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# Ternary ruthenium complex hydrides for 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 CO<sub>2</sub> than any other chemical producing reaction in the world. The demand for decarbonizing the ammonia industry by using green H<sub>2</sub> from H<sub>2</sub>O and the electric power generated from renewable energy sources has stimulated research interests into catalyst development for effective N<sub>2</sub> reduction under mild conditions – a grand scientific challenge. Conventional heterogeneous catalysts based on metallic Fe or Ru mediate dinitrogen dissociation and hydrogenation through a relatively energy-costing pathway. The ternary ruthenium complex hydrides Li<sub>4</sub>RuH<sub>6</sub> and Ba<sub>2</sub>RuH<sub>6</sub> 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 [RuH<sub>6</sub>] anionic centers for non-dissociative dinitrogen reduction, where hydridic H transports electron and proton between the centers, and the Li(Ba) cations for stabilizing N<sub>x</sub>H<sub>y</sub> (x: 0 to 2, y: 0 to 3) intermediates. The dynamic and synergistic involvement of all the components of the ternary complex hydrides facilitates a novel reaction mechanism with a narrow energy span and perfectly balanced kinetic barriers for the multi-step process, leading to ammonia production from N<sub>2</sub>+H<sub>2</sub> with superior kinetics under mild conditions.**

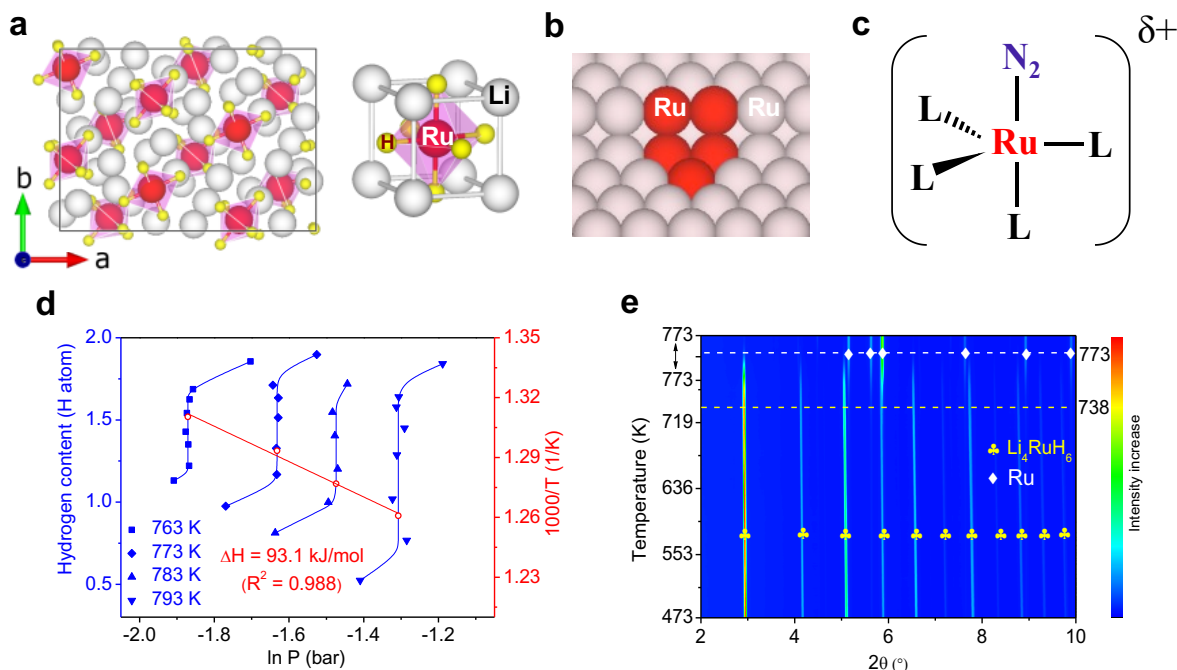
The energetics and mechanism of a catalytic process depend explicitly on the interaction between the reacting species and the active center, which is exemplified in the activation and conversion of N<sub>2</sub> to NH<sub>3</sub> over natural and man-made catalysts. In biological<sup>1-2</sup> or organometallic N<sub>2</sub> fixation<sup>3-5</sup> catalyzed by FeMo(V) cofactor or soluble transition metal (TM) complexes, N<sub>2</sub> 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. Despite operated under ambient conditions, these systems still consume a substantial amount of energy<sup>6</sup>. When the catalysis is carried out on an extended Fe or Ru metal surface, N<sub>2</sub> adsorbs on the active center composed of multiple TM atoms (C<sub>7</sub> or B<sub>5</sub> site of Fe or Ru, respectively) and dissociates exothermically into chemisorbed N atoms followed by a stepwise hydrogenation to NH<sub>3</sub><sup>7-10</sup>. The relatively high kinetic barrier for direct N<sub>2</sub> dissociation and/or strong adsorption of intermediate species on Fe or Ru metal surface render NH<sub>3</sub> synthesis from N<sub>2</sub>+H<sub>2</sub> under near-ambient conditions unattainable<sup>11</sup>. Creating an active center with suitable electronic structure and reacting environment for effective “hydrogenolysis” of N<sub>2</sub> to NH<sub>3</sub> by using H<sub>2</sub> as reductant would synergize

1 the energy input and output in breaking and establishing chemical bonding, and thus endow the  
2 catalysis of narrow energy span<sup>12</sup>. Encouraging attempts have been made via creating isolated or  
3 clustered TM center on an oxide support<sup>13-14</sup>, defect-borne Co<sub>3</sub>Mo<sub>3</sub>N surface<sup>15</sup>, or new catalytic  
4 systems (such as electride/hydride-involved TM particle catalyst, intermetallic catalyst, etc.)<sup>16-19</sup>,  
5 while catalytic hydrogenolysis of N<sub>2</sub> to NH<sub>3</sub> via concerted N-N weakening and N-H forming under  
6 mild conditions has yet to be demonstrated.

7 Recently, gas-phase cluster investigations revealed that laser-generated gaseous clusters such as  
8 [Li<sub>4</sub>FeH<sub>6</sub>]<sup>-</sup> and [Li<sub>5</sub>FeH<sub>7</sub>]<sup>-</sup> etc. from LiH-promoted Fe metal catalyst can undergo stoichiometric  
9 reaction with dinitrogen forming NH<sub>2</sub>-containing clusters<sup>20</sup>. This finding inspired us to investigate  
10 whether the ternary complex hydrides of alkali (or alkaline earth) and transition metals, a series of  
11 compounds belonging to solid-state complexes that often studied in hydrogen storage<sup>21</sup>, would  
12 have the potential to catalyze ammonia formation from N<sub>2</sub> and H<sub>2</sub>. The synthesis of solid-state  
13 Li<sub>4</sub>FeH<sub>6</sub> requires extremely high pressure of 6.1 GPa<sup>22</sup>, but its Ru analogues are stable entities  
14 and can be facily prepared under normal condition<sup>23</sup>. In this article, we report an entirely new  
15 catalyst system, i.e., ternary ruthenium complex hydrides Li<sub>4</sub>RuH<sub>6</sub> and Ba<sub>2</sub>RuH<sub>6</sub>, for ammonia  
16 synthesis from N<sub>2</sub> and H<sub>2</sub>. The ruthenium complex hydrides differ distinctly from the existing  
17 heterogeneous TM catalysts and homogeneous TM complex catalysts in electronic, compositional  
18 and structural properties as well as the reaction mechanism for ammonia synthesis, and exhibit  
19 remarkable catalytic performances under mild conditions, i.e., they outperform all the  
20 heterogeneous catalysts developed to date, and exhibit N<sub>2</sub> + H<sub>2</sub> to NH<sub>3</sub> activities at temperatures  
21 below 373 K! Through a concerted experimental and theoretical investigation, we demonstrate  
22 that catalytic hydrogenolysis of dinitrogen to ammonia could be effectively achieved by ruthenium  
23 complex hydrides under mild conditions, in which all the components of complex hydride, i.e., the  
24 electron-rich [RuH<sub>6</sub>]<sup>4-</sup>, Li/Ba cation and hydridic hydrogen, have a natural synergy during  
25 catalysis. These findings provide new insights into the catalyst design for mild-condition ammonia  
26 synthesis, and may also bridge the gap of heterogeneous and homogeneous nitrogen fixation at the  
27 molecular level.

## 28 Results

29 **Structure and properties of ternary Ru complex hydrides.** The ternary Ru complex hydrides  
30 are a class of mixed ionic-covalent compounds having a general chemical formula of A<sub>x</sub>[RuH<sub>6</sub>] (A  
31 = Li, Na, Mg, Ca or Ba etc., x= 4 or 2)<sup>23-24</sup>. Of particular interests are Li<sub>4</sub>RuH<sub>6</sub> and Ba<sub>2</sub>RuH<sub>6</sub>,  
32 which can be synthesized via reacting Ru metal with LiH or BaH<sub>2</sub>, respectively. Ru in Li<sub>4</sub>RuH<sub>6</sub> is  
33 positively charged based on the XANES spectra (Supplementary Fig. 1), and has a low-valence  
34 state as indicated by charge state analysis<sup>24</sup>. Our Bader charge calculations also reveal that Li  
35 donates electronic charge to [RuH<sub>6</sub>]; H, on the contrary, is negatively charged (Supplementary Fig.  
36 2). The H- and electron-rich [RuH<sub>6</sub>]<sup>4-</sup> anions sit inside the K<sub>4</sub>CdCl<sub>6</sub> (or K<sub>2</sub>PtCl<sub>6</sub>)-type framework  
37 of Li (or Ba) cations with a Ru-Ru distance of 5.09 (5.78) Å (Supplementary Fig. 3). These ternary  
38 ruthenium complex hydrides differ distinctly from the closed packed Ru metal surface and the  
39 isolated molecular Ru complexes in electronic, compositional and structural properties as  
40 illustrated in Figs. 1a, 1b and 1c.



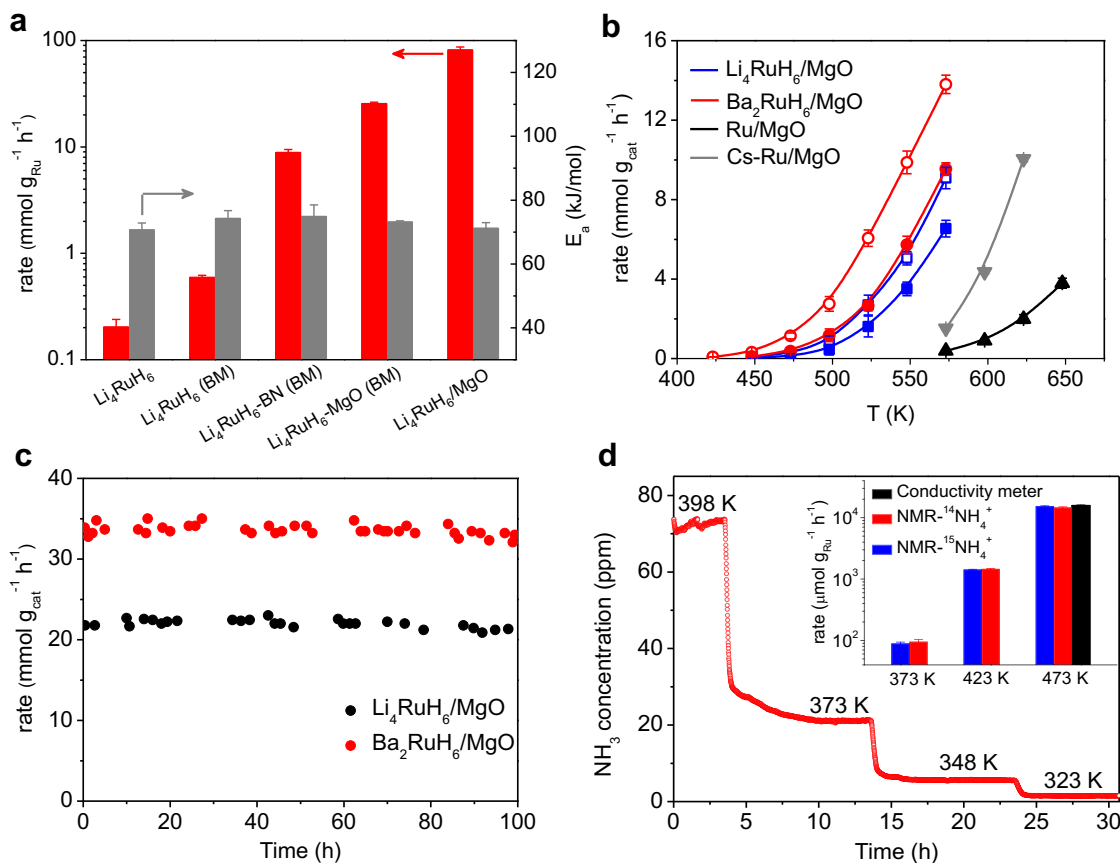
**Fig. 1. Properties of  $\text{Li}_4\text{RuH}_6$ .** **a**,  $\text{Li}_4\text{RuH}_6$  surface and the local coordination of Ru in  $\text{Li}_4\text{RuH}_6$  (Ru-red, H-yellow, Li-white). **b**, Ru (0001) surface (the  $B_5$  site is highlighted in bright red). **c**, The model of molecular Ru complex (L-ligand). **d**, The pressure-composition isotherms of the dehydrogenation of  $\text{Li}_4\text{RuH}_6$  and the corresponding van't Hoff plot, the lines are guide to eye. **e**, *in situ* SR-PXD characterization of  $\text{Li}_4\text{RuH}_6$  sample under atmospheric  $\text{N}_2$ - $3\text{H}_2$  and elevated temperatures (from 473K to 773 K).

Our pressure-composition-isotherm and temperature-programmed reaction measurements reveal that  $\text{Li}_4\text{RuH}_6$  has a large enthalpy change of  $93.1 \text{ kJ mol}^{-1}\text{-H}_2$  in hydrogen desorption (the equilibrium  $\text{H}_2$  desorption pressure is below 0.2 bar at 773 K), and only at high temperatures would  $\text{Li}_4\text{RuH}_6$  decompose to Ru and LiH (Fig. 1d).  $\text{Li}_4\text{RuH}_6$  is also resistant to diluted  $\text{NH}_3$ , i.e., upon feeding a mixture of  $\text{NH}_3$  and  $\text{H}_2$ , the ternary complex hydride remains intact until ca. 673 K (Supplementary Fig. 4a). The *in situ* SR-PXD characterization also reveals that the hydride remains the dominant phase until ca. 651 or 738 K under  $\text{N}_2$  or  $\text{N}_2+3\text{H}_2$  of atmospheric pressure, respectively (Fig. 1e and Supplementary Fig. 4b).  $\text{Ba}_2\text{RuH}_6$  is found to be even more stable than  $\text{Li}_4\text{RuH}_6$  (Supplementary Table 1 and Figs. 4c-d)<sup>25</sup>. These experimental results show that the bulk  $\text{Li}_4\text{RuH}_6$  and  $\text{Ba}_2\text{RuH}_6$  phases will remain stable under the ammonia synthesis conditions applied in this study ( $\text{H}_2$  partial pressure from 0.25 to 7.5 bar, operation temperature from 323 K to 573 K).

**Catalytic performance and kinetic analyses.** The as-prepared bulk-phase  $\text{Li}_4\text{RuH}_6$  and  $\text{Ba}_2\text{RuH}_6$  samples exhibit activities of ca. 150 and 120  $\mu\text{mol g}_{\text{cat}}^{-1} \text{ h}^{-1}$  at 1 bar and 573 K, respectively (Supplementary Fig. 5a). We then reduced the particle sizes of the samples to increase their surface areas. Our experimental results show that ball milling the as-prepared  $\text{Li}_4\text{RuH}_6$  sample with inert dispersers, such as BN and MgO, can effectively reduce its crystalline size from ca. 50 nm to ca. 20 nm ( $\text{Li}_4\text{RuH}_6\text{-BN(BM)}$ ) and 9 nm ( $\text{Li}_4\text{RuH}_6\text{-MgO(BM)}$ ), and enhance the reaction rate by ca. 45 and 125 times, respectively (Fig. 2a). Moreover, for these ball-milled catalysts,  $\text{Li}_4\text{RuH}_6$  phase remained stable after activity test (Supplementary Fig. 6). We further employed MgO as support



1 and synthesized  $\text{Li}_4\text{RuH}_6/\text{MgO}$  and  $\text{Ba}_2\text{RuH}_6/\text{MgO}$  catalysts by introducing Li and Ba to the parent  
2 Ru/MgO catalyst. These supported catalysts (their TEM images and HAADF-STEM  
3 characterizations are given in Supplementary Figs. 7-8) possess the characteristic features (Ru-H  
4 stretch and surface composition) of the bulk-phase hydrides (Supplementary Fig. 9). The  
5  $\text{Li}_4\text{RuH}_6/\text{MgO}$  catalyst shows ca. 400-fold increase in activity from the bulk-phase  $\text{Li}_4\text{RuH}_6$ , but  
6 has a similar apparent activation energy of ca.  $71 \text{ kJ mol}^{-1}$  (0.74 eV) to other  $\text{Li}_4\text{RuH}_6$ -based  
7 catalysts (Fig. 2a and Supplementary Fig. 11a), manifesting an effective exposure of active sites  
8 in the supported catalyst. The supported ternary complex hydride catalysts perform extraordinarily  
9 well under mild conditions and show constant activities for 100 hours, where the activities of  
10  $\text{Li}_4\text{RuH}_6/\text{MgO}$  and  $\text{Ba}_2\text{RuH}_6/\text{MgO}$  at 573 K are more than one order magnitude higher than that  
11 of Ru/MgO even in terms of TOF determined by SSITKA (Figs. 2b and c, Supplementary Table  
12 3). In particular, the  $\text{Ba}_2\text{RuH}_6/\text{MgO}$  outperforms the most active Ru catalysts reported to date, and  
13 its activity at 523 K is over one order of magnitude higher than that of the benchmark Cs-promoted  
14 Ru/MgO catalyst (Table 1 and Supplementary Table 4). Moreover, under 10 bar and a WHSV of  
15  $7500 \text{ ml g}^{-1} \text{ h}^{-1}$ , the yield of ammonia is ca. 8.7 % at 573 K and approaches equilibrium at higher  
16 temperatures for the  $\text{Ba}_2\text{RuH}_6/\text{MgO}$  (Supplementary Fig. 10). Those features indicate the rich  
17 promise of the ternary complex hydrides for practical application in renewable electricity powered  
18 small-scale Haber-Bosch process, which generally requires an active catalyst operating at lower  
19 pressures ( $< 50 \text{ bar}$ ) and lower temperatures ( $< 673 \text{ K}$ ). It is important to note that if the  
20  $\text{Li}_4\text{RuH}_6/\text{MgO}$  and  $\text{Ba}_2\text{RuH}_6/\text{MgO}$  samples are exposed to air, their activities drop significantly to  
21 the level of the Ru/MgO sample. Similarly, the direct introduction of  $\text{Li}_2\text{O}$  to Ru/MgO does not  
22 bring notable changes in activity (Supplementary Fig. 5b). This result demonstrates that the ternary  
23 complex hydride form is of critical importance for the efficient catalysis.



**Fig. 2. Catalytic performances.** **a**, Activities of  $\text{Li}_4\text{RuH}_6$ -based catalysts at 573 K and the corresponding activation energies (Reaction conditions: catalyst loading 30 mg,  $\text{H}_2:\text{N}_2=3:1$ , flow rate  $30 \text{ ml min}^{-1}$ , and 1 bar). **b**, Temperature-dependent  $\text{NH}_3$  synthesis rates of different catalysts (Reaction conditions:  $\text{H}_2:\text{N}_2=3:1$  (filled symbols) or  $\text{H}_2:\text{N}_2=2:3$  (open symbols), others are the same as **a**). **c**, Time dependence of the activities of  $\text{Li}_4\text{RuH}_6/\text{MgO}$  and  $\text{Ba}_2\text{RuH}_6/\text{MgO}$  catalysts (Reaction conditions:  $\text{H}_2:\text{N}_2=2:3$ , 10 bar, others are the same as **a**). Noted that the effluent  $\text{NH}_3$  concentration during stability test is far from that at thermodynamic equilibrium. **d**, Time course of effluent  $\text{NH}_3$  concentration in the outlet gas ( $\text{Ba}_2\text{RuH}_6/\text{MgO}$  catalyst, 200 mg,  $\text{H}_2:\text{N}_2=1:3$ , flow rate  $36 \text{ ml min}^{-1}$ , 1 bar). The inset shows the activities of  $\text{Ba}_2\text{RuH}_6/\text{MgO}$  catalyst in the temperature range of 373-473 K determined by  $^1\text{H}$  NMR measurements of  $\text{NH}_3$  concentration in the outlet gas under a flow of  $^{15}\text{N}_2\text{-H}_2$  or  $^{14}\text{N}_2\text{-H}_2$ . The activity at 473 K was also measured by conductivity meter for comparison. (30 mg,  $\text{H}_2:\text{N}_2=2:3$ , flow rate  $10 \text{ ml min}^{-1}$ , 1 bar). Error bars shown in **a**, **b** and inset figure of **d** represent the standard deviation from three independent measurements.

The most prominent kinetic features of this new class of ternary complex hydride catalysts are the smaller apparent activation energies and the positive reaction orders of  $\text{H}_2$  (Table 1 and Supplementary Figs. 11b-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<sup>10,26</sup>. These features enable the ternary complex 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  $\text{Li}_4\text{RuH}_6/\text{MgO}$  and  $\text{Ba}_2\text{RuH}_6/\text{MgO}$  catalysts present constant increases of turn-over-number (TON) at 448 K and 423 K, respectively, and the turn-on

1 and turn-off NH<sub>3</sub> signals under an alternative feeding of N<sub>2</sub> + H<sub>2</sub> and H<sub>2</sub>. Noted that no ammonia  
 2 was detectable upon feeding N<sub>2</sub> only to Li<sub>4</sub>RuH<sub>6</sub>/MgO showing lattice H cannot work alone for  
 3 ammonia (Supplementary Fig. 12). We subsequently probed the function limit of the hydride  
 4 catalysts by adopting the charge-transfer ionization time-of-flight mass spectroscopy (CTI-  
 5 TOFMS) with low NH<sub>3</sub> detection limit<sup>27</sup>. Under ambient pressure, both the CTI-TOFMS and the  
 6 conductivity meter (the conventional ammonia detection method) gave similar effluent NH<sub>3</sub>  
 7 concentrations of ca. 70 ppm at 398 K and 20 ppm at 373 K from the Ba<sub>2</sub>RuH<sub>6</sub>/MgO catalyzed  
 8 system (Supplementary Fig. 13). The CTI-TOFMS further detected a constant effluent ammonia  
 9 concentration of ca. 5 ppm at 348 K and 2 ppm at 323 K, respectively (Fig. 2d). In order to assert  
 10 the origin of the nitrogen in the produced ammonia, we also performed a series of isotopic labeled  
 11 control experiments and employed <sup>1</sup>H NMR for the quantitative measurements (Supplementary  
 12 Fig. 14). As shown in Fig. 2d inset, feeding the Ba<sub>2</sub>RuH<sub>6</sub>/MgO catalyst with <sup>15</sup>N<sub>2</sub>-H<sub>2</sub> or <sup>14</sup>N<sub>2</sub>-H<sub>2</sub>  
 13 results in nearly identical ammonia production rates, respectively, providing a conclusive evidence  
 14 that the ammonia formed originates from the feeding gas.

15 **Table 1. Catalytic Properties of Ru-based catalysts.**

16

Catalyst	Ru content (wt %)	<i>r</i> <sub>NH<sub>3</sub></sub> <sup>a</sup>		TOF <sup>b</sup>		Reaction order			<i>E</i> <sub>a</sub> (kJ mol <sup>-1</sup> )
		573 K	523 K	573 K	523 K	α(NH <sub>3</sub> )	β(N <sub>2</sub> )	γ(H <sub>2</sub> )	
Li <sub>4</sub> RuH <sub>6</sub> /MgO	8.0	22.0	4.4	20.9	3.9	-0.59	0.91	0.30	71.2
Ba <sub>2</sub> RuH <sub>6</sub> /MgO	5.0	34.0	8.7	59.7	15.3	-0.63	0.92	1.00	63.9
Ru/MgO	8.7	1.7	0.25	1.3	0.2	-0.24	1.12	-0.86	94.8
Cs-Ru/MgO	7.3	5.7	0.60	9.9	1.1	-0.09	1.01	-0.82	112.4

17 <sup>a</sup>NH<sub>3</sub> synthesis rate (mmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>); catalyst loading 30 mg, H<sub>2</sub>:N<sub>2</sub> = 2:3, flow rate 30 ml min<sup>-1</sup>, and 10 bar.

18 <sup>b</sup> TOF (×10<sup>-3</sup> s<sup>-1</sup>) was calculated based on the surface Ru content derived from the average particle size observed by TEM and  
 19 spherical assumption of the particle morphology (Supplementary Table 2). TOFs of these catalysts at 573 K and 1 bar determined  
 20 by SSITKA are shown in Supplementary Table 3.

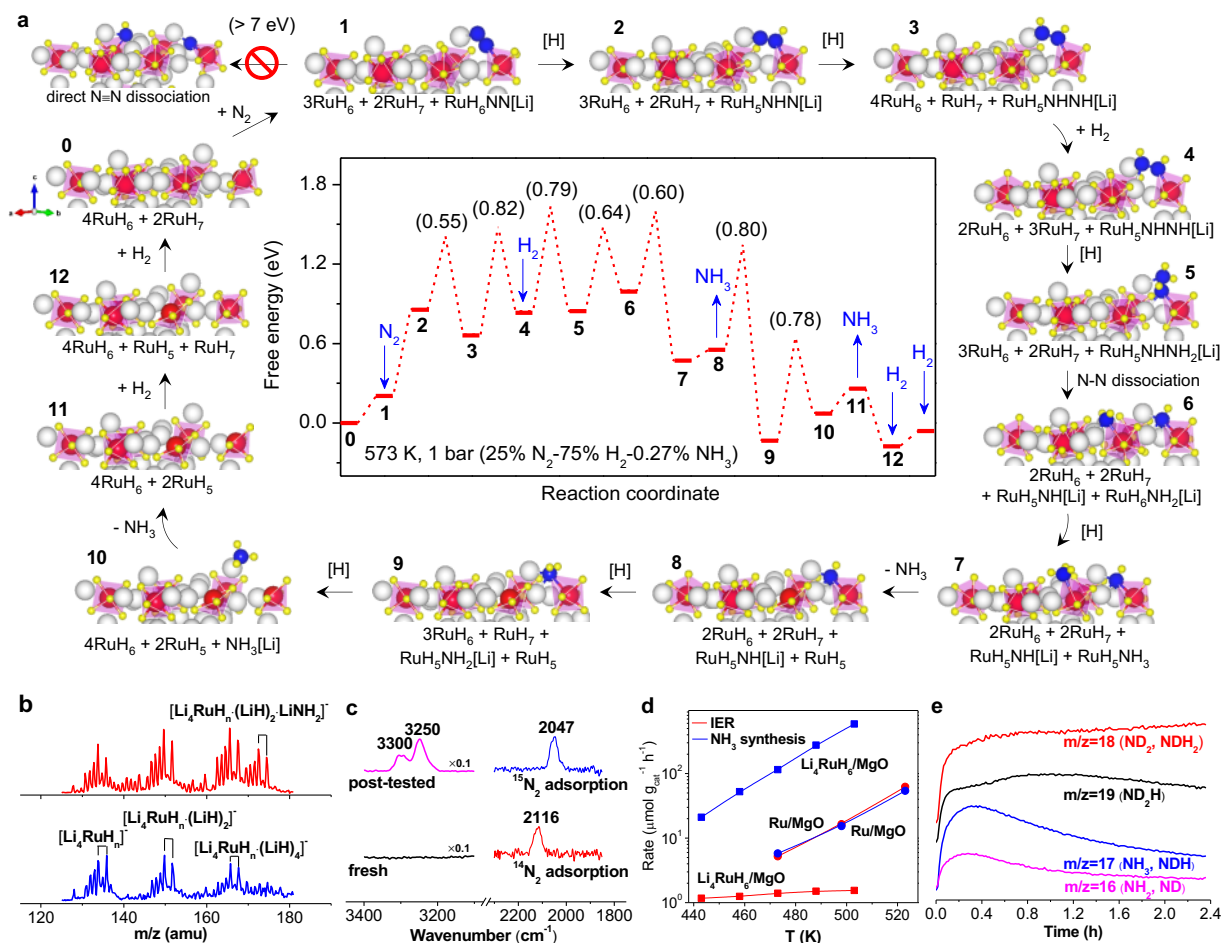
21 **Reaction mechanism.** Hydridic H is a combined source of electron and proton and was found to  
 22 exert profound effects on nitrogen fixation<sup>28</sup>. In enzymatic ammonia synthesis catalyzed by FeMo-  
 23 or FeV-cofactor, the key intermediate was suggested to be a bridging hydride species, which  
 24 undergoes reductive elimination of dihydrogen to create an electron-enriched Fe center capable of  
 25 catalyzing N<sub>2</sub> reduction<sup>1-2</sup>. In homogeneous regime, various molecular TM hydride complexes  
 26 have been investigated for N<sub>2</sub> fixation<sup>5, 29</sup>. Several early TM hydride complexes, such as  
 27 multinuclear Ti or Cr polyhydride complex, not only cleave N<sub>2</sub> but also hydrogenate the  
 28 dissociated N forming imido-nitrido or diimido products<sup>30-32</sup>. While for late TM hydride  
 29 complexes, such as Ru hydride complex [PPh<sub>3</sub>]<sub>3</sub>Ru(H<sub>2</sub>)H<sub>2</sub>, N<sub>2</sub> is usually weakly activated and  
 30 coordinated to the TM site in an end-on mode. No N-H bond formation was observed<sup>5, 33</sup>. As for  
 31 heterogeneous Ru metal catalysts, the surface hydrides would exert a severe poisoning effect that  
 32 defers low-temperature N<sub>2</sub> activation and conversion<sup>26</sup> and the H-associative mechanism is  
 33 suppressed relative to the dissociative mechanism<sup>34-35</sup>. The H-rich ternary Ru complex hydrides,

1 on the contrary, effectively catalyze  $N_2$  and  $H_2$  to  $NH_3$  under mild conditions, reflecting a distinct  
2 electronic configuration and function mechanism of the active center.

3 We thus investigated the mechanism of ammonia formation over  $Li_4RuH_6$  experimentally and  
4 theoretically (Fig. 3). The as-prepared  $Li_4RuH_6$  sample was bombarded with laser to generate  
5 gaseous clusters for mass spectroscopy (MS) analysis. The composition and structure of the  
6 clusters would hint at or correlate with the surface of  $Li_4RuH_6$ <sup>20,36</sup>. Taking into the consideration  
7 of the isotopes of Ru, the clusters with relatively intensive peaks include  $[Li_4RuH_6]^+$  and its  
8 complexes with LiH. Bombarding  $Li_4RuH_6$  in  $N_2$  atmosphere, interestingly, highlights the  
9 production of a set of  $NH_2$ -containing clusters (Fig. 3b).

10 Our DFT calculations show that the  $[RuH_6]$  terminated (110) surface is the most stable low  
11 Miller index surface under operational conditions, and that the surface has an intriguing flexibility  
12 in accommodating excess lithium and hydrogen. As shown in Supplementary Fig. 15, the addition  
13 of excess LiH to the surface composed of six  $Li_4RuH_6$  units is exothermic and results in the  
14 formation of  $[RuH_7]$  complexes at the low-to-moderate temperatures and pressures investigated  
15 here. These data correlate with the observation of LiH affinity to  $[Li_4RuH_6]^+$  in the cluster  
16 experiment (Fig. 3b). It is important to note that certain over-stoichiometry in surface hydrogen  
17 and lithium (two extra LiH) actually induces a preference for  $N_2$  over  $H_2$  adsorption at the active  
18 pentagonal base pyramidal polyhedral  $[RuH_6]$  site. The competitive adsorption of  $N_2$  and  $H_2$  is not  
19 pronounced over  $Ba_2RuH_6$ , however, the addition of excess  $BaH_2$  enhances  $N_2$  adsorption, which  
20 may account for its higher TOF (see Supplementary Fig. 16 and Table 1). Based on the  
21 experimental observation and the theoretical calculations, a model  $Li_4RuH_6$  (110) surface  
22 composed of six  $Li_4RuH_6$  units and stabilized by two extra LiH was adopted to simulate  $NH_3$   
23 formation at 573 K and 1 bar (see Supplementary Fig. 17).

24 The full reaction pathway has been mapped out using DFT calculations and found to be highly  
25 complex, involving no less than 13 intermediate states and multiple adsorption/dissociation and  
26 lattice H transfer processes. Given the complexity and dynamic nature of the surface, a large  
27 number of possible pathways were investigated (a few are shown in Supplementary Fig. 18), where  
28 the one shown in Fig. 3a (and Supplementary Fig. 19) was found to display the minimum energy  
29 span, i.e., the smallest free energy distance between the intermediate state and the transition state  
30 with the highest degree of rate control<sup>12</sup>. The energy span is as low as 1.75 eV under the mild  
31 experimental conditions imposed here, which is substantially lower by  $>1.0$  eV than that observed  
32 on Ru (211)<sup>11</sup>, and in good agreement with the enhanced TOF observed relative to Ru/MgO (Table  
33 1). Further, it is important to stress that although the path involves many activated processes, all  
34 of the kinetic barriers are found to below 79 kJ/mol (0.82 eV).



**Fig. 3. Mechanistic investigations on  $\text{N}_2$  activation and hydrogenation over  $\text{Li}_4\text{RuH}_6$  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 intermediate states are simplified, [H] represents lattice hydrogen transfer. [Li] refers to the involvement of Li cations in stabilizing the  $\text{N}_x\text{H}_y$  intermediates.  $\text{N}_2$  activation on catalyst surface prefers a non-dissociative path with moderate barriers, while the direct dissociation of  $\text{N}_2$  is prohibited by a very high kinetic barrier ( $> 7$  eV) (Supplementary Fig. 20). Color code: Ru-red, H-yellow, Li-white and N-blue. **b**, Mass spectra of clusters generated from  $\text{Li}_4\text{RuH}_6$  sample under a pure He (blue line) and a mixture of  $\text{N}_2$ -He (red line) atmosphere. **c**, DRIFT spectra of the fresh, post-tested, and post- $^{15}\text{N}_2$  and  $^{-15}\text{N}_2$  adsorbed  $\text{Li}_4\text{RuH}_6/\text{MgO}$  samples. **d**, The temperature dependence of  $^{28}\text{N}_2$ - $^{30}\text{N}_2$  isotopic exchange reaction (IER) rates and catalytic  $\text{NH}_3$  synthesis rates of  $\text{Li}_4\text{RuH}_6/\text{MgO}$  and  $\text{Ru}/\text{MgO}$  catalysts. **e**, Reaction time profiles for ammonia synthesis from  $\text{N}_2$  and  $\text{D}_2$  over  $\text{Li}_4\text{RuH}_6$  at 598 K.

Here,  $\text{N}_2$  prefers to chemisorb on the partially positive-charged Ru of  $[\text{RuH}_6]$  site (0-1) in an end-on mode and bends to Li nearby. The N-N bond length is thus elongated to 1.14 Å, which manifests a moderate activation and correlates with our DRIFT observation of a N-N stretching of adsorbed  $\text{N}_2$  at 2116  $\text{cm}^{-1}$  (confirmed by  $^{15}\text{N}_2$  adsorption at 2047  $\text{cm}^{-1}$ ) (Fig. 3c). The DFT calculations show that the direct dissociation of dinitrogen over the surface is strongly kinetically inhibited (Supplementary Fig. 20), which is understandable since Ru in  $\text{Li}_4\text{RuH}_6$  is electron-deficient and the Ru-Ru distance (5.09 Å) is much longer compared with that in Ru metal (2.71 Å),

1 which is unfavorable for the direct dissociation of dinitrogen. The non-dissociative N<sub>2</sub> activation  
2 is also supported by the of kinetic <sup>15</sup>N<sub>2</sub>-<sup>14</sup>N<sub>2</sub> isotopic exchange reaction (IER) experiments over  
3 Ru/MgO and Li<sub>4</sub>RuH<sub>6</sub>/MgO samples, i.e., on the degassed Ru/MgO sample, the IER rates are  
4 comparable to the ammonia synthesis rates evidencing homolytic N<sub>2</sub> splitting on the Ru metal  
5 surface is the main course for N<sub>2</sub> activation. However, the Li<sub>4</sub>RuH<sub>6</sub>/MgO sample has negligible  
6 IER rates in the temperature range of 443 to 503 K, which is in clear contrast to its pronounced  
7 catalytic activity for ammonia synthesis (Fig. 3d and Supplementary Fig. 21). A non-dissociative  
8 pathway is thus expected to prevail over Li<sub>4</sub>RuH<sub>6</sub>.

9 Our theoretical study shows that the hydrogenation of the adsorbed N<sub>2</sub> can happen both from  
10 the gaseous dihydrogen and from the lattice H, where the latter is preferred due to its lower kinetic  
11 barrier. In the full path presented by Fig. 3a, all the hydrogenation steps of the activated dinitrogen  
12 to form NH<sub>3</sub> take place only by lattice Hs, evidencing the role of lattice H in transporting electron  
13 and proton. While the gaseous dihydrogen molecule adsorption replenishes lattice H deficiency of  
14 the surface during the process. Such a mechanistic feature can be at least partially supported by  
15 the H/D isotope experiments, i.e., the H-rich ammonia and its fragments with m/z = 17 and 16 first  
16 increase and then decrease (Fig. 3e) when feeding the Li<sub>4</sub>RuH<sub>6</sub> catalyst with N<sub>2</sub> and D<sub>2</sub>.

17 As shown in Fig. 3, the first hydrogenation of the adsorbed N<sub>2</sub> (**1-2**) happens from the intra-site  
18 H (H from [RuH<sub>6</sub>]-NN) and is endergonic by ca. 0.66 eV without kinetic barrier. The hydridic H  
19 is transferred to the polarized N-N antenna and undergoes reductive protonation forming activated  
20 [RuH<sub>5</sub>]-NHN species, where both N atoms gain electrons from the hydridic H and interact with  
21 neighboring Li (Li-N distance is 1.90 Å) (The Bader charge analyses are given in Supplementary  
22 Fig. 22). The second ([RuH<sub>5</sub>]-NHNH) and the third ([RuH<sub>5</sub>]-NHNH<sub>2</sub>) hydrogenation steps (**2-3**  
23 and **4-5**) occur by the reductive protonation of the lattice Hs transferred from the neighboring  
24 [RuH<sub>7</sub>] sites and assist by surface Li (Supplementary Fig. 23a). The N-N bond dissociates via a  
25 Li-assisted multi-step path with a kinetic barrier of 0.64 eV creating a [RuH<sub>5</sub>]-NH and a [RuH<sub>6</sub>]-  
26 NH<sub>2</sub> species (**5-6**) (Supplementary Fig. 23b). The first NH<sub>3</sub> ([RuH<sub>5</sub>]-NH<sub>3</sub>) formed from the intra-  
27 site H transfer (**6-7**) desorbs from the surface without kinetic barrier (**7-8**). The remaining [RuH<sub>5</sub>]-  
28 NH species then consumes two lattice Hs from two neighboring [RuH<sub>7</sub>] sites and forms [RuH<sub>5</sub>]-  
29 NH<sub>2</sub> (**8-9**) and the second NH<sub>3</sub> species (**9-10**), respectively (Supplementary Fig. 23c). The second  
30 NH<sub>3</sub> species leaves Ru and hangs loosely on the neighboring Li (as [Li]-NH<sub>3</sub>) and then desorbs  
31 from the surface (**10-11**). The surface is then replenished by the second and the third dihydrogen  
32 adsorption and restores the initial state (**11-12** and **12-0**).

33 It is important to note that every N<sub>x</sub>H<sub>y</sub> species formed as well as the transition state between  
34 every step during the process shows strong electrostatic interaction with the neighboring Li cations  
35 on the surface (Li-N distance is in-between 1.90-2.00 Å), i.e., Li cation stabilizes the N<sub>x</sub>H<sub>y</sub> species  
36 and helps reducing the kinetic barriers, which shares some common features with that of N-K  
37 interaction in molecular Fe and U nitride complexes during nitrogen reduction and  
38 functionalization, and that of Li-N interaction in the Li-mediated electrochemical ammonia  
39 synthesis<sup>37-39</sup>. Also noted is that the most stable intermediate predicted is the Li-stabilized [RuH<sub>5</sub>]-  
40 NH<sub>2</sub>, which correlates well with the DRIFT observation of a pair of broad N-H stretches centered  
41 at ca. 3300 and 3250 cm<sup>-1</sup> of the catalyst sample quenched from reaction (Fig. 3c) and the  
42 identification of NH<sub>2</sub>-containing clusters in the cluster reaction (Fig. 3b). This mechanism results  
43 in positive reaction orders with respect to H<sub>2</sub> and N<sub>2</sub> and negative order of NH<sub>3</sub>, agreeing well with  
44 our experimental findings and clearly distinguishing it from existing metallic ruthenium-based  
45 catalysts (Table 1).



## 1 **Conclusions**

2 The ternary ruthenium complex hydride may serve as the very first example of TM complex  
3 compound that can catalyze ammonia formation from dihydrogen and dinitrogen. The non-  
4 dissociative  $N_2$  reduction is realized effectively by the cooperation of multiple electron-rich  
5  $[RuH_{5/6/7}]$  sites, the involvement of lattice hydridic H as proton and electron carrier, and the role  
6 of alkali/alkaline earth metal cation in stabilizing  $N_xH_y$  intermediate species. The dynamic and  
7 synergistic engagement of all the active components of ternary hydride in the catalysis  
8 demonstrates the increased freedom and power in manipulating the energetics of the elementary  
9 steps and thus opens an avenue for the design and development of efficient catalyst tackling the  
10 conversion of kinetically stable molecules.

11

## 1 Methods

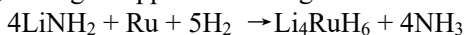
2 All the materials handlings were performed in a glove box filled with purified argon to keep a low water vapor  
3 concentration (< 0.1 ppm) and a low oxygen concentration (< 1 ppm). N<sub>2</sub> (99.999%), H<sub>2</sub> (99.9999%), D<sub>2</sub>  
4 (99.999%), Ar (99.999%), N<sub>2</sub>/H<sub>2</sub> mixture with different molar ratios (99.9999%) were purchased from Dalian  
5 Special Gases Co., LTD.

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

14  
15 **Preparation of ball milled catalyst samples.** Li<sub>4</sub>RuH<sub>6</sub> was ball milled in a H<sub>2</sub>-filled vessel on a Retsch planetary  
16 ball mill (PM 400, Germany) at 150 r.p.m for 3h, and was denoted as Li<sub>4</sub>RuH<sub>6</sub> (BM). Li<sub>4</sub>RuH<sub>6</sub>-BN (BM) or  
17 Li<sub>4</sub>RuH<sub>6</sub>-MgO (BM) was prepared via ball milling Li<sub>4</sub>RuH<sub>6</sub> and BN (Aladdin, 99.9% metals basis, 1~2 μm) or  
18 MgO powder under the same conditions as that of Li<sub>4</sub>RuH<sub>6</sub> (BM), in which the Ru content is ca. 8 wt %. The  
19 MgO sample has a high specific surface area of ca. 534 m<sup>2</sup> g<sup>-1</sup>, which was synthesized according to the literature  
20 report<sup>43</sup>. The crystalline sizes of Li<sub>4</sub>RuH<sub>6</sub>-BN (BM) and Li<sub>4</sub>RuH<sub>6</sub>-MgO (BM) were estimated to be ca. 20 and 9  
21 nm, respectively, by using the Scherrer equation based on the collected PXRD patterns.

22  
23 **Preparation of Ru/MgO catalyst.** Ru metal was deposited on the MgO support according to a urea-based  
24 decomposition precipitation (DP) method as reported in literature<sup>44-45</sup>. The sample was further reduced in pure  
25 H<sub>2</sub> at 673 K for 5 h and was denoted as the Ru/MgO. The Ru content of as-prepared Ru/MgO catalyst was  
26 determined to be 8.7 wt % by inductively coupled plasma mass spectrometry (ICP-AES, PerkinElmer ICP-AES  
27 7300DV). The average Ru particle size of as-prepared Ru/MgO is ca. 3.09 nm (Supplementary Fig. 7).

28  
29 **Preparation of Li<sub>4</sub>RuH<sub>6</sub>/MgO and Ba<sub>2</sub>RuH<sub>6</sub>/MgO catalysts.** Li<sub>4</sub>RuH<sub>6</sub>/MgO catalyst with a Ru loading of ca.  
30 8.0 wt % was prepared as follows. The reduced Ru/MgO was impregnated in a lithium-ammonia solution with  
31 a molar ratio of Li:Ru≈4:1, where Li metal (Macklin, 99.9% metals basis) can be easily converted to LiNH<sub>2</sub> in  
32 the presence of Ru. After evacuating the excess NH<sub>3</sub>, the obtained sample was subsequently treated under 1 bar  
33 of H<sub>2</sub> at 573 K until no ammonia is detectable by the conductivity meter (Mettler Toledo SevenMulti), thus  
34 enabling *in situ* formation of Li<sub>4</sub>RuH<sub>6</sub> on MgO support according to the following reaction:



36 The Ba<sub>2</sub>RuH<sub>6</sub>/MgO catalyst with a Ru content of 5.0 wt % was prepared in a similar way, except impregnating  
37 the Ru/MgO in a barium-ammonia solution.

38  
39 **Preparation of Li<sub>4</sub>RuH<sub>6</sub>/MgO-air and Ba<sub>2</sub>RuH<sub>6</sub>/MgO-air catalysts.** The obtained supported ternary Ru  
40 hydrides were exposed to air for 2 days for sufficient oxidation, then underwent *in situ* reduction by H<sub>2</sub>-N<sub>2</sub>  
41 before catalytic testing. The obtained samples were referred as Li<sub>4</sub>RuH<sub>6</sub>/MgO-air and Ba<sub>2</sub>RuH<sub>6</sub>/MgO-air,  
42 respectively.

43  
44 **Preparation of Li<sub>2</sub>O-Ru/MgO and Cs-Ru/MgO catalysts.** The Li<sub>2</sub>O-Ru/MgO and Cs-Ru/MgO catalysts were  
45 obtained by impregnating Ru/MgO with solutions of LiNO<sub>3</sub> (Kermel, ≥ 99.0%) and CsNO<sub>3</sub> (Guangfu, ≥ 99.0%)  
46 followed by H<sub>2</sub> reduction at 673 K for 5 h. The Li or Cs to Ru molar ratio is ca. 4:1 or 1:1, respectively. The Ru  
47 content of Cs-Ru/MgO catalyst was determined to be 7.3 wt %.

48  
49 **Catalytic reaction tests.** Ammonia synthesis was conducted in a stainless steel fixed-bed reactor with a quartz  
50 liner that operated with the supply of continuous-flow of extra pure N<sub>2</sub>-H<sub>2</sub> mixture gas (>99.9999%). Typically,  
51 30 mg of catalyst was loaded in the liner tube on a bed of quartz wool and subsequently heated at a ramping rate  
52 of 5 K min<sup>-1</sup> under the given pressure and flow rate. The ammonia produced was trapped in a diluted sulfuric

1 acid solution and the proton conductivity was recorded with time by a conductivity meter. The principle of the  
2  $\text{NH}_3$  quantification method has been described previously<sup>46</sup>. The activity data at each temperature was monitored  
3 when the catalytic performance reached a steady-state value. Blank test using the same setup did not give any  
4 measurable activity at temperatures below 673 K and 10 bar.  
5

6 **TEM and STEM-EDS measurement.** Transmission electron microscopy (TEM) images were recorded on a  
7 JEM-2100 microscope, operating at an accelerating voltage of 200 kV. More than 100 particles were measured  
8 from TEM images to determine the average particle size and particle size distributions. The compositions of the  
9 catalyst, including spectral imaging to produce elemental maps were captured using high angle annular dark  
10 field scanning transmission electron microscopy (HAADF-STEM, JEM-2100F) equipped with an energy  
11 dispersive X-ray spectroscopy (EDS) detector.  
12

13 **FTIR measurement.** Fourier transform infrared measurements were conducted on a Bruker Tensor II unit in  
14 the diffuse reflection (DRIFT) mode with a scan resolution of  $4\text{ cm}^{-1}$  and an accumulation of 32 scans each time.  
15

16  **$\text{N}_2$  physisorption.** The Brunauer-Emmet-Teller (BET) specific surface areas of the samples were determined  
17 from nitrogen adsorption-desorption isotherms measured at 77 K using an automatic gas adsorption instrument  
18 (QUADRASORB SI).  
19

20 **Powder X-ray diffraction (PXRD) measurement.** PXRD patterns were collected on a PANalytical X'pert  
21 diffractometer equipped with  $\text{Cu K}\alpha$  radiation (40 KV, 40 mA) for phase identification. The test samples were  
22 loaded in a homemade sample cell that was covered with KAPTON film to avoid air or moisture contamination.  
23

24 ***In situ* synchrotron radiation powder X-ray diffraction (SR-PXD) measurement.** *In situ* SR-PXD  
25 experiments were performed at the diffraction beamline P.02.1, DESY (Hamburg, Germany). The *in situ* cell  
26 and the procedure used were described elsewhere<sup>47</sup>. The wavelength was fixed at ca.  $0.207\text{ \AA}$  and a PerkinElmer  
27 XRD1621 plate image detector (2048\*2048 pixel, each of size  $200*200$  microns) was used to acquire the  
28 patterns, with a sample-to-detector distance of about 1400 mm. The sample was loaded in a sapphire capillary  
29 tube (0.8 mm ID) and placed in a home-made sample holder. The  $\text{Li}_4\text{RuH}_6$  sample was heated from 298 to 773  
30 K with a ramping rate of  $1\text{ K min}^{-1}$  in a stream of flow gas ( $10\text{ ml min}^{-1}$ ). The  $\text{Ba}_2\text{RuH}_6$  sample was heated from  
31 298 to 923 K with a ramping rate of  $6\text{ K min}^{-1}$  in a stream of flow gas ( $5\text{ ml min}^{-1}$ ). The 2D images were then  
32 integrated using FIT2D software.  
33

34 **X-ray absorption (XAS) spectroscopy.** XAS for acquiring X-ray absorption near-edge structure (XANES) at  
35 the Ru K-edge was performed at the BL14W1 beamline of Shanghai Synchrotron Radiation Facility (SSRF),  
36 China. A double Si(311) crystal monochromator was used for energy selection.  $\text{Li}_4\text{RuH}_6$  sample was sealed with  
37 KAPTON film to avoid air contamination before test. The spectra were recorded at room temperature under the  
38 transmission mode. The Athena software package was used for analysis of the data.  
39

40 **Temperature programmed techniques.** Temperature-programmed desorption (TPD) measurements were  
41 conducted in a quartz-lined stainless steel reactor and the exhaust gases were monitored with an on-line mass  
42 spectrometer (MS, Hiden HPR20). Samples (30 mg) were heated in a stream of Ar ( $30\text{ ml min}^{-1}$ ) from room  
43 temperature to desired temperatures at a ramping rate of  $5\text{ K min}^{-1}$ . Temperature-programmed reaction (TPR)  
44 with specific gas was performed with the same apparatus and similar procedures as used in TPD, except the  
45 change of carrier gas.  
46

47 **Pressure-composition-temperature (PCT) measurement.** PCT dehydrogenation experiments were carried out  
48 on a gas reaction controller (Advanced Materials Corporation, USA) loaded with 800 mg of  $\text{Li}_4\text{RuH}_6$  sample.  
49 Static P-C isotherms were determined at temperatures of 763 K, 773 K, 783 K and 793 K, respectively. The  
50 control precision of the sample temperature was  $\pm 1\text{ K}$ . The initial pressure in the sample chamber for hydrogen  
51 desorption was ca. 1 bar.  
52

1 **Monitoring of catalytic synthesis of NH<sub>3</sub> by vacuum ultraviolet (VUV)-lamp-based charge-transfer**  
2 **ionization time-of-flight mass spectroscopy (CTI-TOFMS).** Real-time monitoring of ammonia synthesis at  
3 low temperatures was realized by building an integrated apparatus that consists of the home-built NH<sub>3</sub> synthesis  
4 setup (described above) and the time-of-flight mass spectroscopy equipped with VUV-lamp-based CTI-TOFMS.  
5 Full details of the VUV-lamp-based CTI-TOFMS were described in previous reports<sup>27, 48</sup>. To calibrate the  
6 instrument response (i.e., peak area) with respect to analyte concentration, ammonia standard gas mixture with  
7 concentration of 100 ppmv in syngas (H<sub>2</sub>:N<sub>2</sub>=1:3) was diluted with NH<sub>3</sub>-free syngas (H<sub>2</sub>:N<sub>2</sub>=1:3) to a series of  
8 lower concentrations. Supplementary Fig. 13a shows the calibration curve of the NH<sub>3</sub><sup>+</sup> ions, and the dynamic  
9 range was obtained from 2 ppm to 100 ppm with a good linear correlation coefficient (R<sup>2</sup>=0.996). 200 mg of  
10 catalyst was loaded and tested under a flow of syngas (H<sub>2</sub>:N<sub>2</sub>=1:3, 36 ml min<sup>-1</sup>). The reaction temperature was  
11 varied from 398 K to 323 K and the pressure was kept at 1 bar. The signals of NH<sub>3</sub><sup>+</sup> (17 amu), H<sub>2</sub>O<sup>+</sup> (18 amu),  
12 H<sub>3</sub>O<sup>+</sup> (19 amu) and O<sub>2</sub><sup>+</sup> (32 amu) ions were recorded during the catalytic process. The background signal of  
13 NH<sub>3</sub><sup>+</sup> ion, determined in the same setup but without catalyst loading, was also detected as the baseline.

14  
15 **Gas-phase optical spectroscopy coupled with mass spectroscopy (GOS-MS) experiment.** GOS-MS  
16 experiment was carried out using a homemade instrument with a laser vaporization source and a dual-channel  
17 time-of-flight mass spectrometer (D-TOFMS). Details of the apparatus has been described elsewhere<sup>49</sup>, and  
18 only a brief outline of the experiment is given below. The species were generated via pulsed laser vaporization  
19 cluster source using the second harmonic of a Nd:YAG laser (Continuum Minilite II). The sample was ablated  
20 in the presence of a supersonic beam of carrier gas. The typical stagnation pressure of carrier gas was about 3-5  
21 bar. Under the efficient cooling by supersonic expansion of pulsed carrier gas, the clusters were cooled to ~200  
22 K in the vacuum chamber and reacted with the pulsed gaseous reactants. The cluster ions were analyzed by the  
23 TOF mass spectrometer. Bombarding the surface of Li<sub>4</sub>RuH<sub>6</sub> sample in pure He atmosphere gives a series of  
24 mass peaks. Taking account the contribution of various Ru isotopes<sup>50</sup>, the relatively intense peaks at m/z=134,  
25 136, 150, 152, 166 and 168 amu can be assigned to [Li<sub>4</sub>RuH<sub>4</sub>]<sup>-</sup>, [Li<sub>4</sub>RuH<sub>6</sub>]<sup>-</sup>, [Li<sub>4</sub>RuH<sub>4</sub>(LiH)<sub>2</sub>]<sup>-</sup>, [Li<sub>4</sub>RuH<sub>6</sub>(LiH)<sub>2</sub>]<sup>-</sup>  
26 , [Li<sub>4</sub>RuH<sub>4</sub>(LiH)<sub>4</sub>]<sup>-</sup> and [Li<sub>4</sub>RuH<sub>6</sub>(LiH)<sub>4</sub>]<sup>-</sup> clusters, respectively. A set of LiNH<sub>2</sub>-containing clusters were  
27 observed from the Li<sub>4</sub>RuH<sub>6</sub> sample bombarded in a mixture of N<sub>2</sub>-He (1:9), which are assigned to the  
28 [Li<sub>4</sub>RuH<sub>4</sub>(LiH)<sub>2</sub>LiNH<sub>2</sub>]<sup>-</sup> (m/z=173 amu) and [Li<sub>4</sub>RuH<sub>6</sub>(LiH)<sub>2</sub>LiNH<sub>2</sub>]<sup>-</sup> (m/z=175 amu) clusters, respectively.

29  
30 **N<sub>2</sub> isotope labeling experiment.** The identification and quantification of small amount of produced NH<sub>3</sub> at  
31 lower temperatures should be careful<sup>51</sup>. To verify the origin of NH<sub>3</sub> from N<sub>2</sub> at lower temperatures, isotopic  
32 labeling experiment was carried out using a mixture of <sup>15</sup>N<sub>2</sub> (≥98%, Cambridge Isotope Laboratories, Inc.) and  
33 H<sub>2</sub> as the feeding gas (H<sub>2</sub>:<sup>15</sup>N<sub>2</sub>=2:3). We employed <sup>1</sup>H NMR to measure ammonia production rates from <sup>14</sup>N<sub>2</sub>-  
34 H<sub>2</sub> and <sup>15</sup>N<sub>2</sub>-H<sub>2</sub> following the procedure described in literature<sup>52-53</sup>, where <sup>14</sup>NH<sub>4</sub><sup>+</sup> and <sup>15</sup>NH<sub>4</sub><sup>+</sup> can be  
35 distinguished by the <sup>1</sup>H spectra in which coupling to <sup>14</sup>N is a triplet and coupling to <sup>15</sup>N is a doublet. The <sup>15</sup>NH<sub>3</sub>  
36 or <sup>14</sup>NH<sub>3</sub> produced was trapped in a diluted sulfuric acid solution (pH≈3) and quantified by using <sup>1</sup>H NMR  
37 spectroscopy. For the NMR studies, the pH of the solutions to be tested was adjusted to 2 using concentrated  
38 hydrochloric acid aqueous solution. 5 vol% DMSO-d<sub>6</sub> (99.9 atom % D, 0.03% (v/v) TMS) was added for  
39 deuterium locking and referencing. All NMR experiments were performed at 298 K on a Bruker Advance III  
40 spectrometer operating at a <sup>1</sup>H frequency of 500 MHz. A total of 1000 transient scans were accumulated for each  
41 sample. Calibration samples were prepared with varying concentrations of <sup>14</sup>NH<sub>4</sub>Cl (Aladdin, 99.999%) and  
42 <sup>15</sup>NH<sub>4</sub>Cl (Aladdin, 99 atom%).

43  
44 **H/D isotope experiment.** Ammonia synthesis from N<sub>2</sub> and D<sub>2</sub> over the Li<sub>4</sub>RuH<sub>6</sub> sample was conducted using a  
45 quartz-lined stainless steel reactor connected to a home-made device that can switch instantly between two gas  
46 streams under the same temperature and pressure. Prior to isotopic reaction, the sample (ca. 30 mg) was heated  
47 to 598 K and kept for a while under atmospheric Ar flow (30 ml min<sup>-1</sup>). The mixture of N<sub>2</sub>-D<sub>2</sub> (1:3, 30 ml min<sup>-1</sup>)  
48 was subsequently switched to the sample and the effluent gas was analyzed with a mass spectrometer (MS,  
49 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  
50 the reaction. ND<sub>3</sub> (m/z=20 amu) was hardly differentiated due to an overlap with the fragment of Ar (m/z=20  
51 amu).

1 **N<sub>2</sub> isotopic exchange experiment.** N<sub>2</sub> isotopic exchange reactions were performed using a home-made stainless  
2 steel reactor connected with vacuum-pumping system. The sample was loaded into the reactor in an Ar-filled  
3 glovebox and the loading amount is 30 mg for Ru/MgO or Li<sub>4</sub>RuH<sub>6</sub>/MgO and 225 mg for the bulk-phase  
4 Li<sub>4</sub>RuH<sub>6</sub>. Prior to the exchange reactions, the Ru/MgO sample was degassed at 673 K and held for 2 h under  
5 vacuum. Li<sub>4</sub>RuH<sub>6</sub>/MgO and bulk-phase Li<sub>4</sub>RuH<sub>6</sub> samples were treated in vacuum at 473K. A mixture of <sup>15</sup>N<sub>2</sub>  
6 and <sup>14</sup>N<sub>2</sub> (<sup>15</sup>N<sub>2</sub>:<sup>14</sup>N<sub>2</sub>=1:4.4, total pressure: ca. 0.55 bar) was then introduced to the samples at elevated temperature  
7 for the exchange reaction. The m/z=28, 29, 30 masses were monitored as a function of time to follow the reaction  
8 by using a mass spectrometer. An example of data processing at 473 K was shown in Supplementary Fig. 21.  
9

10 **Steady state isotopic transient kinetic analysis (SSITKA) experiment.** SSITKA was performed by switching  
11 between two streams of 1% Ar in <sup>14</sup>N<sub>2</sub>-H<sub>2</sub> (<sup>14</sup>N<sub>2</sub>:H<sub>2</sub>=1:3) (Argon was used as an inert tracer and internal standard)  
12 and <sup>15</sup>N<sub>2</sub>-H<sub>2</sub> (<sup>15</sup>N<sub>2</sub>:H<sub>2</sub>=1:3). The system and principle of SSITKA experiment for determining TOF have been  
13 described previously<sup>54-55</sup>. Considering the characteristic holdup of ammonia in the reactor during gas switches,  
14 blank transient was also collected by switching from a stream of NH<sub>3</sub>-diluted syngas (N<sub>2</sub>:H<sub>2</sub>=3:1) to a stream of  
15 NH<sub>3</sub>-free syngas under similar conditions without catalyst present in order to ensure a correct estimation of  
16 transient responses. The signals of <sup>14</sup>NH<sub>3</sub><sup>+</sup> (m/z=16 and 17 amu), <sup>15</sup>NH<sub>3</sub><sup>+</sup> (m/z=18 amu), Ar<sup>+</sup> (m/z=40 amu) ions  
17 were recorded during the process. The TOF(SSITKA) was calculated by using <sup>15</sup>NH<sub>3</sub> (m/z=18 amu) signal. The  
18 conversion was kept below 30% of the equilibrium conversion to limit the scrambling of <sup>14</sup>N<sub>2</sub> and <sup>15</sup>N<sub>2</sub>.  
19

20 **Kinetic studies.** The measurements of reaction order of N<sub>2</sub> or H<sub>2</sub> were carried out with a flow of mixed gas (N<sub>2</sub>,  
21 H<sub>2</sub> and Ar) under conditions (573 K, 1 bar, WHSV=60000 ml g<sup>-1</sup> h<sup>-1</sup>), where the effluent NH<sub>3</sub> concentration was  
22 kept constant. Our measurement conditions were far from equilibrium considering that the thermodynamic limit  
23 is ca. 2.1% under these conditions. The loading amount is 30 mg for Li<sub>4</sub>RuH<sub>6</sub>/MgO, Ba<sub>2</sub>RuH<sub>6</sub>/MgO and Cs-  
24 Ru/MgO, and 50 mg for Ru/MgO. The gas compositions of N<sub>2</sub>:H<sub>2</sub>:Ar were 5:50:45, 15:50:35, 25:50:25,  
25 35:50:15, 45:50:5 for determining the N<sub>2</sub> order, and 20:40:40, 20:50:30, 20:60:20, 20:70:10, 20:80 for  
26 determining the H<sub>2</sub> order, respectively. The NH<sub>3</sub> order was determined by changing the flow rate of syngas while  
27 keeping a constant N<sub>2</sub> to H<sub>2</sub> partial pressure. Apparent activation energies were measured under atmospheric  
28 syngas (H<sub>2</sub>:N<sub>2</sub>=3) with a flow rate of 30 ml min<sup>-1</sup>. The temperature range is 523-598 K for Li<sub>4</sub>RuH<sub>6</sub>/MgO (30  
29 mg), 523-573 K for Ba<sub>2</sub>RuH<sub>6</sub>/MgO (30 mg), 573-648 K for Ru/MgO (30 mg) and 573-623 K for Cs-Ru/MgO  
30 (30 mg), respectively.  
31

32 **Theoretical calculations.** For all theoretical calculations in this report we used density functional theory (DFT)  
33 with generalized gradient approximation (GGA) for the exchange-correlation potential, a plane-wave basis set  
34 and the projector augmented wave (PAW) method<sup>56-57</sup> as implemented in the Vienna ab-initio simulation  
35 package (VASP)<sup>58</sup>. In this study, we set a 500 eV energy cut-off for the plane-wave basis. The free energies  
36 were calculated with ideal gas limit approximation<sup>59</sup> and harmonic limit/hindered harmonic limit approximation  
37<sup>60-62</sup> for the gaseous molecules and for the adsorbates respectively. For simulating hydrogen gas in vacuum, we  
38 used a negligible partial pressure of 10<sup>-9</sup> Pa. The kinetic pathways and their corresponding barriers presented  
39 here were determined by the nudge elastic band method (NEB)<sup>63</sup> implemented in VASP. To study the Li<sub>4</sub>RuH<sub>6</sub>  
40 surface, we created slabs containing four layers of the material in the (110) direction (with regards to the  
41 primitive Li<sub>4</sub>RuH<sub>6</sub> cell) and with six Ru-sites on the surface. We imposed 18 Å vacuum above the top layer of  
42 the slabs to avoid the interaction between the periodic images. During every simulation, the ions in the bottom  
43 two layers of these slabs remained fixed.

## 44 **Data availability**

45 All the data supporting the findings of this study are available within the paper and its Supplementary  
46 Information files. The datasets generated during and/or analyzed during the current study are available from the  
47 corresponding author on reasonable request.



## Code availability

All DFT calculations have been performed with the commercial Vienna ab-initio simulation package, VASP software<sup>58</sup> through the open source python library Atomistic Simulation Environment, ASE (<https://wiki.fysik.dtu.dk/ase/>). No new codebase was developed in this project.

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## Author contributions

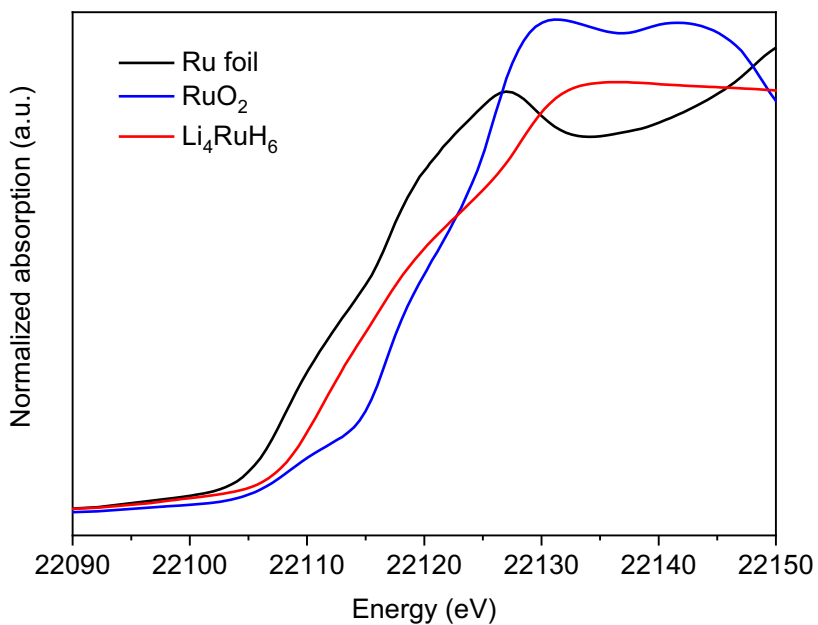
P.C. conceived the idea. P.C. and T.V. supervised the research and wrote the paper. Q.W. conducted most of the experimental work and prepared SI. J.P. conducted DFT calculations and co-prepared SI. J.G. supervised the experimental work. H.H. supervised the theory work. H.X. and L.J. for GOS-MS. L.H.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

## Competing interests

Authors declare no competing interests.



1 **Supplementary information**

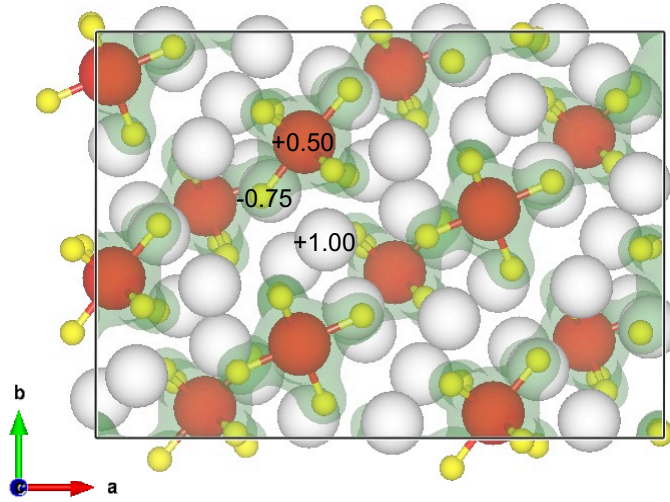


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3 **Supplementary Fig. 1. Normalized XANES spectra at the Ru K-edge for Li<sub>4</sub>RuH<sub>6</sub>, Ru foil**  
4 **and RuO<sub>2</sub>.** The adsorption edge energy of Li<sub>4</sub>RuH<sub>6</sub> is in-between that of Ru and RuO<sub>2</sub>, which  
5 reveals that Ru in Li<sub>4</sub>RuH<sub>6</sub> is positively charged.

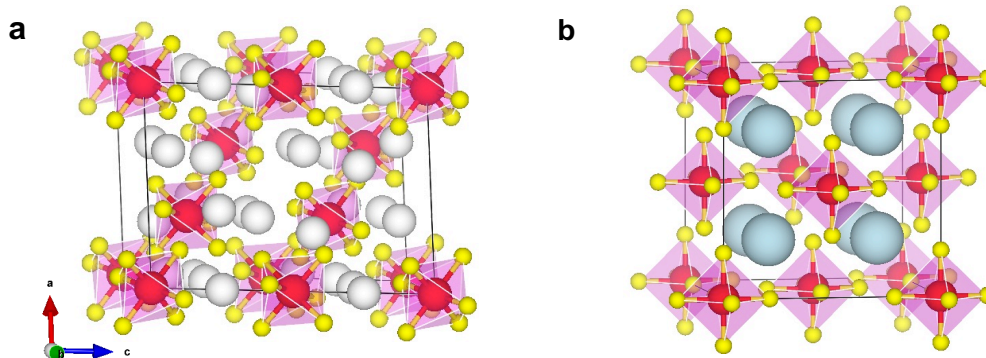
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**Supplementary Fig. 2. Electronic properties of stoichiometric Li<sub>4</sub>RuH<sub>6</sub> surface.** The charge density plot of Li<sub>4</sub>RuH<sub>6</sub> surface with Bader charge analyses on Ru (red), Li (white) and H (yellow).



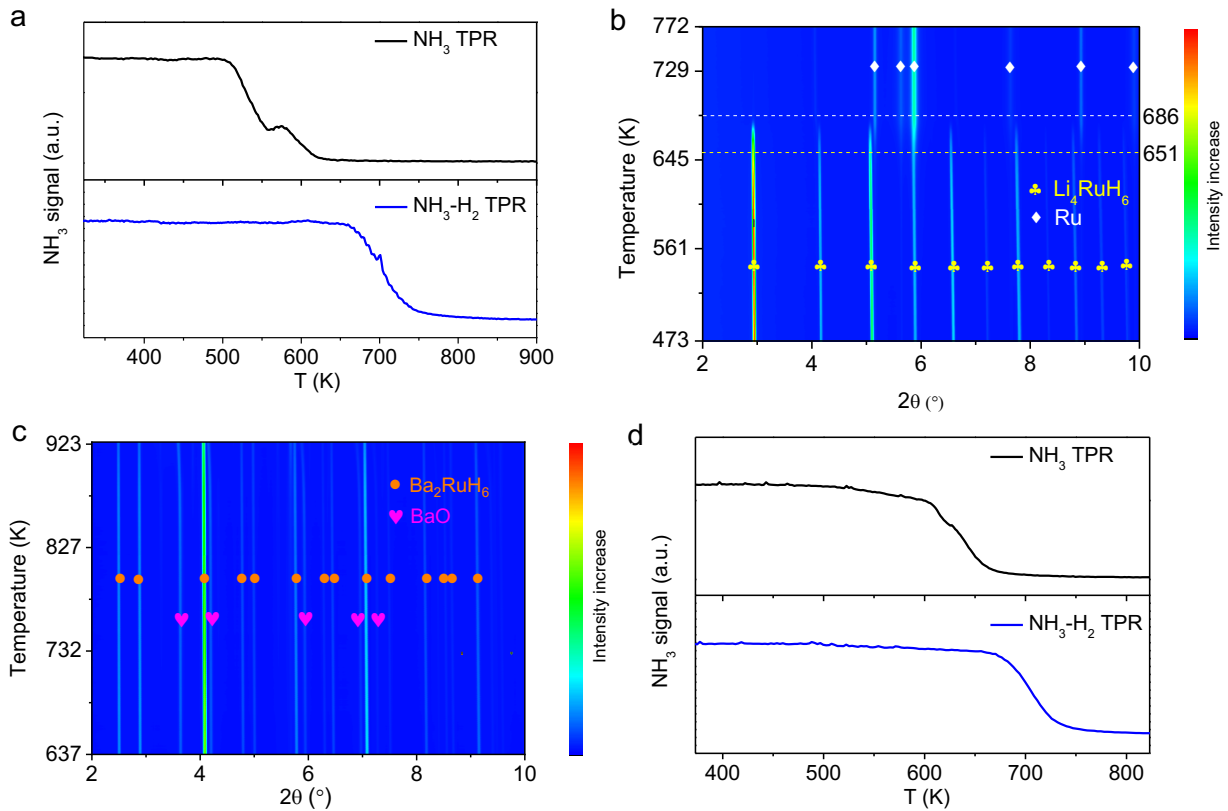
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(a) $\text{Li}_4\text{RuH}_6$		Lattice parameters					Bond distance ( $\text{\AA}$ )		
		a( $\text{\AA}$ )	b( $\text{\AA}$ )	c( $\text{\AA}$ )	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$	$d_{\text{Ru-H}}$	$d_{\text{Ru-Li}}$
Theory (This work)		8.279	8.279	10.169	90	90	120	1.725	2.542
Experiment <sup>1-2</sup>		8.169	8.169	10.025	90	90	120	1.74	
(b) $\text{Ba}_2\text{RuH}_6$		Lattice parameters					Bond distance ( $\text{\AA}$ )		
		a( $\text{\AA}$ )	b( $\text{\AA}$ )	c( $\text{\AA}$ )	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$	$d_{\text{Ru-H}}$	$d_{\text{Ru-Ba}}$
Theory	This work	8.083	8.083	8.083	90	90	90	1.74	3.51
	Refs.	8.052 <sup>3</sup> , 8.092 <sup>4</sup>	8.052 <sup>3</sup> , 8.092 <sup>4</sup>	8.052 <sup>3</sup> , 8.092 <sup>4</sup>	90 <sup>3-4</sup>	90 <sup>3-4</sup>	90 <sup>3-4</sup>	1.74 <sup>3</sup>	3.49 <sup>3</sup>
Experiment <sup>5</sup>		8.028	8.028	8.028	90	90	90		

2

3 **Supplementary Fig. 3. The crystal structures and related parameters of  $\text{Li}_4\text{RuH}_6$  (a) and**  
 4  **$\text{Ba}_2\text{RuH}_6$  (b).** The Ru, Li, Ba and H atoms are presented by red, white, steel grey and yellow  
 5 balls.  
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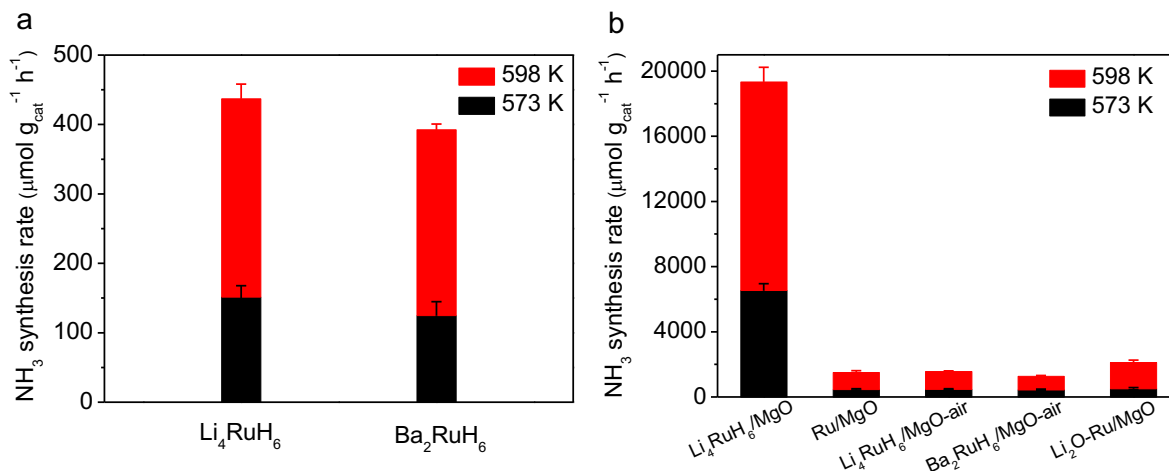
**Supplementary Fig. 4. The stability of bulk  $\text{Li}_4\text{RuH}_6$  and  $\text{Ba}_2\text{RuH}_6$  under different conditions.** **a**, TPR profile of  $\text{Li}_4\text{RuH}_6$  in a mixture gas of  $\text{NH}_3\text{-Ar}$  ( $\text{NH}_3\text{:Ar}=0.5\text{:99.5}$ ) and a mixture gas of  $\text{NH}_3\text{-H}_2\text{-Ar}$  ( $\text{NH}_3\text{:H}_2\text{:Ar}=0.5\text{:75:24.5}$ ). **b**, *In situ* SR-PXD characterization of  $\text{Li}_4\text{RuH}_6$  sample under atmospheric  $\text{N}_2$  and elevated temperatures (from 473 K to 773 K). **c**, *In situ* SR-PXD characterization of  $\text{Ba}_2\text{RuH}_6$  sample under atmospheric  $\text{N}_2\text{-3H}_2$  mixture and elevated temperatures (from 637 K to 923 K). **d**, TPR profile of  $\text{Ba}_2\text{RuH}_6$  in a mixture gas of  $\text{NH}_3\text{-Ar}$  ( $\text{NH}_3\text{:Ar}=0.5\text{:99.5}$ ) and a mixture gas of  $\text{NH}_3\text{-H}_2\text{-Ar}$  ( $\text{NH}_3\text{:H}_2\text{:Ar}=0.5\text{:75:24.5}$ ).

9

The above results show that the  $\text{Li}_4\text{RuH}_6$  phase is stable up to ca. 651 K under  $\text{N}_2$  atmosphere. While upon co-feeding  $\text{H}_2$ , it survives until 738 K (Fig. 1e).  $\text{Li}_4\text{RuH}_6$  is also resistant to diluted  $\text{NH}_3$  at temperature up to 500 K. While upon co-feeding with  $\text{H}_2$ , the temperature pulls ahead to 673 K.  $\text{Ba}_2\text{RuH}_6$  phase is stable up to 923 K under atmospheric  $\text{N}_2\text{-3H}_2$  mixture.  $\text{Ba}_2\text{RuH}_6$  is also resistant to diluted  $\text{NH}_3$  at temperatures up to 550 K. While upon co-feeding with  $\text{H}_2$ , the temperature pulls ahead to 673 K.

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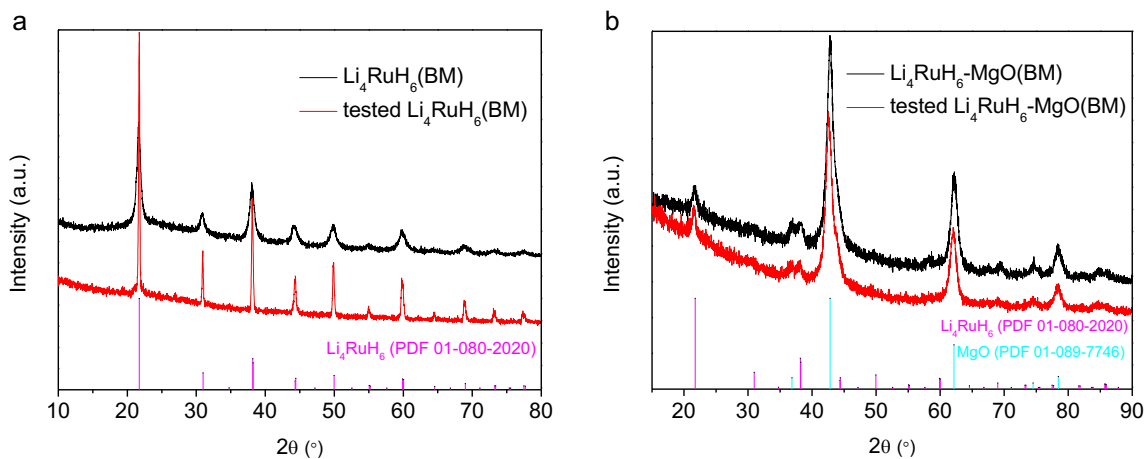
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2 **Supplementary Fig. 5. NH<sub>3</sub> synthesis rates at 573 and 598 K. a,** bulk Li<sub>4</sub>RuH<sub>6</sub> and Ba<sub>2</sub>RuH<sub>6</sub>  
 3 catalysts. **b,** Li<sub>4</sub>RuH<sub>6</sub>/MgO, Ru/MgO, Li<sub>4</sub>RuH<sub>6</sub>/MgO-air, Ba<sub>2</sub>RuH<sub>6</sub>/MgO-air and Li<sub>2</sub>O-Ru/MgO  
 4 catalysts (Reaction conditions: catalyst loading 30 mg, H<sub>2</sub>:N<sub>2</sub>=3:1, flow rate 30 ml min<sup>-1</sup>, and 1  
 5 bar).

6

7 After exposed to air, the hydrides were oxidized and deactivated. The activities of  
 8 Li<sub>4</sub>RuH<sub>6</sub>/MgO-air and Ba<sub>2</sub>RuH<sub>6</sub>/MgO-air samples are thus much lower and are similar to that of  
 9 Ru/MgO.

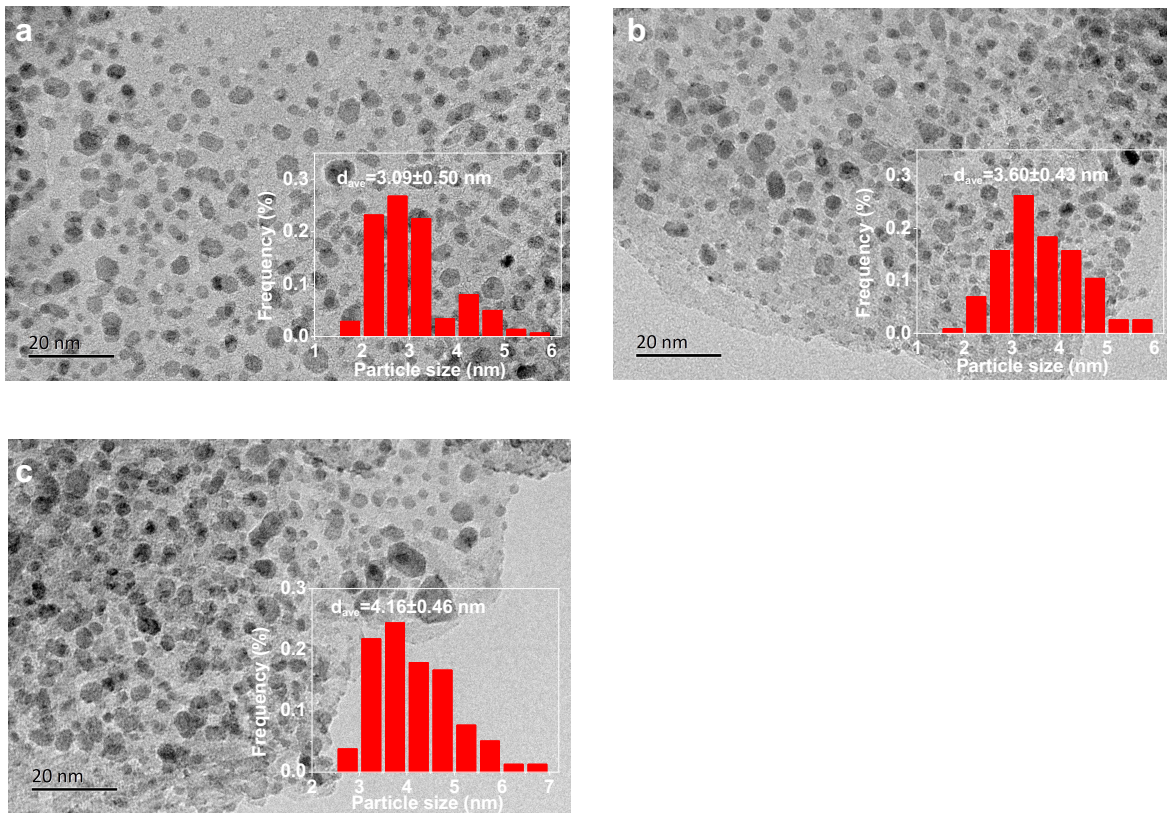
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2 **Supplementary Fig. 6. XRD patterns of ball-milled  $\text{Li}_4\text{RuH}_6$ -based catalysts before (black**  
 3 **curve) and after (red curve) activity test. a,  $\text{Li}_4\text{RuH}_6(\text{BM})$  catalyst. b,  $\text{Li}_4\text{RuH}_6\text{-MgO}(\text{BM})$**   
 4 **catalyst. Reaction conditions:  $\text{H}_2:\text{N}_2=3:1$ , 10 bar, 573 K.**

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**Supplementary Fig. 7. TEM observations. a, Ru/MgO. b,  $Li_4RuH_6/MgO$ . c,  $Ba_2RuH_6/MgO$ .** The inset picture of each image shows the corresponding particle size distribution. The number of particles for each image surveyed was more than 100.

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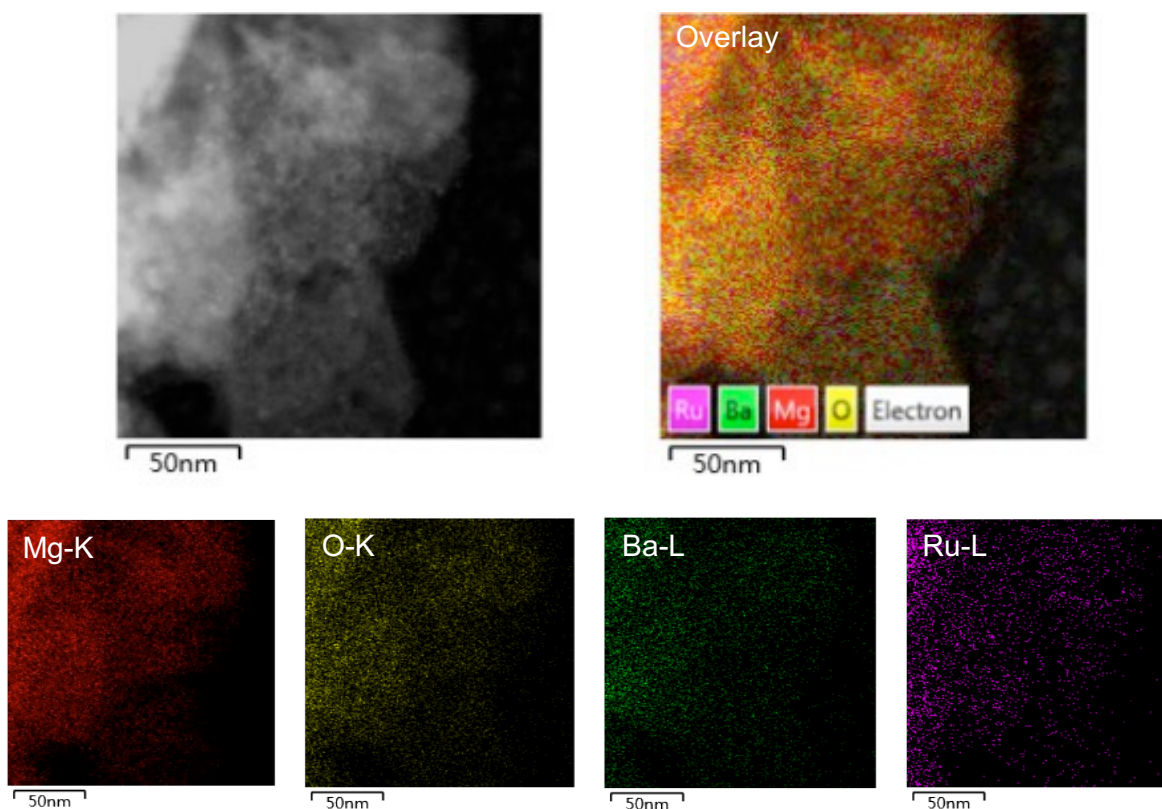
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From the results of particle size distribution analyses, we can see that, after introducing Li and Ba to the parent Ru/MgO catalyst, there is a certain increase in the size of dark particles.

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**Supplementary Fig. 8. HAADF-STEM characterizations of the  $\text{Ba}_2\text{RuH}_6/\text{MgO}$  sample.**

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STEM-EDS maps of Mg-K, O-K, Ba-L and Ru-L, and overlaid Mg, O, Ba and Ru are shown.

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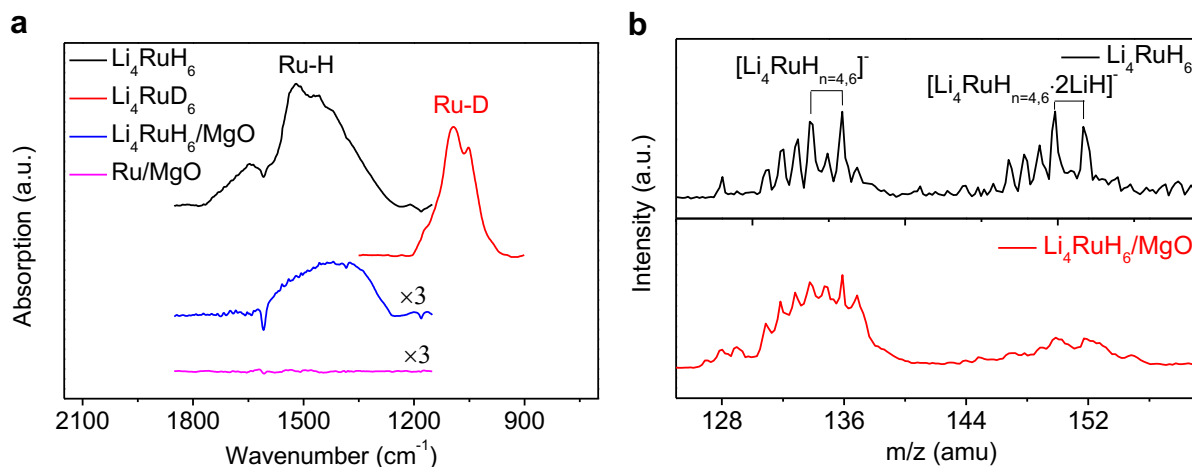
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From the mapping results, we can see that Ba and Ru are in proximity and dispersed evenly over the MgO support.  $\text{Li}_4\text{RuH}_6/\text{MgO}$  sample was not characterized because Li is out of the analysis scope of EDS.

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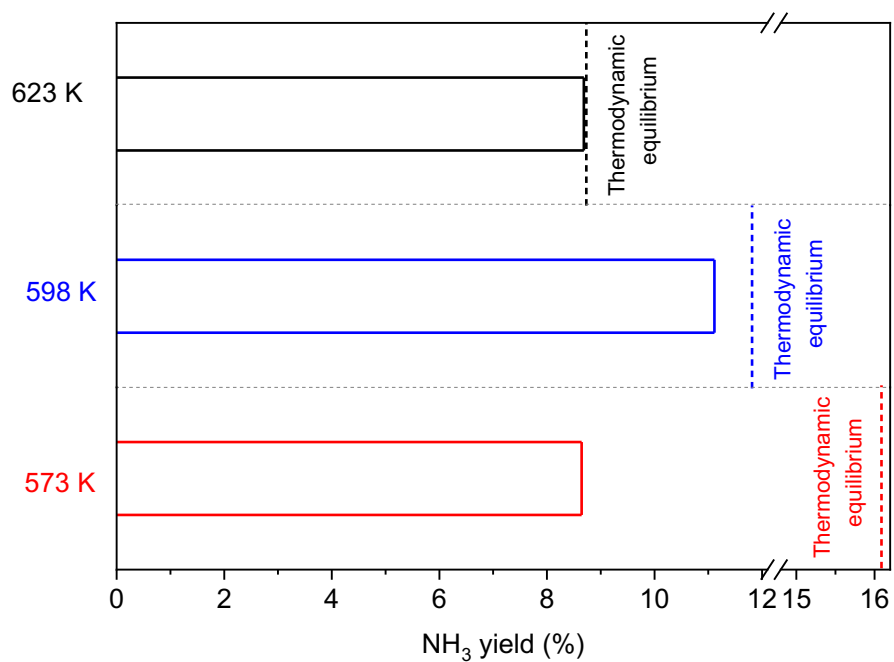
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2 **Supplementary Fig. 9. Characterization of the bulk and supported ternary hydride**  
 3 **catalysts. a,** DRIFT spectra of the as-prepared Li<sub>4</sub>RuH(D)<sub>6</sub>, Li<sub>4</sub>RuH<sub>6</sub>/MgO and Ru/MgO  
 4 catalysts. **b,** Mass spectra of the species produced by pulsed laser vaporization of the Li<sub>4</sub>RuH<sub>6</sub>  
 5 and Li<sub>4</sub>RuH<sub>6</sub>/MgO targets in the presence of a He carrier gas.

6 Li<sub>4</sub>RuH<sub>6</sub> surface has Ru-H stretching vibration in the range of 1200 to 1800 cm<sup>-1</sup>, which is  
 7 confirmed by Ru-D stretch in the deuterated sample. The Li<sub>4</sub>RuH<sub>6</sub>/MgO sample has a similar  
 8 Ru-H stretching range as the bulk sample but somehow with red shift, which might be due to the  
 9 elongated Ru-H bond after the particle size reduction to nanoscale. While for the reference  
 10 sample Ru/MgO, there was no infrared absorption peak in the range of 1800-1200 cm<sup>-1</sup>. The  
 11 mass spectrum of Li<sub>4</sub>RuH<sub>6</sub>/MgO is similar to that of bulk phase Li<sub>4</sub>RuH<sub>6</sub>. These  
 12 characterizations show that the supported catalyst resembles essentially to the bulk-phase  
 13 Li<sub>4</sub>RuH<sub>6</sub>.

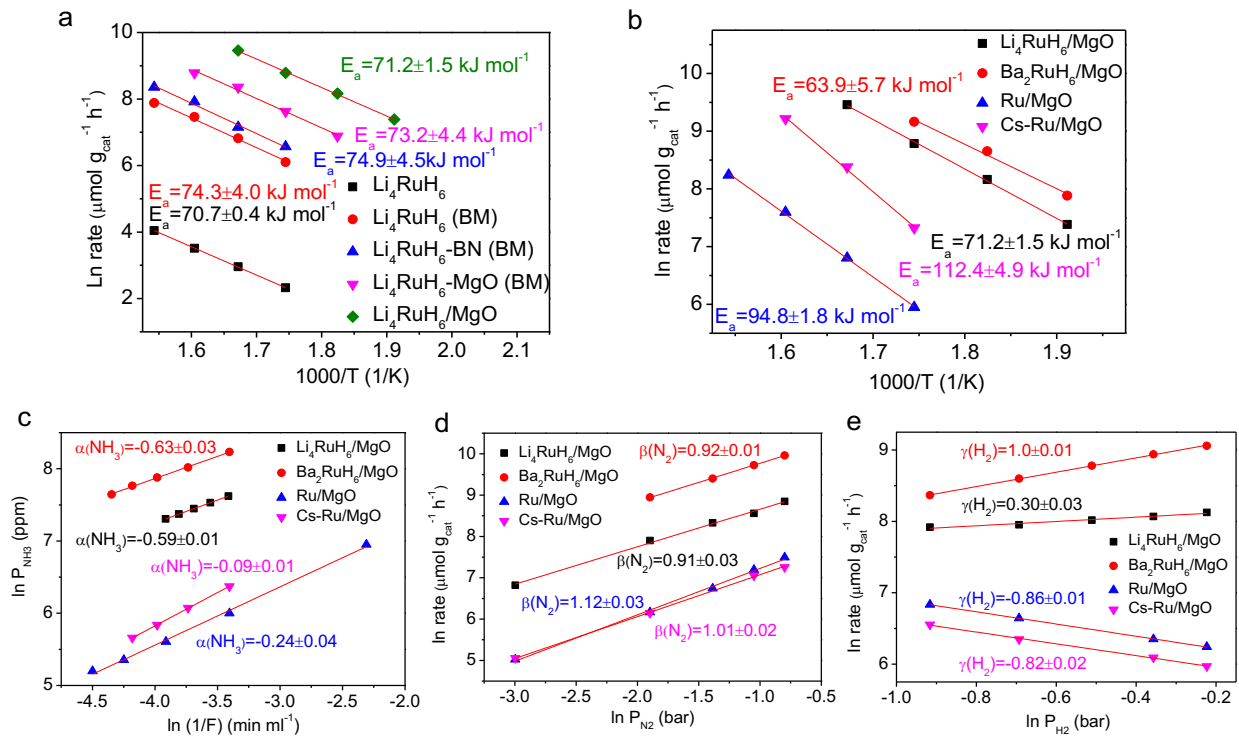
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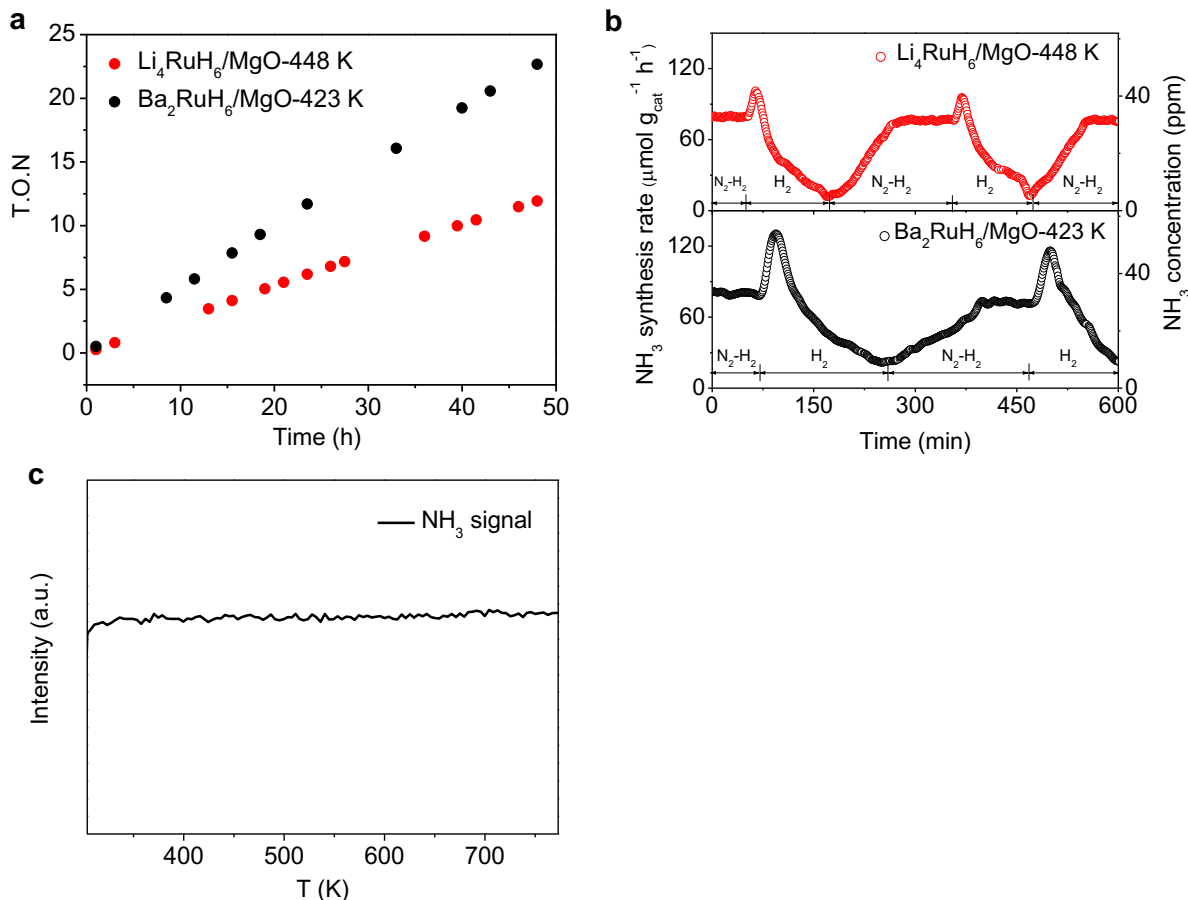
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2 **Supplementary Fig. 10. Temperature dependence of NH<sub>3</sub> yield of Ba<sub>2</sub>RuH<sub>6</sub>/MgO catalyst at**  
 3 **1 MPa.** (Reaction conditions: H<sub>2</sub>:N<sub>2</sub>=2:3, WHSV=7500 ml g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>)



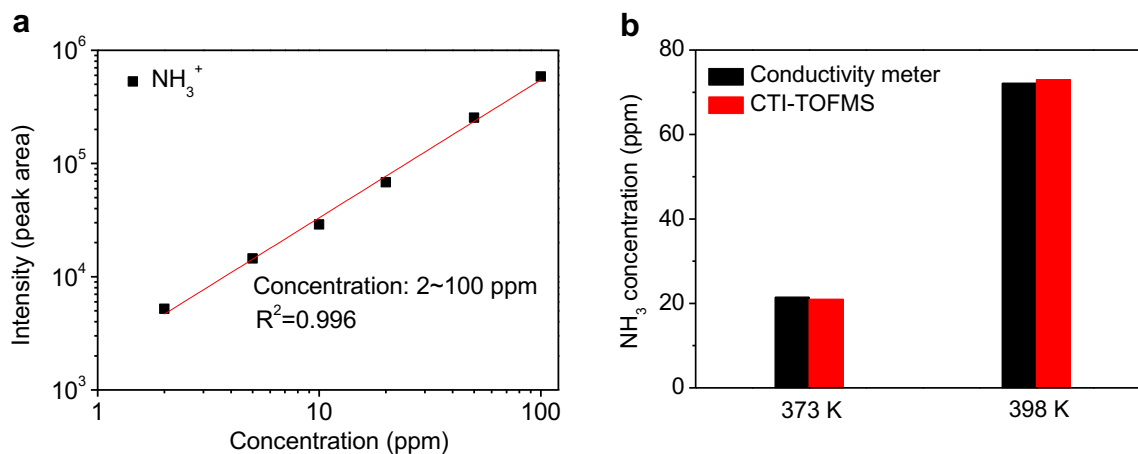
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2 **Supplementary Fig. 11. Measurements of kinetic parameters.** **a** and **b** Arrhenius plots of the  
 3  $\text{Li}_4\text{RuH}_6$ , ball-milled  $\text{Li}_4\text{RuH}_6$  ( $\text{Li}_4\text{RuH}_6$  (BM)), ball-milled mixture of  $\text{Li}_4\text{RuH}_6$  and BN  
 4 ( $\text{Li}_4\text{RuH}_6$ -BN-(BM)), ball-milled mixture of  $\text{Li}_4\text{RuH}_6$  and MgO ( $\text{Li}_4\text{RuH}_6$ -MgO-(BM)),  
 5  $\text{Li}_4\text{RuH}_6/\text{MgO}$ ,  $\text{Ba}_2\text{RuH}_6/\text{MgO}$ , Ru/MgO and Cs-Ru/MgO catalysts. **c** to **e** Dependence of  
 6 ammonia synthesis rates on the partial pressures of  $\text{NH}_3$ ,  $\text{N}_2$  and  $\text{H}_2$ , respectively, under a total  
 7 pressure of 1 bar at 573 K over  $\text{Li}_4\text{RuH}_6/\text{MgO}$ ,  $\text{Ba}_2\text{RuH}_6/\text{MgO}$ , Ru/MgO and Cs-Ru/MgO  
 8 catalysts.



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**Supplementary Fig. 12. Low-temperature catalytic activity and stability.** **a**, Time dependence of NH<sub>3</sub> synthesis TON (based on the amount of surface Ru estimated from the particle size observed by TEM) over Li<sub>4</sub>RuH<sub>6</sub>/MgO and Ba<sub>2</sub>RuH<sub>6</sub>/MgO catalysts at 448 K and 423 K, respectively (Reaction conditions: catalyst loading 30 mg, H<sub>2</sub>:N<sub>2</sub>=2:3, flow rate 30 ml min<sup>-1</sup>, and 1 bar). These data evidence the catalytic formation of NH<sub>3</sub>. **b**, Time course of ammonia synthesis rate of Li<sub>4</sub>RuH<sub>6</sub>/MgO at 448 K and Ba<sub>2</sub>RuH<sub>6</sub>/MgO at 423 K under an alternative feeding of N<sub>2</sub>-H<sub>2</sub> (H<sub>2</sub>:N<sub>2</sub>=2:3) and pure H<sub>2</sub> streams (Reaction conditions: catalyst loading 30 mg, flow rate 30 ml min<sup>-1</sup>, and 1 bar). Upon switching from N<sub>2</sub>-H<sub>2</sub> steam to pure H<sub>2</sub> steam, there is a rapid increase in the NH<sub>3</sub> production rate because the sudden increase of H<sub>2</sub> content (from 40% to 100%) speeds up the release rate of NH<sub>3</sub>. **c**, MS spectrum of the temperature-programmed reaction of N<sub>2</sub> with Li<sub>4</sub>RuH<sub>6</sub>/MgO. No ammonia was detectable showing lattice H cannot work alone for ammonia formation.



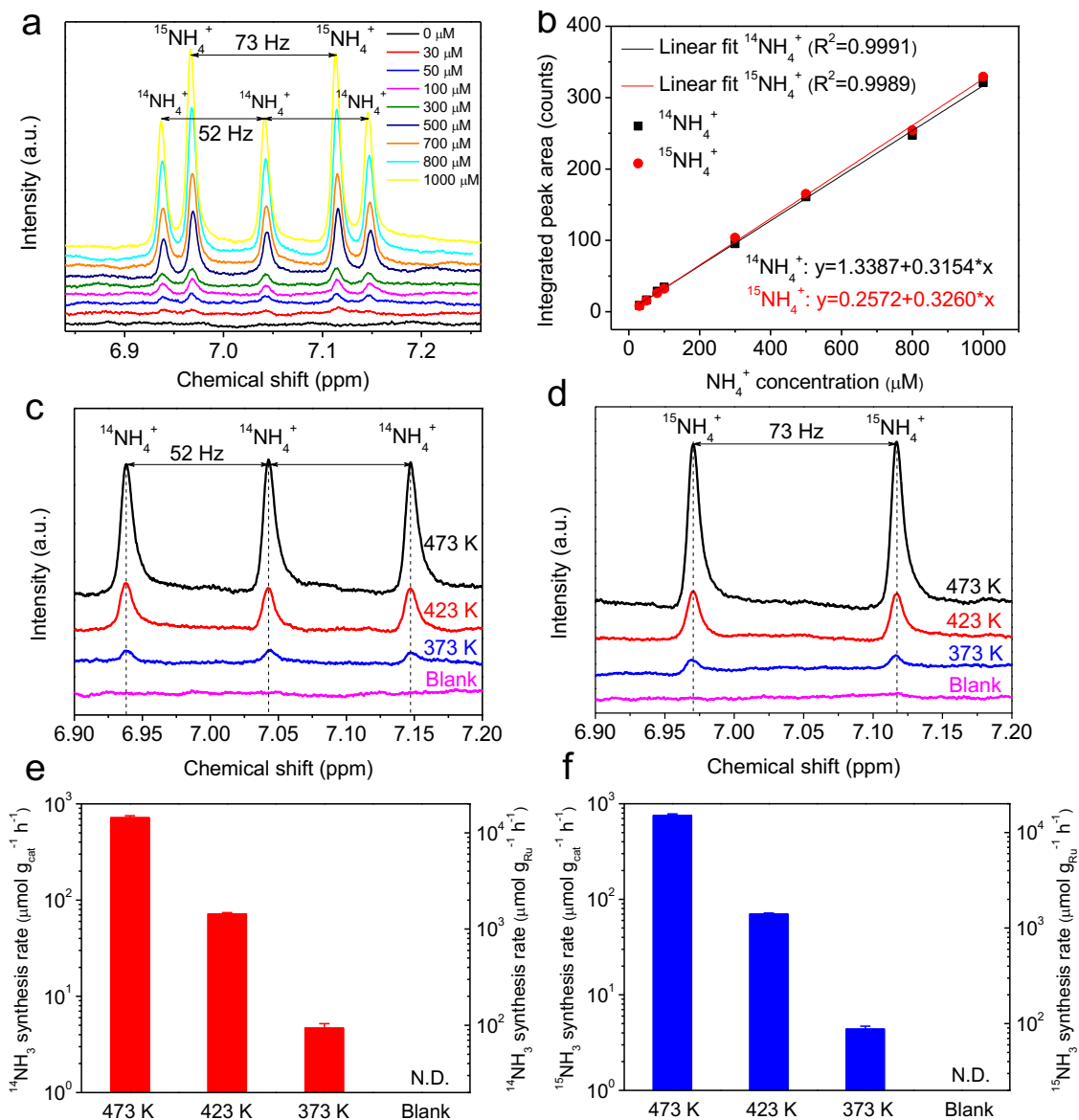
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2 **Supplementary Fig. 13. Low-temperature catalytic performance characterized by CTI-**  
 3 **TOFMS. a**, Linear calibration curve for  $\text{NH}_3^+$  in the concentration range of 2 to 100 ppm of the  
 4 CTI-TOFMS. **b**, Activities of  $\text{Ba}_2\text{RuH}_6/\text{MgO}$  catalyst measured by conductivity meter and CTI-  
 5 TOFMS at 373 and 398 K, respectively (Reaction conditions: catalyst loading 200 mg,  
 6  $\text{H}_2:\text{N}_2=1:3$ , flow rate  $36 \text{ ml min}^{-1}$ , and 1 bar).

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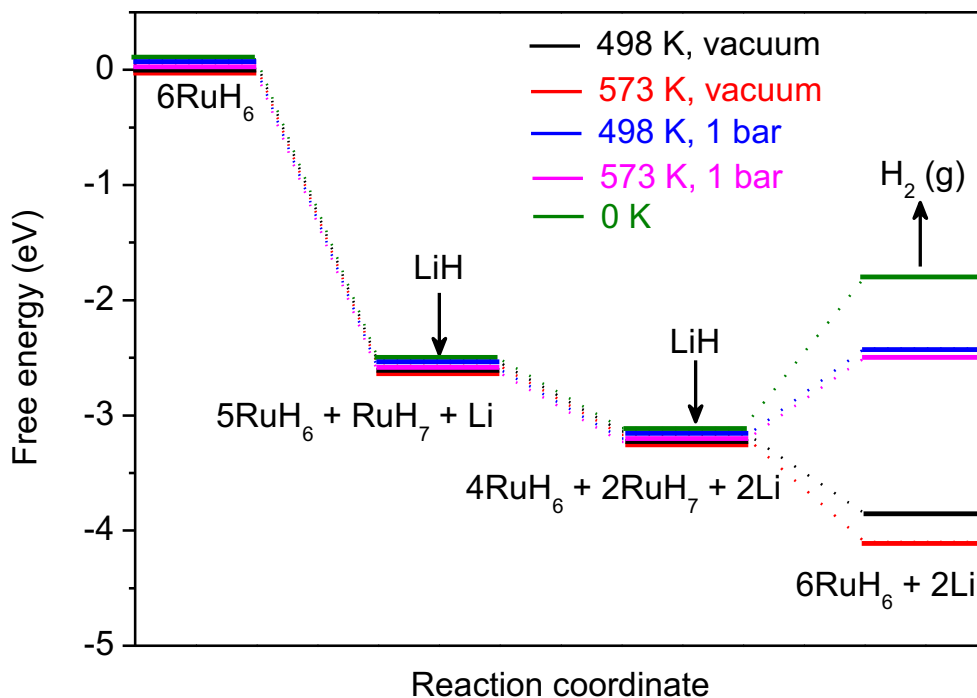
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3 **Supplementary Fig. 14. Quantification of low-temperature  $\text{NH}_3$  synthesis rates using  $^1\text{H}$ -**  
 4 **NMR spectroscopy. a,**  $^1\text{H}$  NMR spectra of a series of  $^{14}\text{NH}_4\text{Cl}$  and  $^{15}\text{NH}_4\text{Cl}$  solutions (with  
 5 equimolar concentrations of  $^{14}\text{NH}_4^+$  and  $^{15}\text{NH}_4^+$ ) with different concentrations. **b,** Linear  
 6 calibration curves for both  $^{14}\text{NH}_4^+$  and  $^{15}\text{NH}_4^+$  in the concentration range of 30 to 1000  $\mu\text{M}$ . After  
 7 absorbing outlet gas at 373 K, 423 K and 473 K, respectively, the sulfuric acid solutions were  
 8 collected for  $^1\text{H}$ -NMR measurements, showing in **c** and **d** are the  $^1\text{H}$ -NMR spectra of  $^{14}\text{NH}_4^+$  and  
 9  $^{15}\text{NH}_4^+$  signals, **e** and **f** are the corresponding  $^{14}\text{NH}_3$  and  $^{15}\text{NH}_3$  synthesis rates derived from  $^1\text{H}$ -  
 10 NMR. Conditions:  $\text{Ba}_2\text{RuH}_6/\text{MgO}$  catalyst 30 mg,  $\text{H}_2 : ^{14}\text{N}_2(^{15}\text{N}_2) = 2 : 3$ , flow rate  $10 \text{ ml min}^{-1}$ ,  
 11 1 bar. 4 mL diluted sulfuric acid solution was used to absorb the produced  $\text{NH}_3$ . The absorption  
 12 time is 10 min at 473 K, 30 min at 423 K and 120 min at 373 K, respectively. Blank experiment  
 13 (without catalyst loading) was performed at 298 K for 120 min, where  $\text{NH}_3$  concentration is  
 14 below the detection limit.

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**Supplementary Fig. 15. The free energy plots of LiH adsorption on the stoichiometric Li<sub>4</sub>RuH<sub>6</sub> surface under different conditions.** LiH dissociates exothermically into surface Li and the H goes to one of the neighboring RuH<sub>6</sub> sites creating a [RuH<sub>7</sub>]. Adding two extra LiH to the surface results in the composition of 4RuH<sub>6</sub> + 2RuH<sub>7</sub> + 2LiH that is thermodynamically stable under the reaction condition applied in this study (373 K to 573 K, ≥ 1 bar). However, adding further LiH will block the surface from N<sub>2</sub> adsorption.

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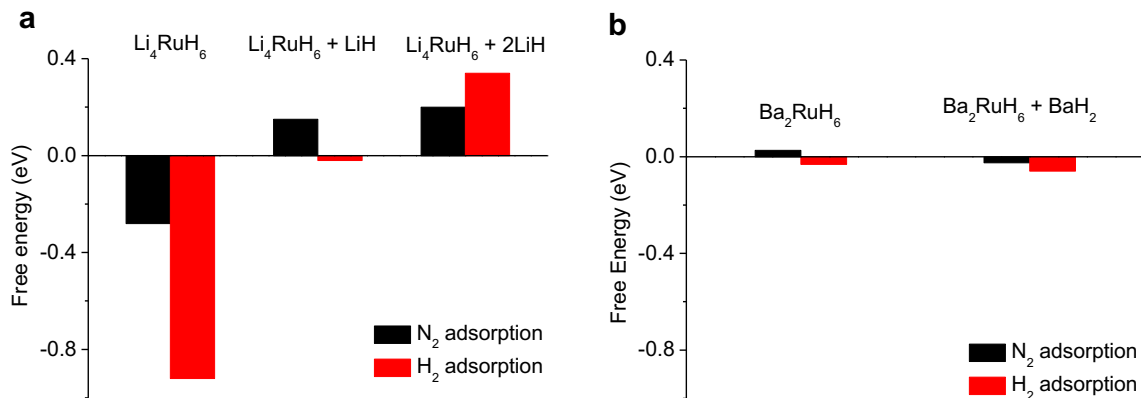
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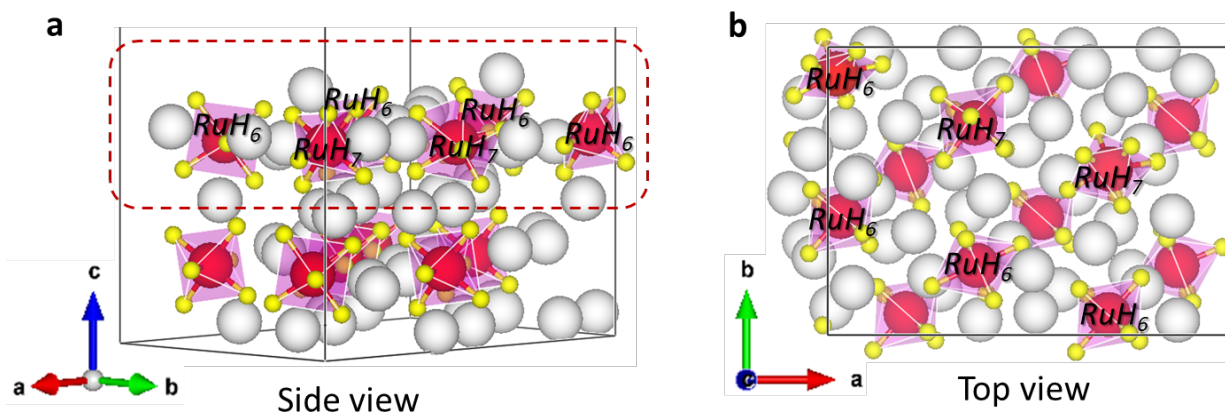




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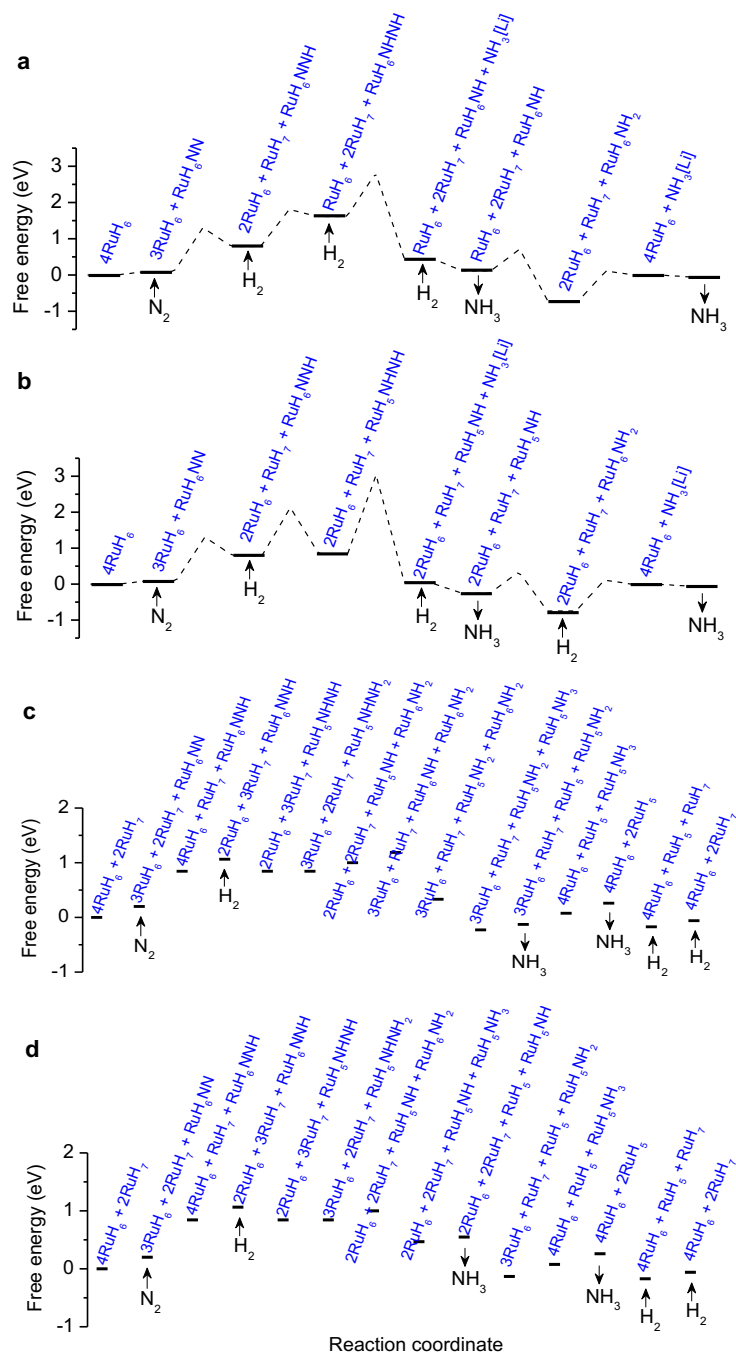
2 **Supplementary Fig. 16. Competitive H<sub>2</sub>(g) and N<sub>2</sub>(g) adsorption on ternary hydride**  
 3 **surface. a**, Li<sub>4</sub>RuH<sub>6</sub> surface with and without extra LiH. **b**, Ba<sub>2</sub>RuH<sub>6</sub> surface with and without  
 4 extra BaH<sub>2</sub>. Our free energy calculations show that H<sub>2</sub> adsorption is strongly favored over N<sub>2</sub>  
 5 adsorption on the stoichiometric Li<sub>4</sub>RuH<sub>6</sub> surface; while on the over-stoichiometric surface  
 6 especially on the Li<sub>4</sub>RuH<sub>6</sub> surface with two extra LiH, N<sub>2</sub> adsorption is preferred to H<sub>2</sub>  
 7 adsorption. The competitive adsorption of N<sub>2</sub> and H<sub>2</sub> is not pronounced over the stoichiometric  
 8 Ba<sub>2</sub>RuH<sub>6</sub>, however, the addition of excess BaH<sub>2</sub> enhances N<sub>2</sub> adsorption, which may account for  
 9 its higher TOF.

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**Supplementary Fig. 17.** The side-view (a) and top view (b) of the model surface of  $\text{Li}_4\text{RuH}_6$  catalyst, in which four  $\text{RuH}_6$  and two  $\text{RuH}_7$  sites are indicated. The top layer of the model (marked with dashed rectangle) is used in Fig. 3a for simple identification.



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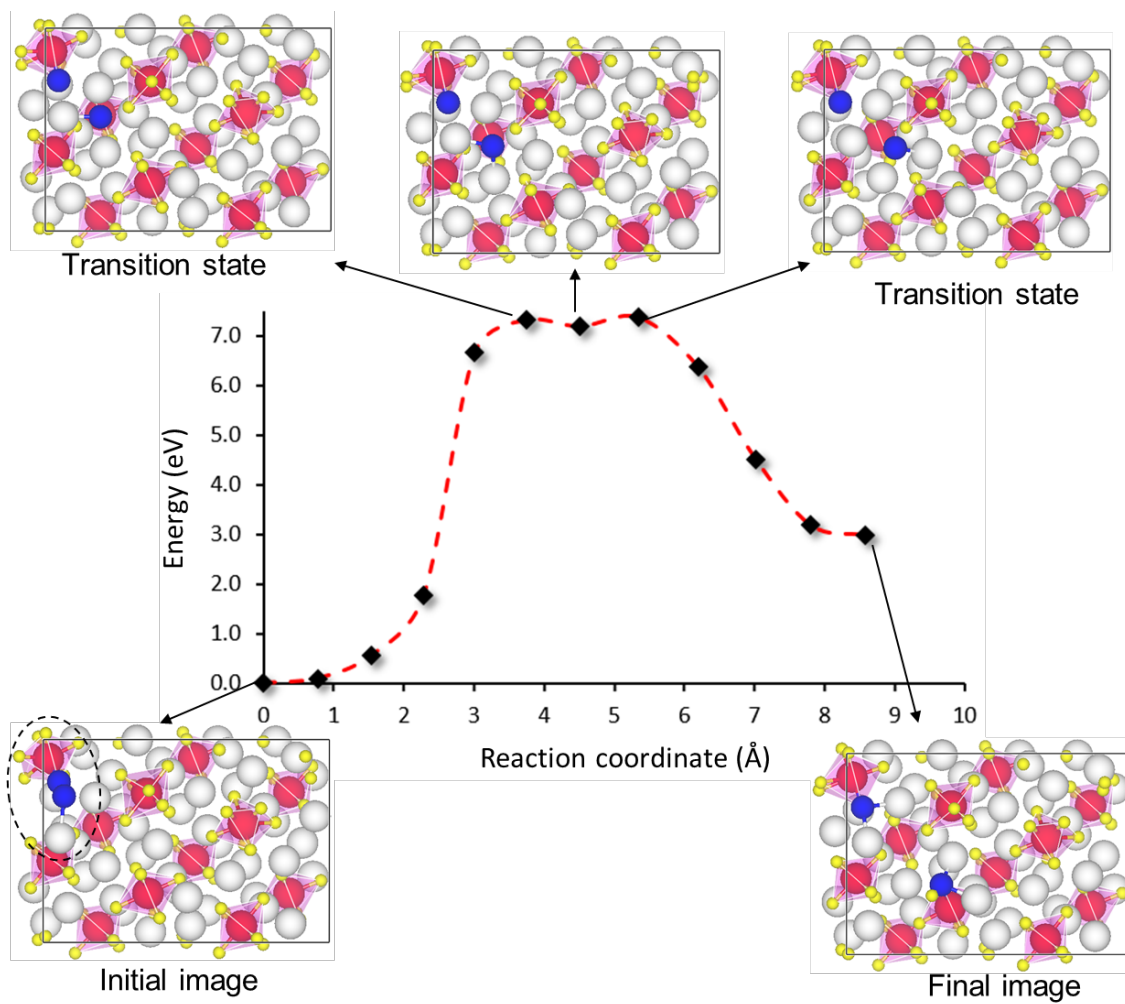
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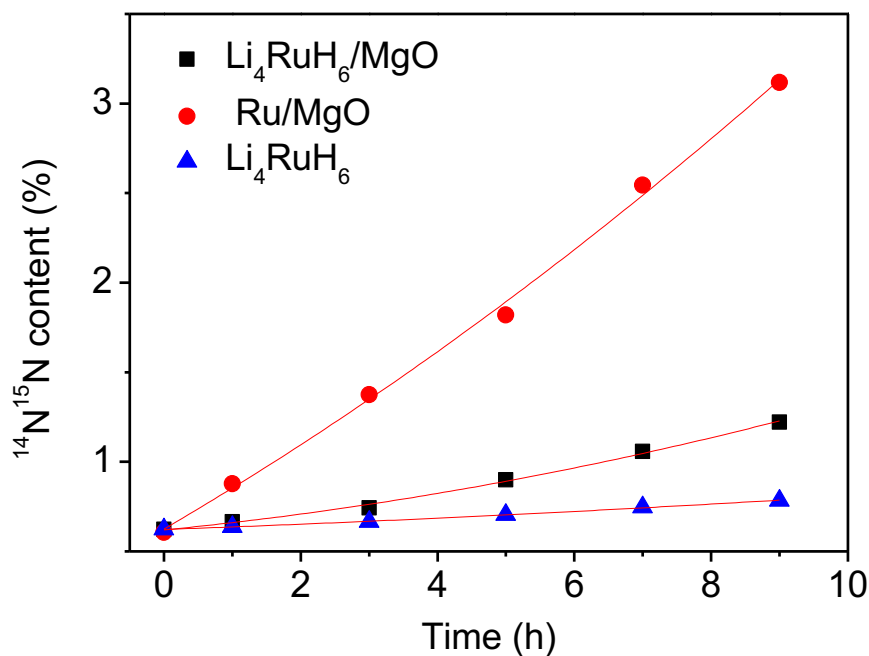
**Supplementary Fig. 18. A few possible pathways for N<sub>2</sub> activation and hydrogenation on Li<sub>4</sub>RuH<sub>6</sub> surface.** The free energy profiles of **a** and **b** are based on a model of Li<sub>4</sub>RuH<sub>6</sub> (110) surface composed of four Li<sub>4</sub>RuH<sub>6</sub> units 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 Li<sub>4</sub>RuH<sub>6</sub> units and stabilized by two extra LiH. All free energy pathways are calculated at 573 K and 1 bar (H<sub>2</sub>:N<sub>2</sub> ratio is fixed at 3, and the concentration of NH<sub>3</sub> is 0.27% that is consistent with the experimental condition.)





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**Supplementary Fig. 20. The detailed kinetic path for direct  $N_2$  dissociation over  $Li_4RuH_6$  surface.**



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Sample	Fitting curve	Correlation coefficient (R <sup>2</sup> )	Initial N <sub>2</sub> exchange rate at 473 K (μmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> )
Li <sub>4</sub> RuH <sub>6</sub> /MgO	$y = 0.620 + 0.0377x + 3.33 \cdot 10^{-3}x^2$	0.996	1.4
Ru/MgO	$y = 0.625 + 0.223x + 6.22 \cdot 10^{-3}x^2$	0.996	5.2
Li <sub>4</sub> RuH <sub>6</sub>	$y = 0.622 + 0.0139x + 4.76 \cdot 10^{-4}x^2$	0.997	0.065

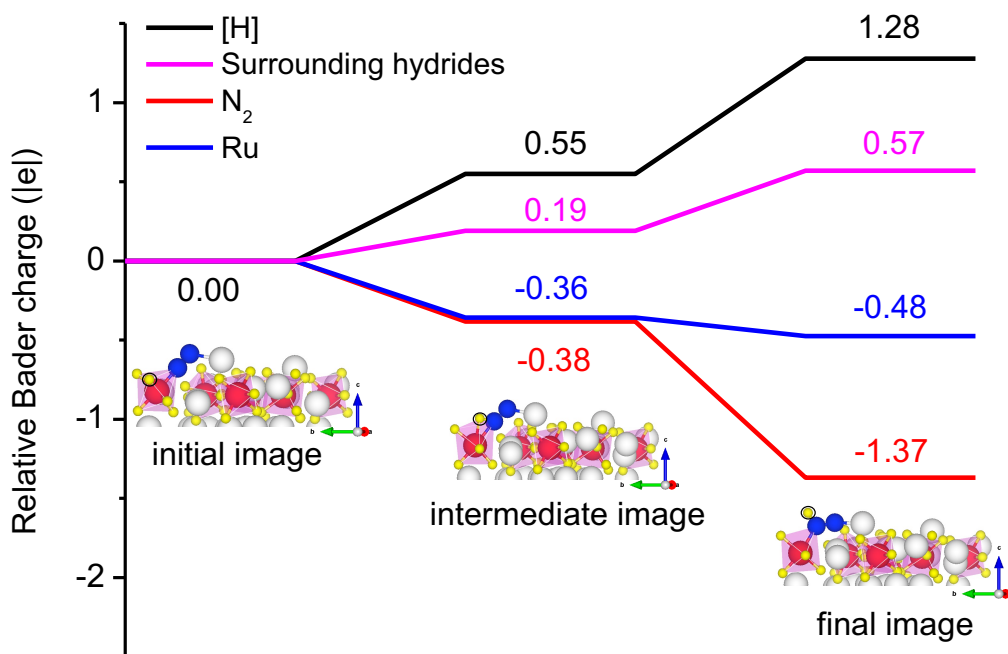
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4 **Supplementary Fig. 21. N<sub>2</sub> exchange reactions.** Time course of <sup>14</sup>N<sup>15</sup>N formation over  
5 Li<sub>4</sub>RuH<sub>6</sub>/MgO, Ru/MgO and Li<sub>4</sub>RuH<sub>6</sub> catalysts at 473 K. The data were fitted by high-order  
6 polynomial curves for easy analysis and the fitting results were shown in the table below the  
7 figure. The initial N<sub>2</sub> exchange rates for Li<sub>4</sub>RuH<sub>6</sub>/MgO, Ru/MgO and Li<sub>4</sub>RuH<sub>6</sub> at 473 K can be  
8 estimated by derivation the fitting curves at the initial time.

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10 It should be noted that the possible inhomogeneity of the Li<sub>4</sub>RuH<sub>6</sub>/MgO sample and its partial  
11 decomposition to LiH and Ru at 473K may contribute to the formation of <sup>14</sup>N<sup>15</sup>N.  
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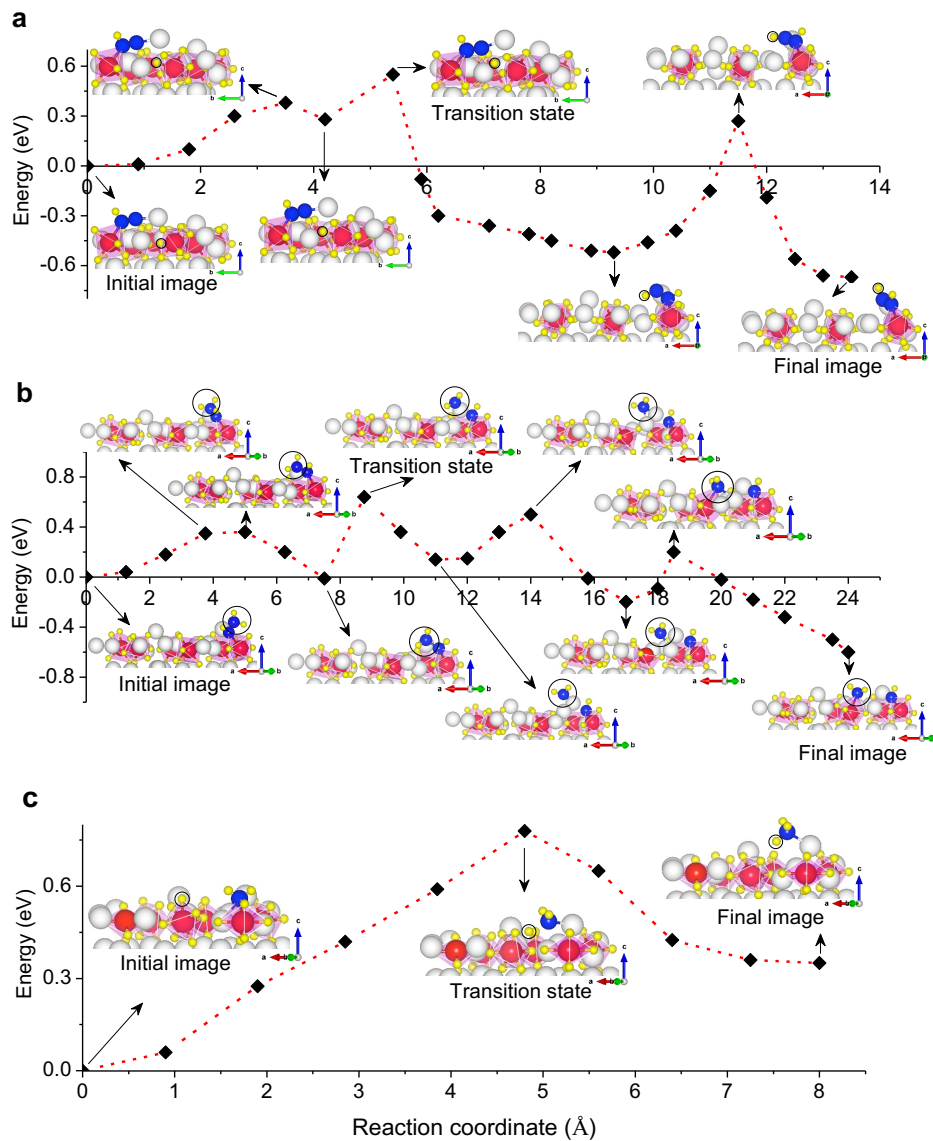
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**Supplementary Fig. 22. Bader charge analyses of the first hydrogenation step (1-2).** In this process, the adsorbed N<sub>2</sub> gains substantial electron from the transiting lattice hydride (denoted as [H]). At the initial stage, the charge state of Ru in [RuH<sub>6</sub>]-N<sub>2</sub> is +0.89; at the final stage, the charge state of Ru in [RuH<sub>5</sub>]-N<sub>2</sub>H is +0.41. The charge state of Ru in [RuH<sub>7</sub>] nearby remains almost constant (ca. +0.4) during the lattice hydride transfer. 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.



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3 **Supplementary Fig. 23. Detailed kinetic paths of some characteristic steps of the catalysis**  
 4 **over  $\text{Li}_4\text{RuH}_6$  surface. a,** Kinetic path of the lattice transfer of step 2-3. Li cations mediate  
 5 lattice H transfer from  $[\text{RuH}_7]$  complex to  $-\text{NHN}$  species that is bonded on  $[\text{RuH}_5]$  site and thus  
 6 forming  $-\text{NHNH}$  species. **b,** Kinetic path of the N-N dissociation step 5-6. The N-N bond  
 7 dissociates via a Li-assisted multi-step path, creating a  $[\text{RuH}_5]-\text{NH}$  and a  $[\text{RuH}_6]-\text{NH}_2$  species. **c,**  
 8 Kinetic path of the second  $\text{NH}_3$  formation step 9-10. Li cations mediate lattice H transfer from  
 9  $[\text{RuH}_7]$  complex to  $-\text{NH}_2$  species and thus forming the second  $\text{NH}_3$ , during which  $\text{NH}_3$  leaves the  
 10  $[\text{RuH}_5]$  site and hangs loosely on the neighboring Li. Noted that for mediating lattice H transfer,  
 11 Li cation has an electrostatic interaction with lattice H at intermediate states, but forms an ionic  
 12 bond with H during its migration. The particular H atom or  $\text{NH}_2$  species of interest is marked by  
 13 a black round ring.

**Supplementary Table 1. Thermodynamic calculations of the reactions for the formation of Li<sub>4</sub>RuH<sub>6</sub> and Ba<sub>2</sub>RuH<sub>6</sub>.** The reaction enthalpy of formation of Li<sub>4</sub>RuH<sub>6</sub> ( $\Delta_r H^0(\text{Li}_4\text{RuH}_6)$ ) is obtained by the corresponding van't Hoff plots in Fig. 1d. The reaction enthalpy of formation of Ba<sub>2</sub>RuH<sub>6</sub> ( $\Delta_r H^0(\text{Ba}_2\text{RuH}_6)$ ) is taken from Ref.<sup>6</sup>. The standard enthalpies of formation of other substances are taken from “NIST Standard Reference Number 69”. Therefore, the standard enthalpies of formation of Li<sub>4</sub>RuH<sub>6</sub> ( $\Delta_f H^0(\text{Li}_4\text{RuH}_6)$ ) and Ba<sub>2</sub>RuH<sub>6</sub> ( $\Delta_f H^0(\text{Ba}_2\text{RuH}_6)$ ) can be evaluated by combining the  $\Delta_r H^0$  and  $\Delta_f H^0$  values.

Reaction	4LiH	+	Ru	+	H <sub>2</sub>	→	Li <sub>4</sub> RuH <sub>6</sub>	$\Delta_r H^0$ (kJ mol <sup>-1</sup> )
$\Delta_f H^0$ (kJ mol <sup>-1</sup> )	-90.5		0		0		-455.1	-93.1
Reaction	2BaH <sub>2</sub>	+	Ru	+	H <sub>2</sub>	→	Ba <sub>2</sub> RuH <sub>6</sub>	$\Delta_r H^0$ (kJ mol <sup>-1</sup> )
$\Delta_f H^0$ (kJ mol <sup>-1</sup> )	-178.3		0		0		-464.1	-107.5

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**Supplementary Table 2. Physicochemical properties of the as-prepared Ru-based catalysts.**

Catalyst	Ru content (wt %)	$S_{\text{BET}}^{\text{a}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$d^{\text{b}}$ (nm)	$D^{\text{b}}$ (%)	Surface Ru content <sup>b</sup> (wt %)
Li <sub>4</sub> RuH <sub>6</sub> /MgO	8.0	245.5	3.60	36.9	2.95
Ba <sub>2</sub> RuH <sub>6</sub> /MgO	5.0	154.1	4.16	32.0	1.60
Ru/MgO	8.7	266.6	3.09	43.0	3.74
Cs-Ru/MgO	7.3	43.0	6.02	22.1	1.61
Li <sub>4</sub> RuH <sub>6</sub>	---	7.2	---	---	---
Ba <sub>2</sub> RuH <sub>6</sub>	---	4.8	---	---	---

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<sup>a</sup>BET specific surface area.

<sup>b</sup>Mean Ru particle size (d), dispersion (D) and surface Ru content were estimated based on TEM data assuming spherical metal particles.

Supplementary Table 3. Activities of as-prepared Ru-based catalysts<sup>a</sup>.

Catalyst	$r_{\text{NH}_3}$ (mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> )	NH <sub>3</sub> pressure (×10 <sup>-3</sup> bar)	TOF <sup>b</sup> (×10 <sup>-3</sup> s <sup>-1</sup> )	$\tau_{\text{cat}}$ (s)	TOF <sup>c</sup> (×10 <sup>-3</sup> s <sup>-1</sup> )	$\theta_{\text{NH}_x}$ <sup>e</sup>
Li <sub>4</sub> RuH <sub>6</sub> /MgO	6.5	2.7	6.2	32.2	31.1	0.200
Ba <sub>2</sub> RuH <sub>6</sub> /MgO	9.5	3.9	16.7	15.1	66.2	0.252
Ru/MgO	0.38	0.16	0.29	---	2.4 <sup>d</sup>	---

<sup>a</sup>Reaction conditions: catalyst loading 30 mg, H<sub>2</sub>:N<sub>2</sub>=3:1, flow rate 30 ml min<sup>-1</sup>, 573 K and 1 bar.

<sup>b</sup>TOF was obtained based on the surface Ru content derived from the average particle size observed by TEM and spherical assumption of the particle morphology.

<sup>c</sup>TOF was determined from SSITKA by inverting the residence time of nitrogen containing species,  $\tau_{\text{cat}}$ , that is associated with the catalyst surface.

<sup>d</sup>TOF of Ru/MgO at 573 K was deduced from its higher temperature data (i.e., TOF(623 K)=0.0118 s<sup>-1</sup> and TOF(673 K)=0.0464 s<sup>-1</sup> determined from SSITKA) based on the Arrhenius plot.

<sup>e</sup>The fractional surface coverage of nitrogen containing species,  $\theta_{\text{NH}_x}$ , was estimated based on TEM data.

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2**Supplementary Table 4. Ammonia synthesis over recently developed Ru-based catalysts.**

Catalysts	Metal content (wt %)	$r_{\text{NH}_3}^{\text{a}}$ (mmol g <sub>Ru</sub> <sup>-1</sup> h <sup>-1</sup> )		WHSV (ml g <sup>-1</sup> h <sup>-1</sup> )	Ref.
		573 K, 10 bar	573 K, 1 bar		
Li <sub>4</sub> RuH <sub>6</sub> /MgO	8.0	275	114	60000	this work
Ba <sub>2</sub> RuH <sub>6</sub> /MgO	5.0	680	276	60000	
Ru/C <sub>12</sub> A <sub>7</sub> :e <sup>-</sup>	1.8	94 (593 K)	41	36000	7
Ru/Ca <sub>2</sub> N:e <sup>-</sup>	1.8	228 (593 K)	93	36000	7
Ru/BaTiO <sub>2.5</sub> H <sub>0.5</sub>	2.5	---	19 (598 K)	66000	8
Ru/Ca(NH <sub>2</sub> ) <sub>2</sub>	10	158 (8 bar)	56	36000	9
Ru/Ba-Ca(NH <sub>2</sub> ) <sub>2</sub>	10	233 (9 bar)	90	36000	10
Ru/Pr <sub>2</sub> O <sub>3</sub>	5	18 (9 bar)	---	18000	11
Ru/La <sub>0.5</sub> Ce <sub>0.5</sub> O <sub>1.75</sub>	5	22	---	72000	12
Ru/BaO-CaH <sub>2</sub>	10	165 (9 bar)	69	36000	13
Ru/BaCeO <sub>3-x</sub> N <sub>y</sub> H <sub>z</sub>	4.5	111 (9 bar)	---	36000	14
Ba-Ru-Li/AC	4.8	---	1.5	62400	15
LaRuSi	37.7	---	4.7 (673 K)	36000	16

<sup>a</sup>Ammonia synthesis rates per gram of Ru under 573 K, 10 bar and 573 K, 1 bar (H<sub>2</sub>:N<sub>2</sub>=3 or 2/3), unless otherwise stated.

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## Supplementary references

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