Ru/MgO and Li₄RuH₆ catalysts at 473 K. The data were fitted by high-order polynomial curves for easy analysis and the fitting results were shown in the table below the figure. The initial N₂ exchange rates for Li₄RuH₆/MgO, Ru/MgO and Li₄RuH₆ at 473 K can be estimated by derivation the fitting curves at the initial time.

It should be noted that the possible inhomogeneity of the Li₄RuH₆/MgO sample and its partial decomposition to LiH and Ru at 473K may contribute to the formation of $^{14}$N$^{15}$N.
Extended Data Fig. 16. Bader charge analyses of the first hydrogenation step (1-2).

In this process, the adsorbed $N_2$ gains substantial electron from the transiting lattice hydride (denoted as $[H]$). It should be noted that the changes in Bader charge (i.e., relative Bader charge) along the path is relative to the initial image. The particular lattice hydride of interest is marked by a black round ring.
Extended Data Fig. 17. Detailed kinetic paths of some characteristic steps of the catalysis over Li$_4$RuH$_6$ surface. a, Kinetic path of the lattice transfer of step 2-3. Li cations mediate lattice H transfer from [RuH$_7$] complex to -NHN species that is bonded
on [RuH₅] site and thus forming -NHNH species. b, Kinetic path of the N-N dissociation step 5-6. The N-N bond dissociates via a Li-assisted multi-step path, creating a [RuH₅]-NH and a [RuH₆]-NH₂ species. c, Kinetic path of the second NH₃ formation step 9-10. Li cations mediate lattice H transfer from [RuH₇] complex to -NH₂ species and thus forming the second NH₃, during which NH₃ leaves the [RuH₅] site and hangs loosely on the neighboring Li. The particular H atom or NH₂ species of interest is marked by a black round ring.

**Extended Data Table 1. Thermodynamic calculations of the reactions for the formation of Li₄RuH₆ and Ba₂RuH₆.** The reaction enthalpy of formation of Li₄RuH₆ (ΔrH₀(Li₄RuH₆)) is obtained by the corresponding van’t Hoff plots in Fig.1d. The reaction enthalpy of formation of Ba₂RuH₆ (ΔrH₀(Ba₂RuH₆)) is taken from Ref. 25. The standard enthalpies of formation of other substances are taken from “NIST Standard Reference Number 69”. Therefore, the standard enthalpies of formation of Li₄RuH₆ (ΔfH₀(Li₄RuH₆)) and Ba₂RuH₆ (ΔfH₀(Ba₂RuH₆)) can be evaluated by combining the ΔrH₀ and ΔfH₀ values.

<table>
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<th>Reaction</th>
<th>4LiH + Ru + H₂ → Li₄RuH₆</th>
<th>ΔrH₀ (kJ mol⁻¹)</th>
<th>ΔfH₀ (kJ mol⁻¹)</th>
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<td>-93.1</td>
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<table>
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<th>Reaction</th>
<th>2BaH₂ + Ru + H₂ → Ba₂RuH₆</th>
<th>ΔrH₀ (kJ mol⁻¹)</th>
<th>ΔfH₀ (kJ mol⁻¹)</th>
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Extended Data Table 2. Physicochemical properties of the as-prepared Ru-based catalysts.

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<th>Catalyst</th>
<th>Ru content (wt %)</th>
<th>S\textsubscript{BET}\textsuperscript{a} (m\textsuperscript{2} g\textsuperscript{-1})</th>
<th>d\textsuperscript{b} (nm)</th>
<th>D\textsuperscript{b} (%)</th>
<th>Surface Ru content\textsuperscript{b} (wt %)</th>
<th>Ru content\textsuperscript{b}</th>
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<tbody>
<tr>
<td>Li\textsubscript{4}RuH\textsubscript{6}/MgO</td>
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<td>245.5</td>
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<tr>
<td>Ba\textsubscript{2}RuH\textsubscript{6}/MgO</td>
<td>5.0</td>
<td>154.1</td>
<td>4.16</td>
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<tr>
<td>Ru/MgO</td>
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<tr>
<td>Cs-Ru/MgO</td>
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<td>6.02</td>
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<tr>
<td>Li\textsubscript{4}RuH\textsubscript{6}</td>
<td>---</td>
<td>7.2</td>
<td>---</td>
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</tr>
<tr>
<td>Ba\textsubscript{2}RuH\textsubscript{6}</td>
<td>---</td>
<td>4.8</td>
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<td></td>
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</tbody>
</table>

\textsuperscript{a}BET specific surface area.

\textsuperscript{b}Mean Ru particle size (d), dispersion (D) and surface Ru content were estimated based on TEM data assuming spherical metal particles.
Extended Data Table 3. Ammonia synthesis over recently developed Ru-based catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Metal content (wt %)</th>
<th>$n_{\text{NH}<em>3}$ (mmol g$</em>{\text{Ru}}$ h$^{-1}$)</th>
<th>WHSV (ml g$^{-1}$ h$^{-1}$)</th>
<th>Ref.</th>
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<tr>
<td>Li$_4$RuH$_6$/MgO</td>
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<td>114</td>
<td>60000</td>
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<td>Ba$_2$RuH$_6$/MgO</td>
<td>5.0</td>
<td>680</td>
<td>276</td>
<td>60000</td>
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<tr>
<td>Ru/C$<em>{12}$As$</em>{0.1}$e$^-$</td>
<td>1.8</td>
<td>94 (593 K)</td>
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<td>36000</td>
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<tr>
<td>Ru/C$_3$N$_2$e$^-$</td>
<td>1.8</td>
<td>228 (593 K)</td>
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<td>36000</td>
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<tr>
<td>Ru/BaTiO$<em>2$H$</em>{0.5}$</td>
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<td>19 (598 K)</td>
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<tr>
<td>Ru/Co(NH$_2$)$_2$</td>
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<td>158 (8 bar)</td>
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<tr>
<td>Ru/Ba/Co(NH$_2$)$_2$</td>
<td>10</td>
<td>233 (9 bar)</td>
<td>90</td>
<td>36000</td>
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<tr>
<td>Ru/Pr$_2$O$_3$</td>
<td>5</td>
<td>18 (9 bar)</td>
<td>---</td>
<td>18000</td>
</tr>
<tr>
<td>Ru/La$<em>{0.5}$Ce$</em>{0.5}$O$_{1.75}$</td>
<td>5</td>
<td>22</td>
<td>---</td>
<td>72000</td>
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<tr>
<td>Ru/Co$_3$O$_2$/CaH$_2$</td>
<td>10</td>
<td>165 (9 bar)</td>
<td>69</td>
<td>36000</td>
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<tr>
<td>Ru/Co$_3$O$_2$/N$_2$H$_2$</td>
<td>4.5</td>
<td>111 (9 bar)</td>
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<td>36000</td>
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<tr>
<td>Ba-Ru-Li/AC</td>
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<td>LaRuSi</td>
<td>37.7</td>
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<td>4.7 (673 K)</td>
<td>36000</td>
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$^a$Ammonia synthesis rates per gram of Ru under 573 K, 10 bar and 573 K, 1 bar (H$_2$:N$_2$=3 or 2/3), unless otherwise stated.
Paper II
A low-temperature reaction mechanism for ammonia synthesis on electron-rich [RuH₆] catalytic centers

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† These authors contributed equally to this work.
ABSTRACT

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 hydrides (Li₄RuH₆ 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.

TOC GRAPHICS
MAIN TEXT

Ammonia is critical to our food production ecosystem\textsuperscript{1,2} and the single most produced polluting chemical (\textasciitilde170 million tons per year)\textsuperscript{3-5}, while also holding the potential to become one of the most promising carbon-free low-cost long term energy carrier\textsuperscript{6,7}. The industrial Haber-Bosch (HB) process employs a Fe-based catalyst, fossil-fuel sourced H\textsubscript{2}, and requires harsh operating conditions (typically 673-723 K and 100-300 bar of pressure). The large-scale and centralized HB process accounts for nearly 2\% of the world’s consumption of fossil fuels\textsuperscript{8} and, consequently, over 1.44\% of the global anthropogenic CO\textsubscript{2} emissions\textsuperscript{5}. The development of small-scale processes that rely on renewable electricity as an energy source to sustainably produce the H\textsubscript{2} 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 mobility\textsuperscript{4,9}. A decentralized, low CAPEX NH\textsubscript{3} synthesis process targeted at emerging markets with significant future population growth needs would also support the core UN sustainability goals.

While direct electrochemical ammonia production represents the Holy Grail, the documented yields remain very far from any kind of commercialization\textsuperscript{10}. 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 under milder reaction conditions than Fe-based catalysts\textsuperscript{11,12}. However, the high activation energy for direct N\textsubscript{2} dissociation and the severe poisoning effect of hydrogen on conventional Ru metal catalyst renders efficient NH\textsubscript{3} synthesis under lower temperatures (< 650 K) and lower pressures (< 50 bar) unattainable\textsuperscript{13}. 
Therefore, there have been many attempts to develop new catalysts for efficiently catalyzing $\text{N}_2+\text{H}_2$ to $\text{NH}_3$ under mild conditions$^{14-17}$.

![Figure 1](image1.png)

**Figure 1.** Comparison of $\text{NH}_3$ synthesis rate and active site structure of ternary Ru complex hydride catalysts and Ru metal catalysts. Reaction conditions: 1 bar of syngas, $\text{N}_2$:H$_2$=1:3, and a weight hourly space velocity (WHSV) of 60000 ml g$^{-1}$ h$^{-1}$.

Recently, we discovered an entirely new class of ammonia catalysts - ternary ruthenium hydrides ($\text{Li}_4\text{RuH}_6$ and $\text{Ba}_2\text{RuH}_6$)$^{18}$ that outperform the benchmark Ru metal catalysts by more than an order of magnitude at temperatures below 573 K (Figure 1). The key to achieving efficient $\text{NH}_3$ synthesis under near-ambient 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 hydride catalysts, Ru is in an ionic state, and $\text{N}_2$ undergoes non-dissociative hydrogenolysis over the hydride (H$^-$) and electron-rich $[\text{RuH}_6]^{4+}$ complex with the aid of the surrounding Li or Ba cations$^{18}$. The dynamic and synergistic engagement of all the components of the ternary hydrides
creates a reaction path with a narrow energy span\textsuperscript{18} and leads to ammonia production with superior activities.

To better understand the catalytic processes of the ternary hydride catalysts and to guide the search for low-temperature ammonia catalysts, we conducted a concerted experimental and computational investigation (please refer to SI for theoretical and experimental method details) to identify the fundamentals of the low-temperature (448 K \( \leq \) T \( \leq \) 573 K) process. We find that the [RuH\textsubscript{6}] catalytic center displays a well-balanced affinity to molecular dihydrogen with respect to dinitrogen and exhibits a shift in activation energy and the reaction order of both hydrogen and ammonia at T \(<\) 500 K. This variation in the kinetic as a function of operating conditions (temperature, reactant partial pressures, etc.) is not a common phenomenon in catalysis but observed in some cases \textsuperscript{19–23}. 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\textsubscript{2} and H\textsubscript{2} are critical for mild-condition ammonia catalysis.

The [RuH\textsubscript{6}] catalytic center in ternary ruthenium hydrides not only outperforms the B5 site of metallic Ru catalysts under the same working conditions, but it also produces NH\textsubscript{3} at low temperatures (Figure 1). Two inherent properties of the [RuH\textsubscript{6}] catalytic center are critical towards the observed outstanding activity at low temperatures: (a) its selectivity for chemisorbing N\textsubscript{2} over H\textsubscript{2} and (b) a self-adjusting mechanism of avoiding hydrogen over-saturation sustaining the N\textsubscript{2} to NH\textsubscript{3} conversion cycle. The catalytically active ternary hydride surface with excess Li and hydrogen (consists of two additional LiH for every six [RuH\textsubscript{6}] centers, i.e., 4RuH\textsubscript{6}+2RuH\textsubscript{7}+2Li) \textsuperscript{18} is energetically moderately selective towards N\textsubscript{2} over H\textsubscript{2} chemisorption. The calculated binding
free energies show that the preferential adsorption of N\textsubscript{2} over H\textsubscript{2} at the [RuH\textsubscript{6}] active center is further enhanced at lower temperatures (Figure 2a). 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\textsubscript{6}] centers. Figure 2b displays the free energy landscape for dissociation of chemisorbed H\textsubscript{2} (state-I) on the [RuH\textsubscript{6}] active center. Although the dissociative chemisorption of H\textsubscript{2} into two lattice Hs is facile, the subsequent transfer of lattice H, as [RuH\textsubscript{7}] (state-II), via a transition state (TS\textsubscript{I-II}), is prohibited by a high activation energy of 1.1 eV (Figure S1) as estimated with nudged elastic band simulations, which is because the Li-mediated H transfer encounters repulsive force from neighboring Hs. Instead, at low temperature, the active center retains the hydrogen atoms to form a [RuH\textsubscript{8}] complex (state-I), which is not a very stable state and can easily desorb H\textsubscript{2} at temperatures above 300 K to release the [RuH\textsubscript{6}] catalytic site for N\textsubscript{2} activation (see Figure 2b). The mechanism of H\textsubscript{2} chemisorption/desorption ensures not all [RuH\textsubscript{6}] centers are converted to [RuH\textsubscript{7}] complexes, even in an H\textsubscript{2}-rich environment. Thus, the catalyst surface is not hydrogen over-saturated by lattice H that bonds firmly to the respective Ru blocking the active sites. This is in contrast to Ru and other late transition metal catalysts, where H-poisoning due to favorable thermodynamics\textsuperscript{24} effectively prevents ammonia production. The opposing behavior between Ru metal and Li\textsubscript{4}RuH\textsubscript{6} catalysts is elegantly captured in the NH\textsubscript{3} formation rate under varying pressure (Figure S2). The lack of hydrogen poisoning effect allows enhanced ammonia production at a higher hydrogen partial pressure on Li\textsubscript{4}RuH\textsubscript{6}.

The chemisorption of H\textsubscript{2} on the ternary hydride surface has unique fingerprints (Figure 2b). The chemisorption of H\textsubscript{2} happens through a physisorbed transition state TS\textsubscript{0-I}, with a negligible barrier of 0.07 eV (Figure S3). The H from the chemisorbed H\textsubscript{2} participates in on-site scrambling with the lattice H on the [RuH\textsubscript{6}] active center. The on-site scrambling of the hydrogen has an insignificant
activation energy of 0.04 eV (Figure S4). Here, we observe a minor reversible adsorption/desorption of H\textsubscript{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 S5 a and b), which reinforces the observation of the chemisorbed nature of the H\textsubscript{2} adsorption on the Li\textsubscript{4}RuH\textsubscript{6} surface. After charging with D\textsubscript{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\textsubscript{2} with lattice H (insert in Figure 2b). A more robust signal of H\textsubscript{2}/HD than D\textsubscript{2} in the TPD profile points out the magnitude of the on-site scrambling of the chemisorbed D\textsubscript{2} with the lattice H.

**Figure 2.** a) The competitive chemisorption of N\textsubscript{2} and H\textsubscript{2} by the [RuH\textsubscript{6}] catalytic center shows selectivity for N\textsubscript{2} over H\textsubscript{2}, which improves at lower temperature and, b) the free energy path of H\textsubscript{2}/D\textsubscript{2} chemisorption/desorption along with on-site scrambling of the chemisorbed H\textsubscript{2}/D\textsubscript{2} on the Li\textsubscript{4}RuH\textsubscript{6} catalytic surface and a prohibitively high barrier (> 1 eV) for chemisorbed H\textsubscript{2} to lattice H transfer demonstrates the mechanism by which [RuH\textsubscript{6}] catalytic center avoids hydrogen over-saturation. The top insertion in (b), shows the TPD profile of deuterated Li\textsubscript{4}RuH\textsubscript{6}.

The variations of reaction energetics as a function of temperature are analyzed by applying the energetic span model, in which the turn over frequency (TOF) determining transition state (TDTS)
and TOF determining intermediate sate (TDI) that maximize the energy span determine the rates and kinetics of the catalytic cycle\textsuperscript{25,26}. Figure 3 (and in Figure S6) shows the development of the free energy path of the catalytic cycle of dinitrogen to ammonia conversion on the Li\textsubscript{4}RuH\textsubscript{6} surface with a lowering of temperature (448 K ≤ T ≤ 573 K). Visualization of the NH\textsubscript{3} formation mechanism on the Li\textsubscript{4}RuH\textsubscript{6} catalyst surface with intermediate states/transition states is provided in Figure S7. The path shows a series of well-balanced and moderate activation energies – all with E\textsubscript{a} \leq 0.82 eV (see Table S1). The change in temperature shifts the TDI and TDTS of the catalytic cycle (Figure 3), with an inflection temperature being at 498 K. The TDTS moves from the transition state 4-5 (TS\textsubscript{4-5}) to TS\textsubscript{3-4} as the temperature is reduced below 498 K.

The Arrhenius plot for ammonia synthesis (Figure 4a) locates this inflection point at 523 K. All measured kinetic parameters for ternary hydride catalyst (Li\textsubscript{4}RuH\textsubscript{6}/MgO) are temperature-dependent (Figure 4) – elucidating the complex temperature dependent switching of TDI/TDTS.

The TDI shifts from state 12 to state 0 as the temperature goes lower than the inflection point. The inserted plot in Figure 3 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 (Figure 3 and Figure S6) 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 and experimentally derived ΔH\textsubscript{a}/E\textsubscript{app} and TOF are listed in Table S2. The value of ΔH\textsubscript{a} at 448 K is 98.2 kJ mol\textsuperscript{-1}. While at 573 K, with state 9 as TDI, the ΔH\textsubscript{a} is calculated to be 72.4 kJ mol\textsuperscript{-1}. An increase in temperature lowers the activation enthalpy and increases the TOF (Table S2). The apparent activation energy for Li\textsubscript{4}RuH\textsubscript{6}/MgO catalyst determined by Arrhenius
plot is $E_{\text{app}} = 71.2$ kJ/mol at temperatures higher than 523 K, and significantly increased value of 102.8 kJ/mol at temperatures below 523 K (Figure 4a). In contrast, there is no change in $E_{\text{app}}$ and other kinetic parameters for conventional Ru catalyst (Ru/MgO) in a wide temperature range (498-648 K).

For Li$_4$RuH$_6$/MgO catalyst, the energetic span and the TOF vary continuously with temperature. The temperature dependent TDI and TDTS modification 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 $\Delta H_a$ 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$_4$RuH$_6$/MgO (Figure 4b-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 in Li$_4$RuH$_6$/MgO. These changes are in stark contrast to the constant values for Ru/MgO, i.e., $-0.23$, $1.12$, and $-0.85$, respectively for H$_2$, N$_2$, and NH$_3$. The kinetic parameters of the ternary Ba-Ru catalyst are also temperature-dependent and show a similar trend with that of the ternary Li-Ru catalyst (Figure S8). 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 ($-0.85$, Figure 4). Moreover, NH$_3$ poisoning effects on the [RuH$_6$] center lessens at lower temperatures, providing a favorable scenario for effective catalysis.
Figure 3. The evolution of the free energy path with the lowering of temperature shifts the TDI and the TDTS of the energetic span model, and the inflection point is at 498 K. For the lower temperature range (< 498 K), the TDI and TDTS are the initial/final state (state-0) and the transition state of the third hydrogenation (TS_{4-5}) on the surface, respectively. In the higher temperature range (>498 K), the TDI and the TDTS are the second H_{2}(g) adsorption (state-12) and the transition state of the first H_{2} (g) adsorption (TS_{3-4}) on the surface. With the increase of temperature, state-9 comes energetically closer to state-12. At 573 K, the TDI and the TDTS are state-9 and TS_{4-5} (Figure S6). The inserted plot shows the schematic presentation of the shift in TDI/TDTS. The TDI and TDTS at different temperature ranges are marked by the square-
circle-symbols, respectively, in the free energy plot and the inserted plot. We apply a fixed total pressure of 1 bar (N₂:H₂=1:3) to generate the free energy paths and barriers using density functional theory based free energy estimations and nudged elastic band method.

Figure 4. Kinetic parameters. a Arrhenius plots of Li₄RuH₆/MgO and Ru/MgO catalysts. b to d dependence of ammonia synthesis rates on the partial pressures of NH₃, N₂, and H₂, respectively, under a total pressure of 1 bar at 573 K (filled symbols) and 498 K (open symbols) over Li₄RuH₆/MgO catalyst and Ru/MgO catalyst. The reaction order of NH₃, N₂, and H₂ is represented by α, β, and γ, respectively.
The present study highlights the dynamic nature of the [RuH₆] catalytic center in enabling mild condition ammonia synthesis. The presence of [RuH₇] complex facilitates the hydrogenation of the activated nitrogen from the surplus lattice hydrides. On the contrary, a too high concentration of [RuH₇] complex on the surface can deactivate the catalyst from dinitrogen adsorption. The high activation energy for lattice H transfer of the chemisorbed H₂ observed in this unique class of material maintains a delicate balance between the availability of lattice hydrogen and active sites. The preferential N₂ chemisorption over H₂ and kinetic blockage of hydrogen over-saturation is key to the success of ternary Ru-hydride systems at low temperatures. Further, a unique temperature-dependent tuning of the reaction order is observed for [RuH₆] catalytic center, leading to a shift in the TDI and TDTS and a corresponding transition from positive to negative reaction order in hydrogen <573 K.

We have been able to achieve a precise temperature resolved atomic-scale understanding of the reaction mechanism at the [RuH₆] catalytic center, its unique thermodynamics, and kinetic aspects that enable exceptional low-temperature activity. This scientific insight needs to be exploited towards optimizing ternary transition metal hydrides as ammonia catalysts as well as exploring a newer class of materials that can replicate the behavior of [RuH₆] catalytic center in the pursuit of renewables powered decentralized room temperature/pressure ammonia synthesis.
ASSOCIATED CONTENT

Supporting Information

The supporting information (SI) files contain details of theoretical and experimental methods; the supporting figure of the kinetic path for chemisorbed H\textsubscript{2} becoming lattice H on Li\textsubscript{4}RuH\textsubscript{6} surface (Figure S1), the pressure-dependent catalytic activity of Li\textsubscript{4}RuH\textsubscript{6}/MgO and Ru/MgO (Figure S2), the kinetic path of H\textsubscript{2} chemisorption on Li\textsubscript{4}RuH\textsubscript{6} surface (Figure S3), the kinetic path of on-site scrambling of chemisorbed H\textsubscript{2} (Figure S4), the TPD profile of fresh and post-treated Li\textsubscript{4}RuH\textsubscript{6} along with ball-milled LiH, Ru and LiH-Ru mixture (Figure S5), the free energy path of N\textsubscript{2} to NH\textsubscript{3} conversion on Li\textsubscript{4}RuH\textsubscript{6} at different temperature, with thermodynamic ad kinetic limits (Figure S6), visualizations of the intermediate steps in the N\textsubscript{2} to NH\textsubscript{3} conversion mechanism on Li\textsubscript{4}RuH\textsubscript{6} surface (Figure S7) and kinetic parameters over Ba\textsubscript{2}RuH\textsubscript{6}/MgO (Figure S8); the supporting tables of activation energy (E\textsubscript{a}) along along the different steps of the free energy path (Table S1), and the theoretical and experimental TOF and ΔHa/Eapp of NH\textsubscript{3} on Li\textsubscript{4}RuH\textsubscript{6} catalyst at different temperature (Table S2)

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Note: The authors declare no competing financial interest

ACKNOWLEDGMENTS: J.P, H.H and T.V. thank the Velux Foundations for financial support through the research center V-Sustain (#9455); Q.W, P.C. and J.G. thank the financial support from National Natural Science Foundation of China (Grant Nos. 21988101, 21633011 and 21922205), Dalian Institute of Chemical Physics (DCLS201702), K. C. Wong Education Foundation (GJTD-2018-06) and 2011-iChEM.
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SUPPORTING INFORMATION FOR

A low-temperature reaction mechanism for ammonia synthesis on electron-rich [RuH₆] catalytic centers

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DETAILS OF THE METHODS:

THEORATICAL CALCULATIONS

We used first-principles based density functional theory (DFT) tool Vienna ab-initio simulation package (VASP)\(^1\) to simulate the system. All the calculations used a revised Perdew-Burke-Ernzerhof approximation (RPBE)\(^2\) for the exchange-correlation potential, a plane-wave basis set with energy cutoff 500 eV, and the projector augmented wave (PAW) method. The DFT energies with the correction from ideal gas limit approximation and harmonic limit/hindered harmonic limit approximation\(^3,4\) for the free molecules, and the absorbates on the catalyst surface respectively generated the free energies reported in this work. The nudged elastic band method (NEB)\(^5\) implemented in VASP used to find the optimal kinetic paths, the transition state, and the related activation energy. The four-layered \(\text{Li}_4\text{RuH}_6\) slab used in this study has a (110) surface (w. r. t the primitive \(\text{Li}_4\text{RuH}_6\) cell) with six Ru-sites on it. An 18 Å vacuum is used above the top layer of the slabs to prevent any interaction between two periodic images. We fixed the ions in the bottom two layers through the simulations.

We applied the energetic span approximation\(^6\) of the exothermal catalytic cycle to calculate turnover frequency (\(\text{TOF}\)) from the energetic span (\(\delta E\)) of the free energy path.

\[
\text{TOF} = \frac{k_B T}{h} e^{-\delta E / k_B T}
\]

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 \(\delta E\).

\[
\delta E = \begin{cases} 
\Delta G_{TDTS} - \Delta G_{TDI}, & \text{if TDTS appears after TDI} \\
\Delta G_{TDTS} - \Delta G_{TDI} + \Delta G_r, & \text{if TDTS appears before TDI}
\end{cases}
\]
The activation enthalpy ($\Delta H_a$) for the catalytic path is back-calculated from the $\delta E$ and the entropy correction ($T\Delta S$).

$$\Delta H_a = \delta E + T\Delta S$$

**EXPERIMENTAL**

**Materials**

LiH (Alfa, 99.4% metal basis), Ru powder (Aladdin, 99.9% metal basis), Ru(NO)(NO$_3$)$_2$ (Alfa, Ru $\geq$ 31.3%), CO(NH$_2$)$_2$ (SCR, $\geq$ 99.0%), Mg(CH$_3$COO)$_2$·4H$_2$O (SCR, $\geq$ 99.0%), C$_2$H$_2$O$_4$·2H$_2$O (SCR, $\geq$ 99.5%), Ba metal (Aldrich, $\geq$ 99% trace metals basis, shot diameter:~2cm), Li metal (Macklin, 99.9% metal basis), CsNO$_3$ (Guangfu, $\geq$99.0%). All the materials handlings were performed in a glove box filled with purified argon to keep a low water vapor concentration (< 0.1 ppm) and a low oxygen concentration (< 1 ppm). H$_2$ (99.9999%), D$_2$ (99.999%), Ar (99.999%), N$_2$/H$_2$ mixture with a molar ratio of 1:3 (99.9999%) were purchased from Dalian Special Gases Co., LTD.

**Preparation of ball-milled LiH, ball-milled Ru powder and ball-milled LiH-Ru mixture**

Ball-milled LiH was prepared by ball milling LiH on a Retsch planetary ball mill (PM 400, Germany) at 150 r.p.m for 3 hours. Ru powder was also ball-milled at 150 r.p.m for 3 hours and then heated at 753 K for 10 hours under 10 bar of H$_2$, and the obtained sample was denoted as ball-
milled Ru powder. The ball-milled LiH-Ru mixture was prepared by ball milling a mixture of LiH and Ru powder in a 4:1 molar ratio at 150 r.p.m for 3 hours.

**Preparation of fresh Li₄RuH₆, post-treated Li₄RuH₆ and deuterated Li₄RuH₆ samples**

Fresh Li₄RuH₆ sample was synthesized by the calcination of ball-milled LiH-Ru mixture under 10 bar of H₂ at 753 K for 10 hours, as has been described in earlier reports⁷,⁸. The post-treated Li₄RuH₆ sample was prepared as follows. The fresh Li₄RuH₆ was first dehydrogenated under atmospheric Ar up to 493 K and then rehydrogenated under atmospheric H₂ at 393 K for 2 hours. At last, the obtained sample was cooled to room temperature for use. The deuterated Li₄RuH₆ sample was prepared in a similar way, except rehydrogenating the dehydrogenated Li₄RuH₆ under atmospheric D₂.

**Preparation of Ru/MgO, Cs-Ru/MgO, Li₄RuH₆/MgO and Ba₂RuH₆/MgO catalysts**

Ru/MgO and Cs-Ru/MgO reference catalysts with Ru content of 8.7 wt% and 7.3 wt%, respectively, were prepared following the procedure described in the earlier report⁹. Li₄RuH₆/MgO catalyst with a Ru loading of 8.0 wt% was prepared according to the following steps: firstly, the Ru/MgO sample was impregnated in a lithium-ammonia solution with a molar ratio of Li:Ru=4:1, where Li metal can be easily converted to lithium amide (LiNH₂) in the presence of Ru. After removal of excess NH₃, the solid residue was then hydrogenated at 573 K to allow *in situ* formation of Li₄RuH₆ on MgO support according to the reaction 4LiNH₂ + Ru + 5H₂ → Li₄RuH₆ + 4NH₃.
Ba$_2$RuH$_6$/MgO catalyst with a Ru loading of 5.0 wt% was prepared in a similar way, except impregnating the Ru/MgO in a barium-ammonia solution.

**Catalytic activity test**

Activity test was performed on quartz-lined stainless steel fix-bed reactor under a continuous flow of N$_2$-H$_2$ mixture gas. Typically, 30 mg of catalyst was loaded in the liner tube on a bed of quartz wool and subsequently heated at a ramping rate of 5 K min$^{-1}$ under the given pressure and flow rate. The ammonia production rate was measured by a conductivity meter (Mettler Toledo SevenMulti), and the principle of this NH$_3$ quantification method has been described previously$^{10}$. The activity data at each temperature was monitored under steady-state conditions.

**Temperature programmed desorption (TPD) measurements**

Temperature-programmed desorption (TPD) measurements were performed on a stainless steel reactor with a quartz liner and the exhaust gases were monitored with an on-line mass spectrometer (Hiden HPR20). Typically, 30 mg sample was loaded and heated in a stream of Ar (30 ml min$^{-1}$) from room temperature to the desired temperature at a ramping rate of 5 K min$^{-1}$, and the signals of H$_2$ (m/z=2), HD (m/z=3) and D$_2$ (m/z=4) were recorded.
Kinetic studies

N\textsubscript{2} and H\textsubscript{2} reaction order measurements were carried out with a flow of mixed gas (N\textsubscript{2}, H\textsubscript{2} and Ar) under a total pressure of 1bar and a weight hourly space velocity (WHSV) of 60000 ml g\textsuperscript{-1} h\textsuperscript{-1}, during which the effluent NH\textsubscript{3} concentration was kept constant. For Li\textsubscript{4}RuH\textsubscript{6}/MgO (or Ba\textsubscript{2}RuH\textsubscript{6}/MgO), the loading amount is 30 mg at both 573 K and 498 K (or 473 K). For Ru/MgO, the loading amount is 50 mg at 573 K and 100 mg at 498 K, respectively. The reaction order of N\textsubscript{2} was determined through changing the partial pressure of N\textsubscript{2} while keeping a constant partial pressure of H\textsubscript{2}, and the reaction order of H\textsubscript{2} was measured at a constant N\textsubscript{2} pressure while changing the partial pressure of H\textsubscript{2}. The reaction order of NH\textsubscript{3} was determined by changing the flow rate of syngas (N\textsubscript{2}:H\textsubscript{2}=1:3) while keeping constant pressure. Apparent activation energies were measured under atmospheric syngas (N\textsubscript{2}:H\textsubscript{2}=1:3) with a flow rate of 30 ml min\textsuperscript{-1}. The temperature range is 448-598 K for Li\textsubscript{4}RuH\textsubscript{6}/MgO (30 mg), 448-573 K for Ba\textsubscript{2}RuH\textsubscript{6}/MgO (30 mg) and 598-648 K for Ru/MgO (30 mg), respectively. All the kinetic measurements were performed under conditions far from equilibrium.
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**Figure S1.** Kinetic path of the chemisorbed dihydrogen forming two lattice hydrogens. Color code: Li-green, Ru-red, and H-yellow. A black round ring marks particular H from the [RuH₆+H₂] complex is transferring to neighbouring [RuH₆] complex and results into two [RuH₇] complex.
Figure S2. Pressure dependence of the catalytic activities of Li$_4$RuH$_6$/MgO and Ru/MgO catalysts at 573 K. Reaction conditions: 10 bar, N$_2$:H$_2$=3:2, WHSV=60000 ml h$^{-1}$ g$^{-1}$. 
Figure S3. Kinetic path of chemisorption of H\(_2\)(g) on the Li\(_4\)RuH\(_6\) surface. Color code: Li-green, Ru-red, and H-yellow. A black round ring marks the particular H\(_2\) of interest.
**Figure S4.** Kinetic path of on-site scrambling of hydrogen from chemisorbed dihydrogen and the lattice hydrogen. Color code: Li-green, Ru-red, and H-yellow. A black ring marked the particular chemisorbed H₂ pairs.
Figure S5. a, TPD profiles of fresh Li$_4$RuH$_6$, ball-milled LiH, ball-milled Ru powder, and ball-milled LiH-Ru mixture (LiH:Ru=4:1) (The ball-milled Ru powder was heated under 10 bar of H$_2$ at 753 K for 12 hours). b, TPD profiles of fresh Li$_4$RuH$_6$ and post-treated Li$_4$RuH$_6$ samples.
Figure S6. The gradual development of the free energy path with changing reaction temperature.

The reaction temperature ranges between 598 K (thermodynamic limit of the reaction) and 448 K (kinetic limit of the reaction, below which the rate of the reaction becomes trivial). The inserted figure on the top right is the free energy of the reaction ($\Delta G_r$) with varying temperatures. At 598 K, the reaction becomes unfavorable as $\Delta G_r$ becomes positive.
Figure S7. Visualization of the NH$_3$ formation mechanism on the Li$_4$RuH$_6$ catalyst surface. The intermediate state or transition state enclosed by broken rectangle is the TDI/TDTS at different reaction temperatures. Color code: Li-green, Ru-red, H-yellow, and N-blue.
Table S1. The activation energy ($E_a$) of the steps along the proposed free energy path.

<table>
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<tr>
<th>Steps</th>
<th>$E_a$ (eV)</th>
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<tr>
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<tr>
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<tr>
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<td>11-12</td>
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</tr>
<tr>
<td>12-0</td>
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</tr>
</tbody>
</table>
Table S2. The theoretical TOF and $\Delta H_a$ and the experimental TOF and $E_{\text{app}}$ of NH3 on Li$_4$RuH$_6$ catalyst at different temperatures.

<table>
<thead>
<tr>
<th></th>
<th>573 K</th>
<th>448 K</th>
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</thead>
<tbody>
<tr>
<td>Exp. TOF (s$^{-1}$)</td>
<td>0.006</td>
<td>3.0×10$^{-5}$</td>
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<tr>
<td>Theo. TOF (s$^{-1}$)</td>
<td>0.011 (TDI is state 9)</td>
<td>0.001</td>
</tr>
<tr>
<td>Exp. $E_{\text{app}}$ (kJ mol$^{-1}$)</td>
<td>71.2</td>
<td>102.8</td>
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<tr>
<td>Theo. $\Delta H_a$ (kJ mol$^{-1}$)</td>
<td>72.4 (TDI is state 9)</td>
<td>98.2</td>
</tr>
<tr>
<td></td>
<td>47.4 (TDI is state 12)</td>
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</table>
Figure S8. Kinetic parameters over Ba2RuH6/MgO catalyst. a, Arrhenius plots in the temperature of 573-448 K. b to d dependence of ammonia synthesis rates on the partial pressures of NH3, N2, and H2, respectively, under a total of the pressure of 1 bar at 573 K (filled circles) and 498 K (open circles).
4. Vanadium oxynitrides as electrocatalyst

The 2nd project done in this PhD focused on using computational catalysis methods for exploring new stable, selective, and active electrocatalyst vanadium oxynitride for renewable electricity based sustainable and distributed ammonia production. This work was done independently, but the idea was triggered by recent experimental observation that the very promising vanadium nitride electrocatalyst is actually inactive and oxygen incorporation activated it. Thus the goal of this project was to create an understanding of how oxygen affects the mechanism, activity, selectivity, and stability.

First, the bulk and surface properties are thoroughly studied to compensate for the lack of any such existing results, followed by the N2RR mechanism, and the thermodynamic pathway was established. DFT based simulations were used to show why a moderate quantity of oxygen is necessary for stabilizing the material and keeping the catalytic site and surface active. The surface is nitrogen reach and stays so during catalysis. The electro-catalytic pathway takes a vacancy mediated Mars van Krevelen pathway. The catalyst surface is poisoning protected, as revealed from the thermodynamic analysis. Large kinetic barrier towards anion migration not only stabilized the surface but also keeps the nitrogen vacancy site available for N2 adsorption by stopping self-annihilation.
Paper III
Vanadium oxynitrides as stable catalysts for electrochemical reduction of nitrogen to ammonia: the role of oxygen

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Abstract

Electrochemical reduction of nitrogen to ammonia can potentially replace the existing centralized fossil fuel-based Haber-Bosch process with small, decentralized units relying on electrical energy from renewable sources, thus supporting a sustainable food and energy infrastructure. Recent activities in the development of transition metal nitride electrocatalysts for this reaction have shown promise, but oxynitrides remain unexplored. We have performed a rigorous computational study of the highly promising vanadium oxynitride (VNO) to establish for the first time the nitrogen reduction pathway in oxynitrides and the role of the mixed anions that can lead to improved stability of the active surface-states, activity, and selectivity over hydrogen evolution. The catalytic properties are best enhanced at low oxygen content (12.5%), due to optimal balance between consecutive protonation preference at N-sites over V-sites, low onset potential (0.4V-RHE), and facile N$_2$ adsorption at N-vacancy sites. The critical N-vacancy active sites are protected from self-annihilation by the mixed-valency anions, large kinetic barriers, and site blocking by O*/OH*/H* due to highly favorable N$_2$ absorption.

Introduction

Activation of dinitrogen from the atmosphere to produce ammonia via biological and industrial processes sustains life on earth as we know it. Ammonia is an essential chemical feedstock for the synthesis of nitrogen-based fertilizers that enables farmers to feed billions of more people than our planet could otherwise not support\cite{1,2}. Ammonia is also building block for manufacturing other synthetic chemicals, medicaments, dyes,
explosives, and resins. Liquid NH$_3$ contains 17.6 wt% hydrogen, is easy to transport and store - thus, it can be a carbon-free energy carrier as well\cite{3,4}. Ammonia is the world's most-produced chemical at 170 million metric tons per year. Although nitrogen is abundant raw material for ammonia production, the large bond energy (940.95 kJ mol$^{-1}$) of N≡N bond makes N$_2$ reduction reaction (N$_2$RR) extremely difficult. Industrial-scale NH$_3$ production relies on the Haber–Bosch process\cite{5}, where the H$_2$ feedstock is normally produced from fossil fuels, and each metric ton of NH$_3$ produced will emit ~1.9 metric tons of CO$_2$. Also, high-temperature (620–820 K) and high-pressure (150–350 atm) production conditions imply only capital-intensive centralized production, while the consumption is distributed quite uniformly over all populated areas on earth. Less developed regions are dependent on inefficient and expensive supply from centralized sources and thus pose a risk to equitable growth. Small-scale devices that produce ammonia onsite could alleviate some of these problems by producing fertilizer on-demand at the point of usage\cite{6}. However, such devices would require a much simpler and near-ambient condition process. An electrochemical route to NH$_3$ production from N$_2$, H$_2$O, and renewable energy sources can revolutionize a green NH$_3$ production industry by cutting down fossil fuel consumption and reducing the carbon footprint of agricultural activities\cite{7}. It can provide decentralization of the process and thus reduce the waste and transportation-related impacts as well. Electrochemical N$_2$RR works well with the intermittency of renewable energy sources like wind and solar power, as ammonia can be produced and stored\cite{8} when excess renewable electricity is generated over user demands.

Given the impact of discovering highly active and stable electrocatalyst for ammonia production, the field has seen intense research activity across the world\cite{9–17}. Platinum
group metal catalysts are often used as catalysts because of their stability in acidic environments, but they generally have low Faradaic efficiencies (FE < 0.1%) for N\textsubscript{2}RR. This is attributed to the scaling relation between various surface adsorbed intermediates in the N\textsubscript{2}RR and the competing hydrogen evolution reaction (HER), which is always favored across different metals\textsuperscript{[18]}. As an alternative to noble metal catalysts, non-precious metal catalysts and metal-free carbon catalysts have been explored broadly as N\textsubscript{2}RR electro-catalysts. Among them, transition metal nitrides (TMN) has been proposed as being both active and highly conductive\textsuperscript{[19–25]}. Nitrides have a potential advantage of being able to form ammonia by a Mars–van Krevelen (MvK) mechanism, in which a surface N atom is reduced to NH\textsubscript{3} and the surface vacancy thus created is repopulated with N\textsubscript{2}. This is followed by the removal of the extra N-atom as ammonia through consecutive protonation. Hence, the catalyst surface is regenerated rather than adsorbing N\textsubscript{2} directly to the catalyst surface. It has been observed experimentally that the best yield rate and Faradic efficiencies are obtained for transition metal oxynitrides (TMON) compared to pure nitride catalysts\textsuperscript{[22,26–28]}. Existing theoretical work\textsuperscript{[21,29,30]} has focused on the N\textsubscript{2}RR mechanism on nitride surfaces, and have not studied the atomic mechanism, thermodynamic limitations on oxynitrides in details. For example, vanadium nitride, which has been investigated theoretically\textsuperscript{[29]}, does not display good long term stability\textsuperscript{[31–33]} in the N\textsubscript{2}RR electrochemical environment as nitrogen and vanadium leach into typical electrolyte solutions, thus limiting its application in ammonia electro-synthesis through N\textsubscript{2}RR. In fact, some experiments indicate that pure nitrides might actually be just decomposing towards ammonia evolution\textsuperscript{[32,34]}, and recent spectroscopic characterization identifies that pure vanadium nitride is inactive for N\textsubscript{2}RR\textsuperscript{[22,34]}, while oxynitride variety
shows good activity\cite{22,26}. It is hypothesized that only the surface N sites adjacent to a surface O show activity for the N$_2$RR\cite{33}. The most recent studies on other TMONs\cite{26–28} further strengthen the necessity of oxygen/nitrogen co-existence for favorable N$_2$RR activity and stability.

A detailed understanding of the structural details, stability, N$_2$RR mechanism and the thermodynamic pathway is lacking for TMON N$_2$RR catalysts. Such fundamental insights are critical for further development and optimization of TMON electro-catalysts for N$_2$RR. Here, we have performed a rigorous study of the structural aspects of bulk and surface VNO to identify the beneficial chemical properties towards nitrogen reduction over pure vanadium nitride. We also establish the impact of oxygen in stabilizing and keeping the catalytic site and surface active.

**Result and discussion**

**VON bulk structure**

The structure of VON has been resolved with multiple experimental techniques to be stable cubic rock-salt phase (for VO$_x$N$_{1-x}$ with nitrogen-rich compositions x< 0.5)\cite{35–37}. The nitrogen-rich composition of the cubic VO$_x$N$_{1-x}$ can be explained from the fact that the pure vanadium nitride (VN) exists in a cubic rock-salt structure, where pure vanadium oxide does not have a stable cubic phase. The most stable vanadium oxide is V$_2$O$_5$ with an orthorhombic crystal structure. Therefore, the reported stable rock-salt phase of VO$_x$N$_{1-x}$ is compositionally closer to vanadium nitride than vanadium oxide. However, the most stable (and active) composition of VO$_x$N$_{1-x}$ is not yet well defined. To determine the crystal structure and thermodynamically favorable composition, we have calculated the
mixing enthalpy of rock-salt VN and VO phases. Based on a 32 atom supercell, all possible 1610 unique symmetry inequivalent VON structural configurations were simulated considering ferromagnetic and antiferromagnetic interaction. Based on these total energy calculations, low energy structures were identified for the full range of O/N ratio. The resultant convex hull with varying O-concentration (x%) is demonstrated in Figure 1a using VO rock-salt as a reference. If pure V$_2$O$_5$ is used as a reference for vanadium oxide (Figure S1), the calculated cubic phases are higher in energy, but the rock-salt structures have been shown experimentally to be metastable for limited-to-moderate oxygen content, possibly due to large ion/vacancy migration barrier and related surface stabilization as discussed below. Experimental evidence also suggests N/O ratio > 1 in the ternary phase diagram of V, N, and O$^{[35]}$.

**Figure 1.** a The mixing energy of VN and VO phases and b distorted polyhedral in VON compared to pure VN and pure VO (V: golden yellow, O: red and N: blue).
We find a non-uniform distribution of N and O in the crystal structure of the minimum energy configurations for different N/O compositions (Figure S2) along the convex hull. There is a sharp disparity in the chemical interaction of O and N with V in VON. The charge density analysis shows that the degree of covalency for the N-V bond is more pronounced than the V-O bond (Figure S3). This disparity between O and N anions also results in distorted polyhedral around V cations (Figure 1b). Table-S1 contains the lattice parameters and the cell volume of the lowest energy configurations of VO$_x$N$_{1-x}$ with different N/O ratios. The combined effect of the difference in the chemical nature of V-O and V-N bonds and non-uniform distribution of N/O breaks the crystal symmetry in VO$_x$N$_{1-x}$, although structure remains close to cubic rock-salt.

VON surface composition and stability

![Graph showing the relationship between oxygen concentration and Gibbs free energy change (ΔG) with a peak in Gibbs free energy at around 20% oxygen](image)

**Figure 2.** Presence of oxygen in low concentrations enhances surface stability by hindering Vanadium leaching from the surface
We studied (100) surfaces of the lowest energy configurations from the convex hull with different N/O compositions (O<50%). The cleaving of bonds makes the surface atoms chemically different from the bulk, and the stability of the surface depends on the surface composition and atomic ordering. Both VO and VN are known to display non-stoichiometry mainly due to the presence of a significant amount of V-vacancies along with anion vacancies. It is important to note that the formation and stabilization of anion surface vacancies are not detrimental, but the opposite in this case, as they are the active sites for N\(_2\) adsorption and continuation of the N\(_2\)RR by MvK mechanism. The V-vacancy formation, on the other hand, can cause structural instability and inactivity of the catalytic surface. Eq-1, represents the V-vacancy (\(V^{vac}\)) formation along with metallic vanadium (\(V_{metal}\)) from the surface metal site (\(V^*\)).

\[
V^* \rightarrow V^{vac} + V_{metal}
\]  

(1)

O on the nitride surface is reported to be unstable under N\(_2\)RR conditions. Any O on the nitride surface is reduced and removed as water long before the system attends the N2RR onset potential\(^{[29]}\). Hence, in the working condition of N\(_2\)RR, O will mostly be in the bulk while the surface will contain N and V atoms of the VON. Therefore in the N\(_2\)RR study of VON, we focused on these surfaces. Figure 2 shows the relative stability regarding the V-vacancy formation energy of stoichiometric surfaces for the N-rich composition (x=0% to x=43.75%) on the convex hull. The top layer of these surfaces consists of N and V atoms, while the O atoms populate the subsurface layers (Figure S4). The stability of the V atoms on the surface increase with an increasing amount of O concentration in the system and reaches a peak at x=18.75% and followed by a decreasing trend. For O concentrations x=6.25% to x=37.5%, the surface V-atom display enhanced stability.
compared to pure VN (x=0). It confirms the positive influence of oxygen on the stability of the catalytic surface.

Catalysis on VON surface

Reduction of N\(_2\) to NH\(_3\) occurs on the cathode surface, and the overall electrochemical reaction is:

\[
N_2(g) + 6(H^+ + e^-) \rightarrow 2NH_3(g) \tag{2}
\]

The corresponding anode reaction that acts as a proton source is:

\[
3H_2(g) \leftrightarrow 6(H^+ + e^-) \tag{3}
\]

The main challenge in N\(_2\)RR selectivity is the competition with hydrogen evolution reaction, which often have lower overpotential than N2RR.

Selectivity over HER

In a MvK mechanism, a surface N (\(\ast^N\)) gets protonated thrice to release one molecule of NH\(_3\) leaving an N-vacancy (\(\ast^{N-vac}\)) on the site (eq. 4-7).

\[
\ast^N + 6(H^+ + e^-) \rightarrow \ast^N H + 5(H^+ + e^-) \tag{4}
\]

\[
\ast^N H + 5(H^+ + e^-) \rightarrow \ast^N 2H + 4(H^+ + e^-) \tag{5}
\]

\[
\ast^N 2H + 4(H^+ + e^-) \rightarrow \ast^N 3H + 3(H^+ + e^-) \tag{6}
\]

\[
\ast^N 3H + 3(H^+ + e^-) \rightarrow \ast^{N-vac} + NH_3(g) \uparrow + 3(H^+ + e^-) \tag{7}
\]
A competing hydrogen transfer step is hydrogenation of the V-site \((\ast^V)\) instead of N-site (eq. 8). It is important to note that the hydrogen will not be protonic, but hydridic, as discussed below.

\[
\ast^V + (H^+ + e^-) \rightarrow \ast^V H
\]  

(8)

H* on protonated N and H* on V has a very different chemical nature. H* on protonated N takes a positive oxidation character, while H* on V takes a negative oxidation character (hydride ion). Table-S2 contains the Bader charges calculated for different H. The bond length of N-H is \(~1.0\text{Å}\), and V-H is \(~1.70\text{Å}\) (Figure 3). In the case of V, the hydride ion can react with a proton from water (eq. 9) or H from neighboring protonated N site (eq.10) to evolve hydrogen. The existence of H* with anionic and cationic character in the neighboring sites is unstable and reacts spontaneously with each other to form H\(_2\) (Figure S5). The possible mechanism of HER from protonated V-site is schematically represented in Figure 3a.

\[
\ast^V H + \ast^V \rightarrow \ast^V + H_{2(g)} ↑
\]  

(9)

\[
\ast^V H + \ast \rightarrow \ast + \ast + H_{2(g)} ↑
\]  

(10)

Figure 3b, shows the energy comparison of the VON surface with protonated N and hydrogenated V sites. We found that on the VON surface, protonation of N-site is strongly preferred over V, especially for a lower concentration of O. With increasing O-concentration, the energy difference between these two protonation paths decreases. In Figure 3c, we have compared formation energy after second hydrogen transfer, one at the N and V sites respectively, or both at the N site. This plot clearly shows the strong thermodynamic drive towards the formation of a consecutive protonation at N-site rather
than the formation of protonated one N-site along with one V-site, which leads to HER. The results presented in Figures 3b and c together has declined the possibility of HER and confirmed selectivity of the VON surface for N₂RR.

**Figure 3.** a Mechanism of HER from protonic and hydride hydrogen, b relative energy of –NH over –VH, and c energetically strong preference of –NH₂ formation over –NH–VH. d linear correlation between the free energy of fist protonation and N-vacancy formation
According to the MvK mechanism, the N-site that started getting protonation will eventually form one molecule of NH₃, leaving a surface N-vacancy in its place. A linear correlation is observed between the free energy of the first protonation (\(\ddagger H^+\)) and N-vacancy formation (\(\ddagger N_{vac}\)) on the VON surface with O concentration 0 to 37.5% (Figure 3d).

**Activity: N₂RR by MvK mechanism on VON**

In the MvK mechanism, the N-vacancy formation due to the creation of one molecule of NH₃ from the surface N (eq. 4 – 7) is followed by the absorption of one N₂ molecule at the vacant site. N₂ adsorption on the vacancy site can happen in two ways: associative and dissociative mechanism. In an associative MvK, the N-N bond remains intact during the adsorption process and starts to dissociating only after the protonation of the topmost N of the adsorbed N₂. Eq. 11-15 describes the associative MvK, in which gaseous N₂ bound to the vacancy is represented as (\(\ddagger N_{vac}\) N₂). The protonation of the topmost N atom of the vacancy bound N₂ leads to the formation of NH₃(g) and a regenerated catalytic surface (\(\ddagger N_{vac}\) N) which is equivalent to (\(\ddagger N\)).

\[
\ddagger N_{vac} + N₂(g) + 3(H^+ + e^-) \rightarrow \ddagger N_{vac} N₂ + 3(H^+ + e^-) \tag{11}
\]

\[
\ddagger N_{vac} N₂ + 3(H^+ + e^-) \rightarrow \ddagger N_{vac} NNH + 2(H^+ + e^-) \tag{12}
\]

\[
\ddagger N_{vac} NNH + 2(H^+ + e^-) \rightarrow \ddagger N_{vac} NNH₂ + (H^+ + e^-) \tag{13}
\]

\[
\ddagger N_{vac} NNH₂ + (H^+ + e^-) \rightarrow \ddagger N_{vac} NNH₃ \tag{14}
\]
In a dissociative MvK, the N-N bond dissociates directly during the adsorption process, and one of the N atoms then fills up the vacancy site while the second N atom bonds with the neighboring V ion of the vacancy site. Eq. 16–20 demonstrate the dissociative MvK. Here, after dissociation of N$_2$(g), the N replenishing the vacancy site and the N binding to the neighboring metal site is denoted as (∗$^{N-\text{vac}}$ N) and (∗$^{V}$ N), respectively.

\[
\text{∗}^{N-\text{vac}} \text{NNH}_3 \rightarrow \text{∗}^{N-\text{vac}} \text{N} + \text{NH}_3(g) \uparrow = \text{∗}^N + \text{NH}_3(g) \uparrow
\]  

Here, we calculate the free energy of all chemical and electrochemical steps considering zero-point energy correction ($\Delta E_{\text{ZPE}}$) and the change in entropy ($\Delta S$) for the adsorbate and the gaseous molecules. Eq. 21 shows the free energy estimation, where the reaction energy is ($\Delta E$).

\[
\begin{align*}
\text{∗}^{N-\text{vac}} + \text{N}_2(g) + 3(H^+ + e^-) & \rightarrow \text{∗}^{N-\text{vac}} \text{N} + \text{∗}^{V} \text{N} + 3(H^+ + e^-) \\
\text{∗}^{V} \text{N} + 3(H^+ + e^-) & \rightarrow \text{∗}^{V} \text{NH} + 2(H^+ + e^-) \\
\text{∗}^{V} \text{NH} + 2(H^+ + e^-) & \rightarrow \text{∗}^{V} \text{NH}_2 + (H^+ + e^-) \\
\text{∗}^{V} \text{NH}_2 + (H^+ + e^-) & \rightarrow \text{∗}^{V} \text{NH}_3 \\
\text{∗}^{V} \text{NH}_3 & \rightarrow \text{∗}^{V} + \text{NH}_3(g) \uparrow
\end{align*}
\]
\[ \Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S \]  

(21)

Figure 4. a Free energy path is showing the preference of dissociative MvK over associative one and b stronger binding energy of N with V favors N-N dissociation on the VON surface.

The free energy path of NH\(_3\) formation on the VON surface according to associative MvK and dissociative MvK is presented in Figure 4a. The result shows that the associative MvK path is energetically more demanding than the dissociative MvK. The free energy path is defined at 0V in the reversible hydrogen electrode (RHE) scale, and the largest positive step determines the reducing potential required. Strong bonding between V and N lowered the energy of the absorbed state of N\(_2\) following dissociation of the N-N bonds (Figure 4b). Our results match with the previous studies on vanadium nitride, which show that (100) facet of the rock-salt mono-nitrides preferred dissociative N\(_2\) adsorption.
compared to the associative adsorption\textsuperscript{[20]}. The energy barrier of dissociating N-N bond directly upon adsorption at the vacancy site is only 0.3 eV in the case of VN, which is easily activated at ambient conditions. For the rest of this study, we, therefore, focus on the dissociative MvK pathway. Figure 5a presents the free energy path of N$_2$RR on the VON surface with an O-concentration of 12.5%. The free energy paths for VON with 0 to 37.5% O content are presented in the supplementary Figure S6a to S6g. The highest electrochemical step in these paths is typically related to the first protonation of the surface N (\textsuperscript{*}N$H$), except for the VON surface with x = 6.25\% (Figure S6b) and 18.78\% (Figure S6d), where the second protonation step (\textsuperscript{*}2N$2H$) is the highest electrochemical step. Figure 5b shows the onset potential (vs RHE) required for N$_2$RR for different VON surfaces. Increasing the O contents in the VON slab increases the onset potential insignificantly. The lowest onset potential is found for the slab with an O concentration range from 0\% to 12.5\%, which is only \textasciitilde0.4V. N$_2$ adsorption on the vacancy site is a non-electrochemical step (eq. 17), and if the step is endothermic, the energy needs to be provided by the surrounding environment. Therefore, it is desirable to have exothermic N$_2$-adsorption. Figure 5c demonstrates the free energy of N$_2$-adsorption on the VON surfaces with varied O-concentrations. The plot shows that for pure VN (x=0\%), the free energy required for the N$_2$-adsorption is 0.6eV and endothermic in nature. Increasing O-concentration in the VON slab improves the situation, and the free energy of N$_2$-adsorption decreases. For VON slabs with x =12.5, 31.25 and 37.5\%, N$_2$-adsorption on the vacancy site is exothermic and hence expected to be a spontaneous process (Figure 5c). The N$_2$-adsorption energy depends explicitly on the surface coverage of N vacancies. Here, the energetics are calculated with 12.5\% surface coverage of N vacancies (Figure
We observed that by increasing the surface coverage of N vacancies from 12.5% to 25%, the N$_2$-adsorption energy decreases by 0.7 eV (Figure S7) on the VN surface. Based on these results, we can conclude that the VON surface with an x=12.5% composition, is expected to be the best catalyst for N$_2$RR considering both activity and selectivity over HER, as well as spontaneous absorption of N$_2$ at the vacancy site.

It is important to note that although oxygen is not explicitly present in the top layer of the catalyst surface, it indirectly affects the vanadium and nitrogen electronic states and manipulates the binding free energy of the adsorbates. This effect can be understood from the d-band theory of adsorption energies. For example, the variation in the d-band center (Figure S8 a and b) of V bonded with N ion from the N$_2$ adsorbed and dissociate at N-vacancy on the VNO surface with increasing oxygen content correlates well to the N$_2$ adsorption (Figure 5c).
Figure 5. a free energy path of N\textsubscript{2}RR (at x=12.5\%), b onset potentials, c N\textsubscript{2} adsorption energy on the N-vacant site at different Oxygen concentrations (x).

Shielding of N-vacancy site against poisoning

According to the MvK mechanism, the N-vacancy formed by protonation of surface N-site to NH\textsubscript{3}, needs to be replenished by a gaseous N\textsubscript{2} molecule (eq. 17) to complete the N\textsubscript{2}RR cycle. For this, N-vacancies must be sufficiently stable on the surface and not get poisoned by other species like OH\(^{\ast}\) or water molecule. Further, there is also the possibility of this vacancy site to migrate towards bulk and self-annihilate.
Figure 6. self-annihilation of the N-vacancy site on the surface by a migration of N atom from the sub-surface and b migration of O atom from the subsurface.

Self-annihilation

The bulk of the VON slab contains both N and O anions. Nitrogen vacancy created during the initial stages of the MvK mechanism can get self-annihilated by migration of N or O atoms from the subsurface layers. Figure 6a and b displays the thermodynamic and kinetic barriers for a sub-surface N-ion and O-ion to migrate on the vacancy site. The results show that vacancy migration towards subsurface is thermodynamically feasible in both the case. The thermodynamic barrier for the N-migration from sub-surface to surface vacancy site is positive but low (average ~0.5eV) for all the O compositions. In the case of sub-surface O, the migration is thermodynamically downhill, but the kinetic barriers are insurmountable (1.2-2.8 eV) for both the type of migration and expected to keep vacancy kinetically stable on the surface.

Poisoning with O*/OH*/H*

Multiple species compete with N$_2$ for being adsorbed at the nitrogen-vacancy side. In an aqueous electrolyte system under reducing conditions, H*, O*, OH*, and water molecules
can block the reaction site preventing catalytic activity. The calculated binding free energy trend confirms that adsorption of N\textsubscript{2} is significantly preferred over O*/OH*/H* adsorption at the nitrogen-vacancy site (Figure 7a). This supports the continual reaction cycle for ammonia production via the dissociative MvK mechanism. Our detailed mechanistic analysis points out that the catalyst surface layer should consist of V and N atoms, while O atoms stay in the subsurface layer, supporting the catalyst activity through electronic interaction and stabilization of non-stoichiometry. The calculated potential for removal of oxygen atoms from the top layer via protonation and water formation is much more positive than the reducing potential required for N\textsubscript{2}RR (Figure 7b). Thus any O*/OH* species that might populate top layer would get removed very fast at the operating potential.

![Figure 7. a N\textsubscript{2} is preferentially adsorbed at the vacancy site over O*/OH*/H* for x<25% oxygen content. b O from the top layer is removed as water at much before the VON surface reaches N\textsubscript{2}RR potential.](image-url)
Conclusion

TMONs are one of the most promising classes of inorganic transition metal compound electrocatalysts for nitrogen reduction to ammonia using renewable electricity at near-ambient conditions. The challenges of pure transition metal nitrides are overcome in this class of materials due to chemical interaction originating from anion substitution and stabilization of the active surface defect sites. We address the lack of knowledge of the structural details like anion ordering, surface (defect) stability, and structure as well as unearth hitherto unknown mechanism by which TMONs are far superior electrocatalysts in terms of selectivity, stability, and activity towards electrocatalytic nitrogen reduction.

We conclude that <25% oxygen content leads to a kinetically stable cubic rock salt structure and surfaces that suppress leaching and other structural transformation hampering the catalytic activity, while a high oxygen concentration is detrimental to both stability and catalytic activity. The most catalytically active surfaces contain only nitrogen and vanadium due to thermodynamic stability as well as the removal of surface oxygen by protonation. VON surfaces for low oxygen content show remarkable selectivity over HER due to a thermodynamic preference for repetitive protonation at the nitrogen site over the vanadium site leading to ammonia release. Ammonia evolution follows a dissociative Mars van Krevelen mechanism. The onset potential for 12.5% O containing VNO is only ~0.4V, while keeping the surface facile for N\textsubscript{2} absorption at the nitrogen-vacancy site, unlike other low oxygen-containing compositions and pure VN. The anion-vacancy sites are critical for continued ammonia production and remain shielded from lattice ion-based self-annihilation due to large kinetic barriers for anion migration. Also, the surface is protected against O*/OH*/H* poisoning due to the thermodynamic
preference for N$_2$ absorption and fast electrochemical removal of surface oxygen at potentials relevant for N2RR. Our study establishes a fundamental understanding of the catalytic behavior of VNO for ammonia electro-synthesis. Along with the explanation of why the oxynitride phase can sustain catalytic activity and other beneficial effects of oxygen substitution. Finally, it also identifies the optimal N/O ratio in VNO for further investigation and experimental validation.

Computational details

Density functional theory-based simulations were performed with plane wave basis set and projector-augmented wave based implementation in VASP$^{[41]}$ package. Revised Perdew-Burke-Ernzerhof (RPBE)$^{[42]}$ with Pade Approximation is used as an exchange correlation functional. The wave functions are expanded in plane waves with an energy cutoff of 500 eV for bulk and 350 eV for surface simulations. The first Brillouin zone is sampled with 4x2x2, 7x5x2, and 2x2x1 Monkhorst–Pack k-point mesh for the 32 atom VNO supercell (1x2x2), V2O5 unit cell and VNO surfaces respectively. In the periodic repeating unit cell used for surface simulation, 18 Å of vacuum is used in the z-direction to minimize any interaction under periodic boundary conditions. The bottom two layers are fixed during atomic relaxations, and top two layers were optimized including any adsorbate until forces on each free atom are lower than 0.003 eV/Å. Gaussian smearing of 10 meV is used for the electronic states. The lattice parameters are optimized for bulk calculations and are provided in Table S1. For surface calculations, lattice parameters are kept fixed.
To estimate the change in free energy under an applied potential for protonation steps, the free energies are calculated using the computational hydrogen electrode (CHE) model[43]. It is a simple linear model that approximates free energy change to the applied potential for an elementary electrochemical reaction step. The free energies of molecules are calculated within the ideal gas approximation. Phonon modes for adsorbates that are used for evaluation of zero-point energy and entropy (Table S3) are done with performing small-displacement energy/force calculations in all three directions and all adsorbate atoms. References for water, ammonia, hydrogen, and nitrogen molecules are used for adsorption free energy calculations. We use the nudged-elastic band method[44] as implemented in VASP with a tolerance of 0.03 eV /Å. All computation was managed, processed, and visualized with an atomistic simulation environment (ASE)[45].

Acknowledgments

J.P, H.H and T.V. thank the EU project ARENHA (“Advanced materials and Reactors for ENergy storage tHrough Ammonia”) #862482 for the financial supports.

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Supplementary Information for:

Vanadium oxynitrides as stable catalysts for electrochemical reduction of nitrogen to ammonia: the role of oxygen

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Figure S1. The mixing enthalpy of VN and VO with respect to V$_2$O$_5$. 
Figure S2. Crystal structures of minimum energy configuration with different N/O compositions along the convex hull of the mixing enthalpy calculated for rock-salt VN and VO phases (V: green, O: red and N: blue).
Figure S3. Charge density plot of (001) cross-section of VON (x=12.75%) showing the disparity in the chemical bonding between V-N and V-O (V: green, O: red and N: blue).
Table-S1: Cell parameters of the lowest energy configurations of VON with different N/O ratio.

<table>
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<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
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<th>β (°)</th>
<th>γ (°)</th>
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Figure S4. (100) slab cleaved from VON crystal with oxygen concentration \(x=0\%\) to \(x=43.75\%\), (b) (V: green, O: red and N: blue).
Figure S5. Free energy of HER from hydride ion and proton located at the neighboring V and N on the VON surface.

Table-S2: Bader charges on different H ions

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<tr>
<td>$^{N-vac} H$</td>
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Table-S3: Zero point energy and entropy correction for the gaseous molecules and adsorbates used in the free energy calculations of VON surface at ambient condition (300K and 1atm pressure).

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<tr>
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Figure S6. Free energy path of dissociative MvK NER on VON with x=0% to x=37.25%
Figure S7. The effect of surface coverage of N-vacancy on N-adsorption energy.
Figure S8. a) d-band partial density of states of V ion on the surface, bonded with N from N2 adsorbed on the N-vacancy site for varying oxygen content in VNO and (b) calculated d-band center (with respect to Fermi level)
5. Conclusion and outlook

5.1. Conclusion

Computational studies of novel thermal and electrocatalysts done in this PhD project led to breakthroughs in the design of ammonia evolution catalysts that are highly active in ambient conditions.

It was proven that the ternary ruthenium hydrides Li\textsubscript{4}RuH\textsubscript{6} and Ba\textsubscript{2}RuH\textsubscript{6} represent an entirely new class of catalysts containing electron- and H-rich [RuH\textsubscript{6}] anionic centers that produce ammonia through a previously non-described mechanism non-dissociative mechanism. The unique property of these catalysts originates from (a) hydridic H transporting electrons and protons (b) cations stabilizing N\textsubscript{x}H\textsubscript{y} (x: 0 to 2, y: 0 to 3) intermediates. The reaction mechanism is very complex, but it is balanced through multiple synergistic chemical effects such that ammonia can be produced below 450K. The hydride compounds are the very first example of bulk solid state transition metal complex compounds that can catalyze ammonia formation at such mild conditions. The [RuH\textsubscript{6}] catalytic center activates N\textsubscript{2} preferentially and avoid hydrogen over-saturation in mild conditions by delicately balancing H\textsubscript{2} chemisorption and N\textsubscript{2} activation. The unprecedented yield at low temperatures is caused by a shift in the rate-determining reaction intermediates and transition states, where the reaction orders in hydrogen and ammonia change dramatically.

Vanadium oxynitride – a member of unexplored oxynitride electrocatalyst, were studied in detail for bulk surface properties like optimal composition, anion ordering, surface (defect) stability, as well as establish the currently unknown vacancy mediated ammonia evolution mechanism on VNO. It is shown than compared to VN, VNO is a far superior electrocatalyst in terms of selectivity, stability, and activity towards electrocatalytic nitrogen reduction. We conclude that \textasciitilde12.5\% oxygen content leads to (a) kinetically stable catalyst surfaces that suppress leaching and other structural transformation hampering the catalytic activity (b) show remarkable selectivity over HER due to a thermodynamic preference for repetitive protonation at the nitrogen site and (c) onset potential of only \textasciitilde0.4V. The anion-vacancy sites are critical for continued ammonia production and remain shielded from lattice ion-based self-annihilation due to large kinetic barriers for anion migration.
5.2. Outlook

Insights gained through this PhD project on ternary hydrides should open the floodgates for new research activity from theoretical and experimental groups worldwide in further exploration of this novel catalyst family. Hydrides need to be studied as an active catalyst going away from the current trend of using it as catalyst support only. The excellent performance of ternary Ru hydrides will definitely exert a strong influence on the whole field of catalysis as it shows the power of lattice hydride ions as the hydrogen source for reductions reactions.

Following the footstep of the hydride thermos-catalysts, Results on VNO electrocatalyst, while very promising, need experimental validation of activity and selectivity, especially for acceptably high current density. The work on oxynitride also pioneered computational studies on multi-anion bulk electrocatalysts. Following this lead, it will be worth to study extensive other transition metal oxynitrides and possibly other multi-anionic systems with or without nitrogen. This can very well be the breakthrough to pave the path towards ambient pressure temperature conversion of nitrogen into ammonia through a distributed process. However, this is only the inceptive study. Detailed research is needed for optimization and scalability before such catalysts can be used for process engineering. It is hoped the excellent results obtain in this thesis inspire such activity.
6. References


