

## Materials and Methods

### 1. Materials.

Cerium dioxide ( $\text{CeO}_2$ ), Iron(III) chloride ( $\text{FeCl}_3$ ), Lithium hydride ( $\text{LiH}$ ), Titanium Dioxide ( $\text{TiO}_2$ ), Magnesium oxide ( $\text{MgO}$ ) and Ruthenium(III) Chloride Hydrate ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ ) were purchased from Aladdin. Anhydrous ethanol (AR grade) and Concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) were purchased from Sinopharm Chemical Reagent Co, Ltd. All chemicals in the experiments were used without further purification. The purities of  $\text{H}_2$ ,  $\text{N}_2$  and Ar are all 99.995%.

### 2. Catalyst preparation

**Ru-CeO<sub>2</sub>/Li:** The commercial  $\text{CeO}_2$  was pre-calcined at 723 K under vacuum for 3 hours to remove the adsorbed impurities. First, 0.0513 g of  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  ferric chloride (7 wt%) was dissolved in 40 mL of anhydrous ethanol, then 0.5 g of vacuum treated commercial  $\text{CeO}_2$  was added. After dispersion by ultrasonic, the solution was impregnated and stirred for 5 h in nitrogen atmosphere. The Ru-Ce precursor was obtained by means of rotation evaporation at 313 K and overnight vacuum drying named Ru-CeO<sub>2</sub>.

Take a certain amount of  $\text{LiH}$  and Ru-CeO<sub>2</sub> in the molar ratio of 6:1, grind and mixed them evenly. The mixture was put into a sealable reactor, heated up to 673K at 3.3 K/min in vacuum, and calcined for 2 h. After cooling down to room temperature, the obtained atropurpureus powders were washed with deionized water 6-8 times to completely remove unreacted  $\text{LiH}$ , then dried in vacuum. The catalyst named Ru-CeO<sub>2</sub>/Li. The BET surface area of the as-synthesized Ru-CeO<sub>2</sub>/Li was measured to be 5.89 m<sup>2</sup>g<sup>-1</sup>. The other catalysts with different Ru loaded were named Ru(1%)-CeO<sub>2</sub>/Li, Ru(3%)-CeO<sub>2</sub>/Li, Ru(5%)-CeO<sub>2</sub>/Li, Ru(9%)-CeO<sub>2</sub>/Li respectively.

**CeO<sub>2</sub>/Li:** Take a certain amount of  $\text{LiH}$  and  $\text{CeO}_2$  in the molar ratio of 6:1, grind and mixed them evenly. The mixture was put into a sealable reactor, heated up to 673K at 3.3 K/min in vacuum, and calcined for 2 h. After cooling down to room temperature,

the obtained yellowish-green powders were washed with deionized water 6-8 times to completely remove unreacted LiH, then dried in vacuum. The BET surface area of the as-synthesized CeO<sub>2</sub>/Li was measured to be 15.97 m<sup>2</sup>g<sup>-1</sup>.

**Ru-TiO<sub>2</sub>/Li or Ru-MgO:** The commercial TiO<sub>2</sub> (MgO) was pre-calcined at 723 K under vacuum for 3 hours to remove the adsorbed impurities. The R-@TiO<sub>2</sub>/Li or Ru-MgO was obtained by the similar preparation method to Ru-CeO<sub>2</sub>/Li.

### 3. Characterization

The powder X-ray diffraction (XRD) patterns were performed on a Bruker D8 Advance Davinci X-ray diffractometer with monochromator Cu K $\alpha$  radiation ( $\lambda=1.5418$  Å) from 10° to 80°. Transmission electron microscopy (TEM) images were measured using a Tecnai G2 S-Twin F20 at the acceleration voltage of 200 kV. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis were collected using a Helios NanoLab 600I from FEI Company. X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo ESCALAB 250 X-ray photoelectron spectrometer with a monochromated X-ray source (Al K $\alpha$   $h\nu=1486.6$  eV). The energy scale of the spectrometer was calibrated using Au4f<sub>7/2</sub>, Cu2p<sub>3/2</sub>, and Ag3d<sub>5/2</sub> peak positions. The standard deviation for the binding energy (BE) values was 0.1 eV. Argon ion etch for one minute. The electron paramagnetic resonance spectra (EPR) were obtained on a JES-FA 200 EPR spectrometer. The details of the instrumental parameters were as follows: scanning frequency: 9.45 GHz; scanning width: 800 mT; scanning power: 0.998 mW; scanning temperature: 293 K. Fourier transform infrared (FTIR) spectroscopy was performed on a Bruker VERTEX 80 V spectrometer. The Brunauer-Emmett-Teller (BET) surface areas of the samples were measured from the adsorption of N<sub>2</sub> at 77 K by using a Micromeritics ASAP 2020M system. Raman spectra of samples was analyzed on a Renishaw inVia Confocal Raman spectrometer equipped with a solid-state laser of 532 nm as the excitation source. Inductively coupled plasma (ICP) analyses were carried out on an iCAP 7600

ICP-OES instrument. The temperature programmed desorption (TPD) and temperature-programmed reduction (TPR) were performed on an Autochem II 2920 apparatus (Micromeritics, USA). Quantitative samples were usually loaded and pre-treated in an inert gas flow at 400 °C for 1 h. After cooling to 50 °C, the samples were saturated with a flow of 25 mL min<sup>-1</sup> 10% N<sub>2</sub>/He, 10% H<sub>2</sub>/Ar for 60 min. After being purged with inert gas for 1 h, the samples were heated from 50 °C to 400 °C with a heating rate of 10 °C/min under inert gas atmosphere, and the desorbed N<sub>2</sub>, H<sub>2</sub> was determined using a thermal conductivity detector. Ammonia production efficiency was measured by the WFSM-3060 catalyst evaluation device from Tianjin Xianquan Industry and Trade Development Ltd. Ammonia concentration was measured by ion chromatography (IC) on a PIC-10 produced by Qingdao Puren Instrument Ltd.

#### 4. Catalytic Measurements

The catalytic reactions were conducted in a fixed-bed flow system with a gas flow of H<sub>2</sub>:N<sub>2</sub> (3:1) at a flow rate of 60 ml min<sup>-1</sup>. Specifically, a mixture of 15 mg of Ru-CeO<sub>2</sub>/Li and 500 mg of quartz sand (140 mesh) was loaded into the reactor in the glove box and then pre-treated in a stream of H<sub>2</sub>:N<sub>2</sub> (3:1) at 1.0 MPa under a temperature program of 5 K/min up to 673 K and then holding at 673 K for 1 h. After the system is stable, the reaction was monitored under steady-state conditions of temperature (523-773 K) with a flow rate of 60 ml min<sup>-1</sup> under 1.0 MPa. The produced ammonia was trapped in 0.25 mM sulphuric acid solution and the amount of NH<sub>4</sub><sup>+</sup> generated in the solution was determined using an ion chromatograph.

#### 5. Kinetic measurements

All the kinetic measurements were carried out in the fixed-bed flow system with a flow of mixed gas (N<sub>2</sub>, H<sub>2</sub>) under conditions far from equilibrium and the reaction temperature was fixed at 673K,. According to Arrhenius formula:

$$\ln r = \ln k + \alpha \ln P_{\text{NH}_3} + \beta \ln P_{\text{N}_2} + \gamma \ln P_{\text{H}_2}.$$

In the measurement of  $N_2$  reaction order, the partial pressure of  $H_2$  in the reaction gas was kept constant to test the rate of ammonia synthesis under different partial pressure of  $N_2$ . Since the partial pressure of  $NH_3$  in the reaction product is very small, the  $\alpha \ln P_{NH_3}$  term can be ignored, so the above equation can be further transformed into:

$$\ln r = K_1 + \beta \ln P_{N_2}.$$

Meanwhile, the reaction order of  $H_2$  can be measured by

$$\ln r = K_2 + \gamma \ln P_{H_2}.$$

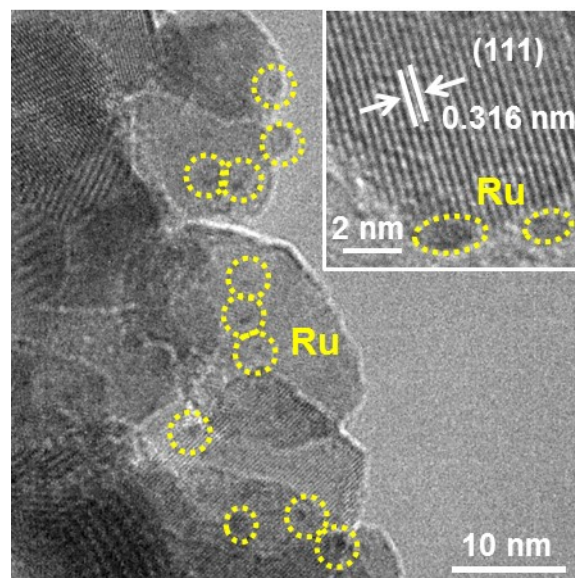
Table S1. Composition of different catalysts (based on ICP measurements)

Samples	Ce:Li (mole:mole)	Ru (wt%)
Ru-CeO <sub>2</sub> /Li	0.8	6.6
CeO <sub>2</sub> /Li	0.9	/
Ru-CeO <sub>2</sub>	/	6.1
Ru-MgO	/	6.3

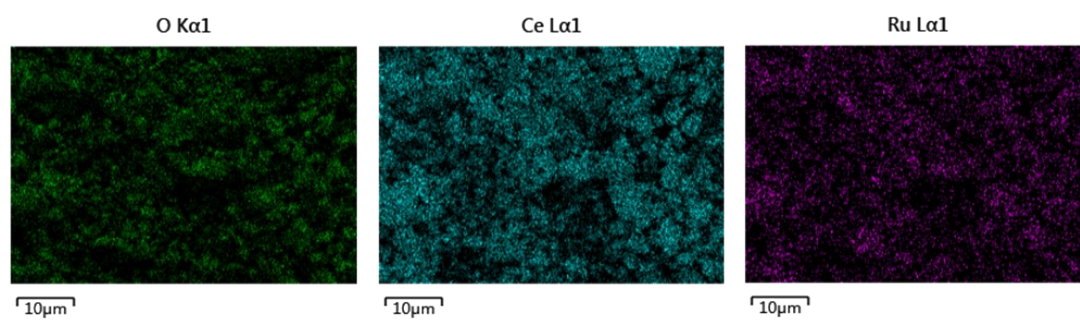
Table S2. Representative works on ammonia synthesis based on Ru-modified catalysts.

Samples	Rate ( $\mu\text{mol g}^{-1} \text{h}^{-1}$ )	Reaction conditions	sccm ( $\text{ml min}^{-1}$ )	Ref.
Ru-CeO <sub>2</sub> /LiH	33000	1MPa, 400 °C	60	This work
Ru/CeO <sub>2</sub> -w	22620	1MPa, 400 °C	60	S1
Ru(5%)-Pr <sub>2</sub> O <sub>3</sub>	19000	1MPa, 400 °C	60	S2
Ru(5%)/CeO <sub>2</sub>	7200	0.9MPa, 400°C	60	S2
Ru(1.8%)/LaScSi	1800	1MPa, 400 °C	60	S2
Ru(9.1%)-Ba/AC	8285	1MPa, 400 °C	60	S3
Ru(6%)-Cs/MgO	12117	1MPa, 400 °C	60	S3
Ru(4%)/C12A7:e <sup>-</sup>	6089	1MPa, 400 °C	60	S3
Ba-Ru(4.8%)-Li/AC	19600	1MPa, 400 °C	60	S4
Ru(1%)/CeO <sub>2</sub> -BH	5454	1MPa, 400 °C	60	S5
Ru(3%)/Ti <sub>0.18</sub> -Ce	18912	0.9MPa, 400°C	60	S5
Ru(7.8%)/Y <sub>5</sub> Si <sub>3</sub>	4100	1MPa, 400 °C	60	S6
Ru(3%)/CeO <sub>2</sub>	22075	1MPa, 400 °C	60	S7
Ru(5%) NPs/CeO <sub>2</sub>	28000	1MPa, 400 °C	60	S8
Ru(1.8%)/Ca <sub>2</sub> N:e <sup>-</sup>	3386	0.1MPa, 340 °C	60	S9
Ru(2.0%)/CaH <sub>2</sub>	4002	0.1MPa, 340 °C	60	S10

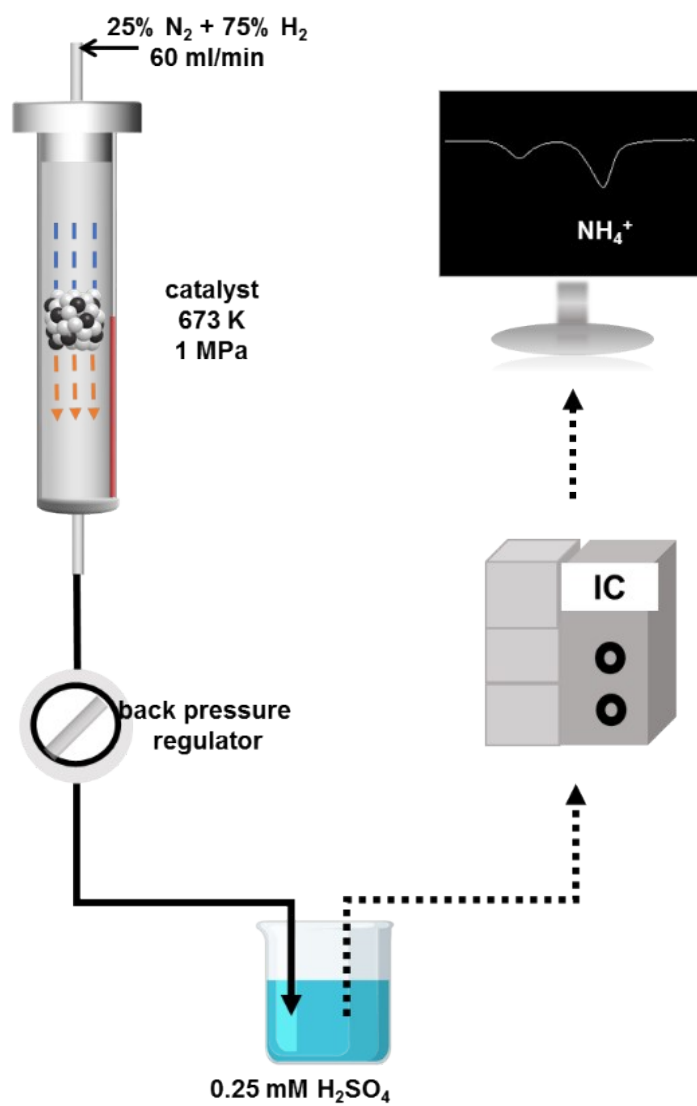




**Figure S1.** HRTEM images of Ru-CeO<sub>2</sub>/Li.

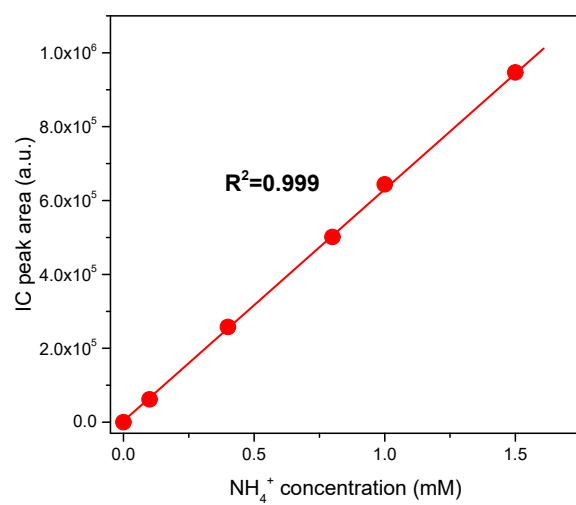


**Figure S2.** SEM-EDX elemental mapping profiles of Ru-CeO<sub>2</sub>/Li for oxygen, cerium and ruthenium.

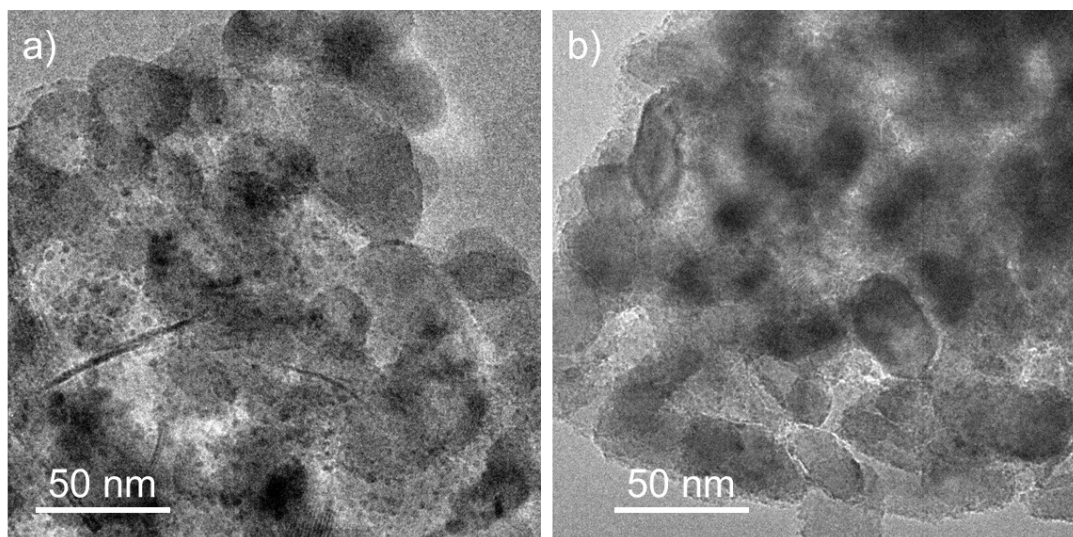


**Figure S3.** Schematic diagram of the catalytic system.

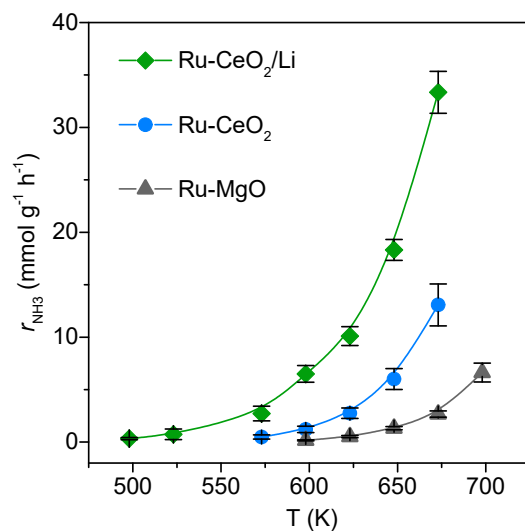




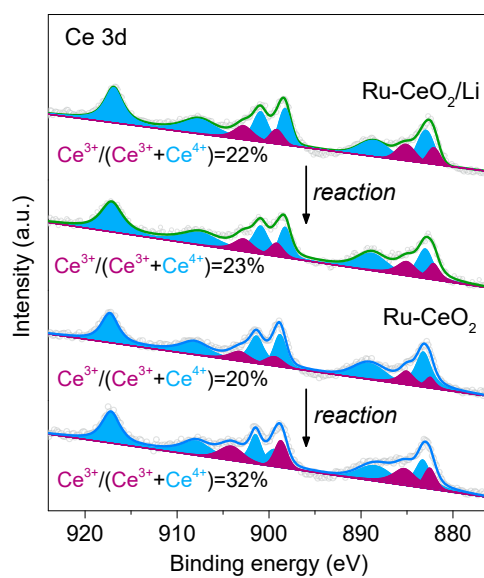
**Figure S4.** The calibration curve of NH<sub>4</sub><sup>+</sup> using the ion chromatograph method.



**Figure S5.** TEM images of (a) Ru-MgO and (b) Ru-TiO<sub>2</sub>/Li.



**Figure S6.** Ammonia synthesis rate as a function of temperature.



**Figure S7.** XPS spectra of Ce 3d for Ru-CeO<sub>2</sub> and Ru-CeO<sub>2</sub>/Li before and after the reactions.

## References:

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