Supporting Information for

Electronic promoter or reacting species? The role of $LiNH_2$ on Ru in catalyzing NH_3 decomposition

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Materials and Methods

Materials

$LiNH_2$ (Aldrich, 95.0%), $RuCl_3 \cdot xH_2O$ (Aladdin, 97%), Lithium rod (Alfa Aesar, 99.9%), KNO_3 (Alfa Aesar, 99.0%), were used without further treatment. CNTs, having a mean diameter of 20 nm and BET surface area of 104 $m^2\ g^{-1}$ were supplied by Professor H. B. Zhang's group in Chemistry Department, Xiamen University, China. NH_3 gas was purified by anhydrous CaO before used for catalytic test. As Li metal and $LiNH_2$ are sensitive to moisture and oxygen, sample preparation and loading were conducted in a glove box filled with Argon.

Preparation of Li_2NH. Li_2NH was prepared by heating commercial $LiNH_2$ at 773 K under vacuum for 5 hours.

Preparation of Ru-$LiNH_2$. A mixture of $RuCl_3 \cdot xH_2O$ and $LiNH_2$ with a given weight

ratio was ball milled at 150 rpm in an agart jar at 323 K on a Retsch planetary ballmill (PM400) under Ar atmosphere for 3h. Then the solid residue was purified by stirring it in dry THF (30 ml) followed by centrifugation for 3 times to remove LiCl. The purified product was dried under vacuum and stored in glove box.

Preparation of MgO. MgO was obtained via thermal decomposition of $MgC_2O_4 \bullet 2H_2O$ in Ar flow according to reference.[1]

Preparation of supported Ru catalysts. CNTs or MgO supported Ru catalysts were prepared by the incipient wetness impregnation of CNTs or MgO with acetone solution of $RuCl_3 \bullet xH_2O$.[2] The weight ratio of Ru to CNTs or MgO is *ca.* 0.05, respectively. Prior to test, the samples were reduced in H_2 (30 ml min^{-1}) at 673 K for 2 hours.

Preparation of K or $LiNH_2$-promoted Ru/MgO catalysts. The K promoted-Ru/MgO catalyst was prepared by the dispersion of the prepared Ru/MgO in a KNO_3 aqueous solution, followed by drying in Ar. The atomic ratio of K/Ru in the catalyst is *ca.* 2.[3] The $LiNH_2$-Ru/MgO catalyst was prepared by impregnating the prepared Ru/MgO in an Li-ammonia solution. Li metal converted to $LiNH_2$ in the presence of Ru. The atomic ratio of Li to Ru is *ca.* 11.5:1.

Catalyst testing. Ammonia decomposition reactions were performed in a continuous-flow fixed-bed quartz reactor (inner diameter = 4 mm). Typically, 30 mg of catalyst or its precursor was loaded, and the temperature was raised at a ramping rate of 2 K min^{-1}. The gas composition was analyzed using on-line gas chromatograph (GC-2014C, Shimadzu) equipped with a Porapak N column, a 5A molecular sieve column and

TCD detector. Ammonia conversion data reported here were collected after 30 min time-on-stream at the corresponding temperature.

XANES and EXAFS measurements. Spectra at Ru K-edge were recorded at the BL14W beamline of Shanghai Synchrotron Radiation Facility (SSRF, electron energy of 3.5 GeV and ring currents of 300 mA). Samples were pressed into pellets and then sealed with KAPTON film on both sides to avoid air contamination.

XRD measurements. XRD patterns were recorded on a PANalytical X'pert diffractometer using a homemade sample cell covered with KAPTON film to avoid air contamination.

TG measurements. TG measurement was performed on a Netsch 449C TG unit. Small loading of *ca.* 5 mg was used. Argon was used as carrier gas and the ramping rate was set on 2K min^{-1}.

FTIR measurement. FTIR measurement was performed on a Varian 3100 unit in DRIFT mode. The resolution is 4 cm^{-1}.

Temperature-Programmed techniques. Temperature-programmed reactions were performed in a tubular quartz reactor and the exhaust gases were analyzed by an on-line mass spectrometer (Hiden HPR20). Samples were heated in a flow of Ar (30 ml min^{-1}) from room temperature to desired temperatures.

Computational details. All calculations were performed with the Vienna ab initio simulation package (VASP).[4] Projector-augmented-wave (PAW) potentials[5] were employed in connection with the PBE gradient-dependent exchange-correlation functions.[6] An energy cutoff of 500 eV was used to guarantee a good convergence for

the total energies and forces. The convergence criterion for energy is 10^{-5} eV/atom. For the structural optimization, full relaxation of cell volume and atomic positions was performed until the forces were less than 0.01 eV/Å. A periodic slab of eight atomic layers (256 atoms for the pristine Li_2NH surface) were used to simulate the Li_2NH (110) surface, for which atoms in the bottom four layers were fixed. For the Brillouin zone integrations, the k points were chosen using a 3x3x1 Monkhorst-Pack mesh.[7]

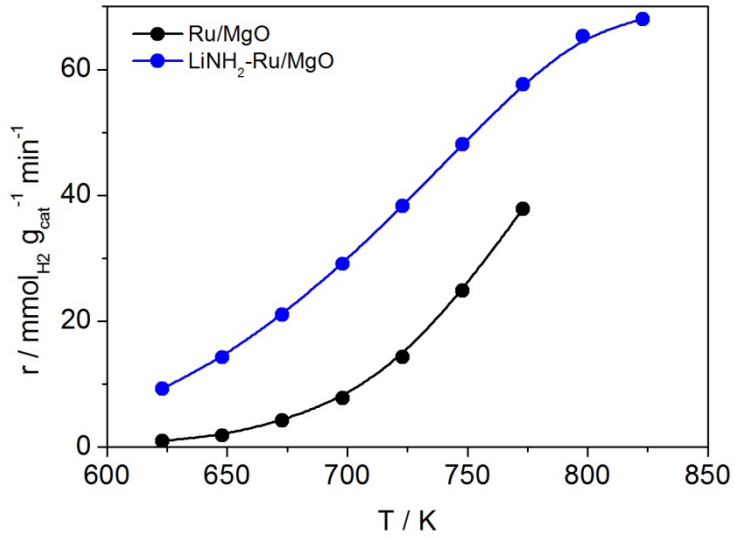


Figure S1. Temperature dependences of the activities of Ru-based catalysts under pure NH_3 flow with WHSV = 60,000 $ml_{NH3}\ g_{cat}^{-1}\ h^{-1}$.

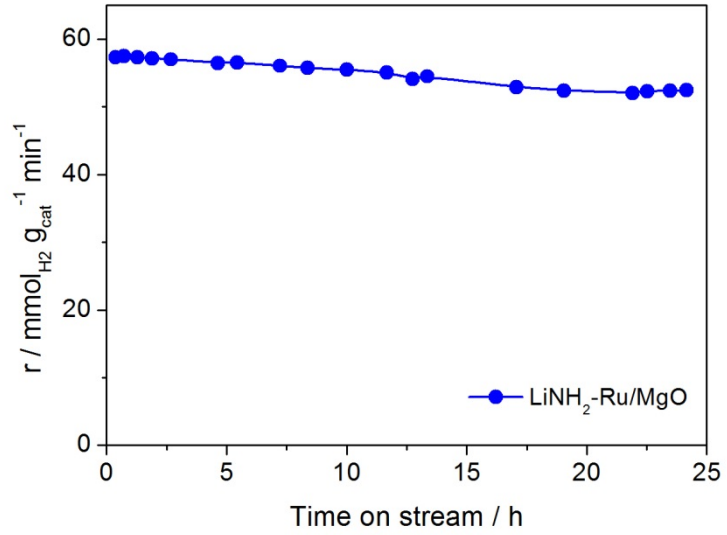


Figure S2. Stability test of the $LiNH_2$-Ru/MgO under pure NH_3 with WHSV = 60,000 $ml_{NH3}\ g_{cat}^{-1}\ h^{-1}$ at 773 K.

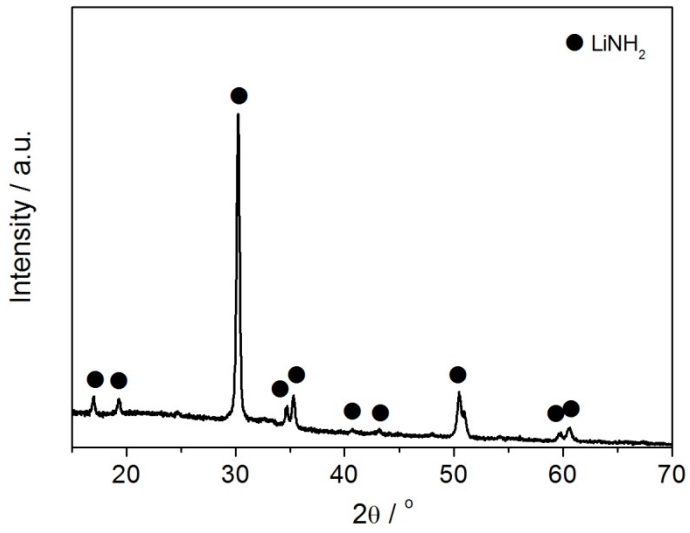


Figure S3. XRD pattern of as-prepared 5 wt% Ru-$LiNH_2$ sample.

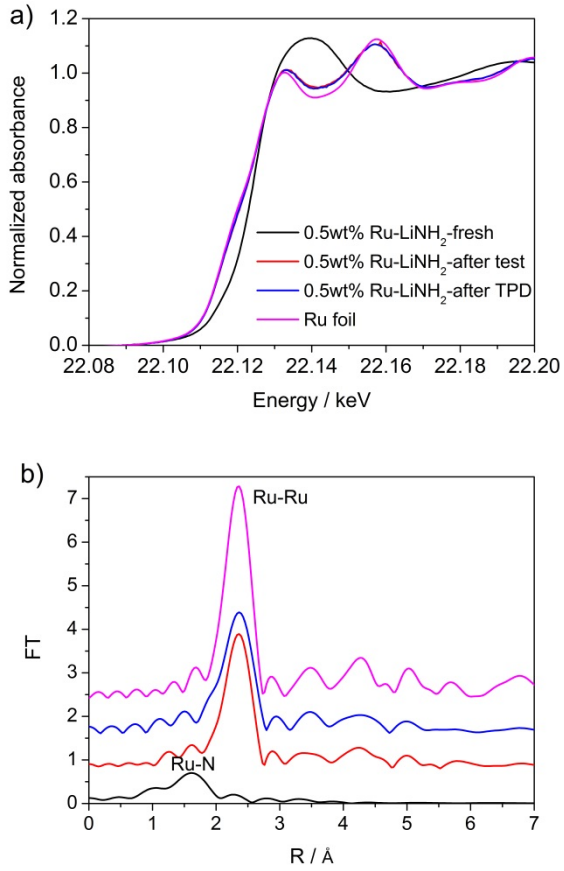


Figure S4. Ru K-edge XANES (a) and EXAFS (b) spectra of Ru-containing samples. To facilitate the measurement and to have uniform chemical state of Ru, 0.5 wt% Ru loading was adopted.

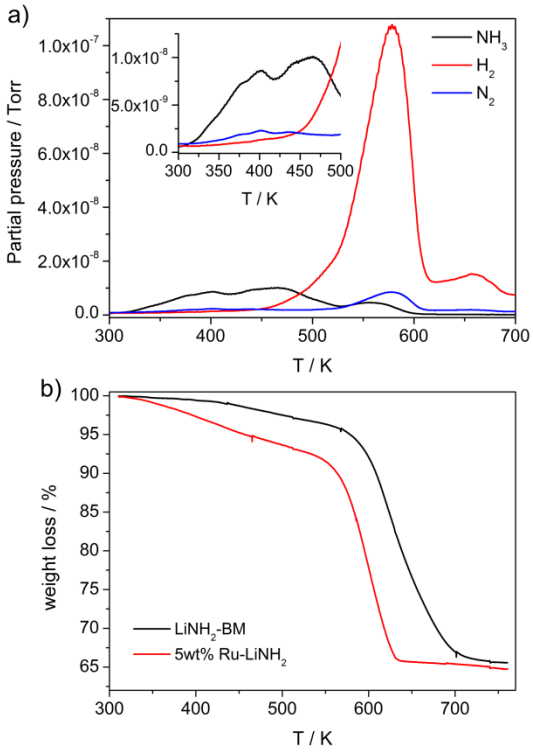


Figure S5. Characterization of the interaction of Ru and $LiNH_2$. (a) Temperature-programmed-decomposition profile (TPD) of 5 wt% Ru-$LiNH_2$, the inset is the enlarged portion of the temperature range of 300-500 K, and (b) TG measurements of 5 wt% Ru-$LiNH_2$ and $LiNH_2$ samples.

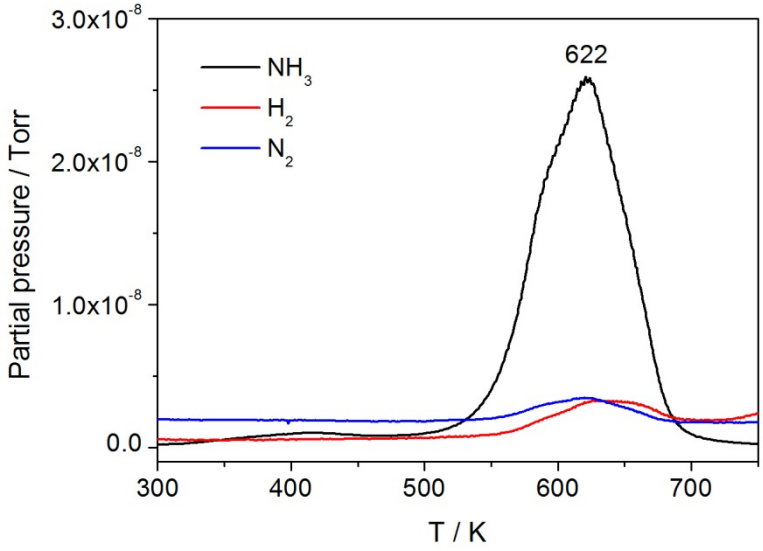


Figure S6. Temperature-Programmed-Decomposition (TPD) profile of $LiNH_2$ sample after ball milling. Reaction condition: sample loading – 20 mg, carrier gas – Ar, flow rate – 40 ml min^{-1}, ramping rate – 2K min^{-1}.

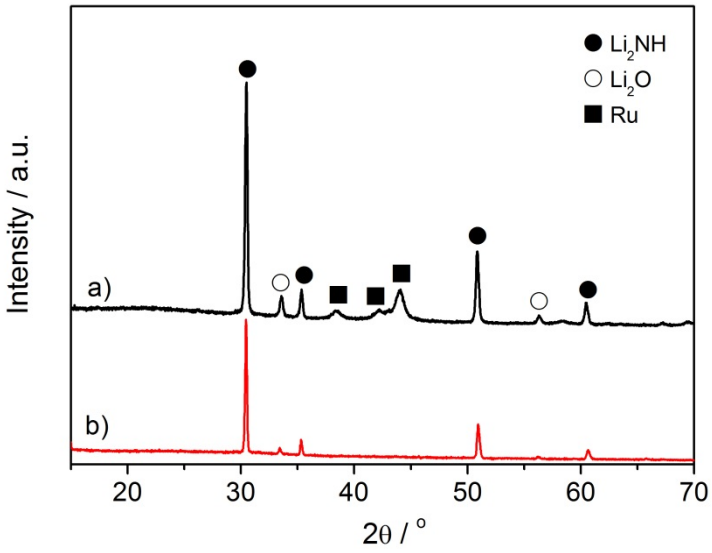


Figure S7. XRD patterns of post-TPD samples of 5 wt% Ru-$LiNH_2$ sample (a) and $LiNH_2$ (b). Reaction condition: sample loading – 20 mg, carrier gas – Ar, flow rate – 40 ml min^{-1}, heating to 723 K, ramping rate – 2K min^{-1}.

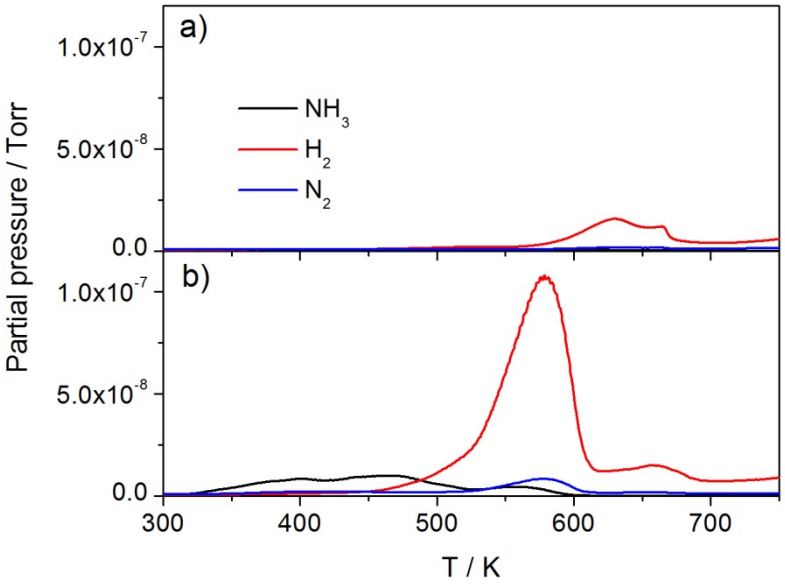


Figure S8. Temperature-Programmed-Decomposition (TPD) profiles of Ru-Li_2NH sample (a) prepared by ball milling Ru and Li_2NH with a molar ratio of 1:2, and 5 wt% Ru-$LiNH_2$ (b). Reaction condition: sample loading – 20 mg, carrier gas – Ar, flow rate – 40 ml min^{-1}, ramping rate – 2K min^{-1}.

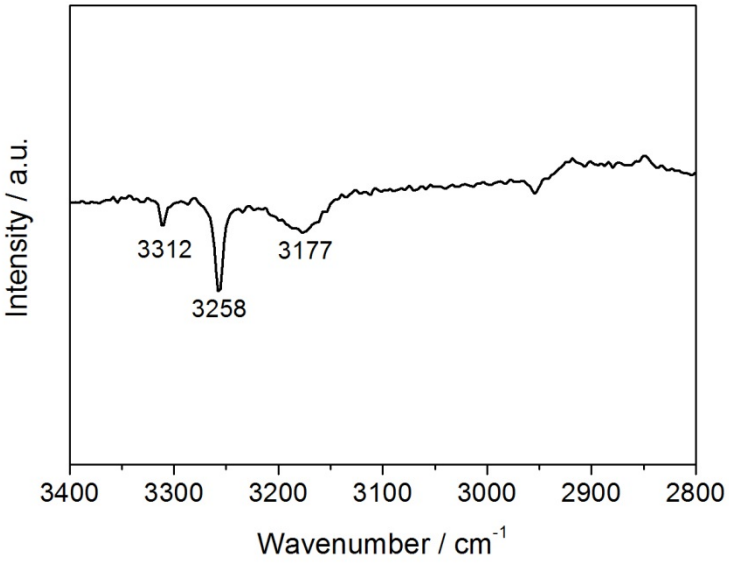


Figure S9. FTIR spectrum of $LiNH_2$-Ru/MgO after testing for decomposition of 5% NH_3/Ar. The sample was collected after reaction at 673 K followed by cooling rapidly to room temperature. The IR bands at 3258 and 3312 cm^{-1} are stretching vibrations of $LiNH_2$ and the band at 3177 cm^{-1} is the stretching vibration of Li_2NH.

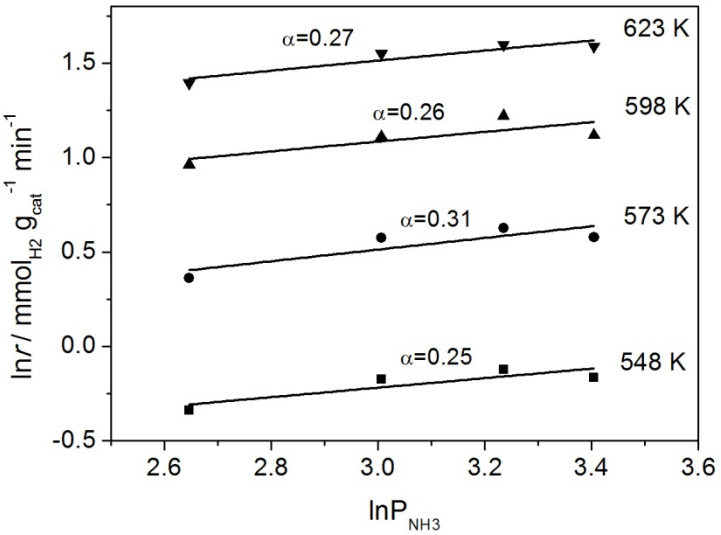
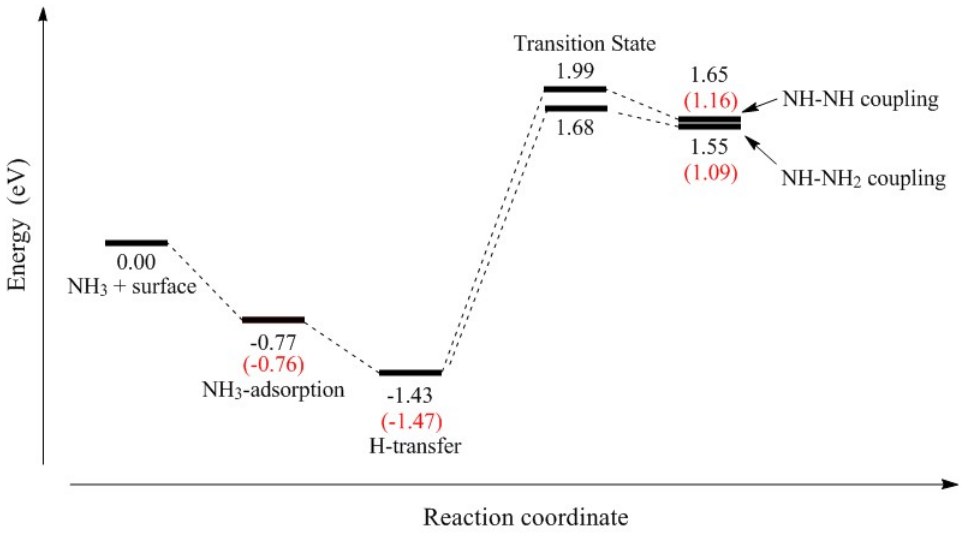
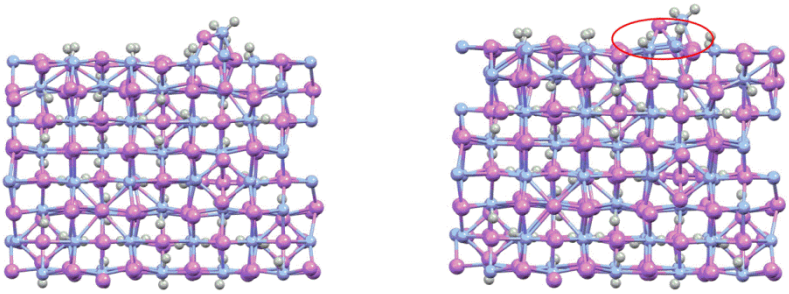


Figure S10. NH_3 reaction order α over 5 wt% Ru-$LiNH_2$ at different reaction temperatures. Reaction condition: sample loading – 30 mg, NH_3/Ar flow rate – 30 ml min^{-1}.

a)



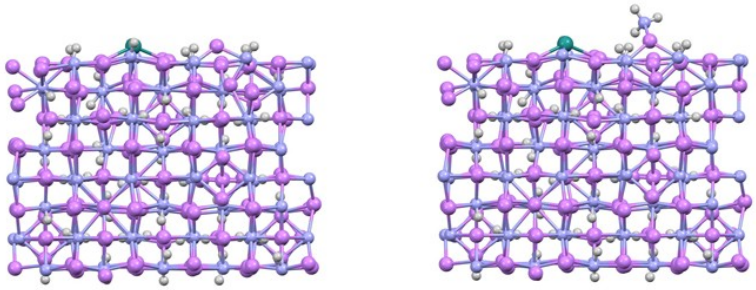
b)



Transition state of NH-NH coupling

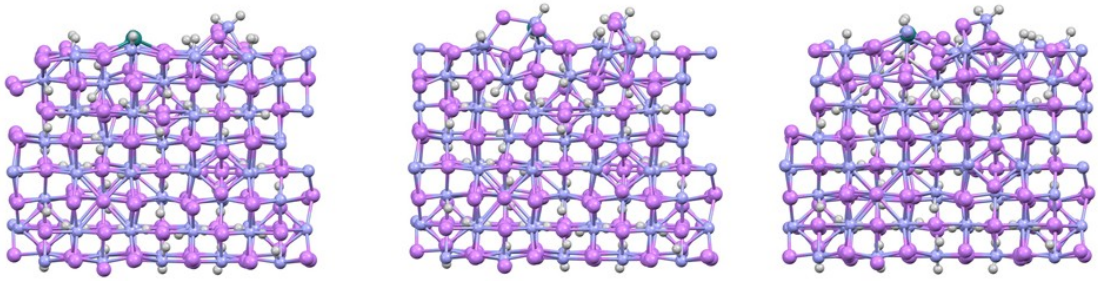
Final state of NH-NH coupling

c)



Ru-doped Li_2NH (110)

NH_3 adsorption



H transfer

NH-NH coupling

NH-NH_2 coupling

Figure S11. (a) Reaction pathway of NH_3 adsorption on the pristine and Ru-doped Li_2NH (110) surface and the follow-up NH-NH and NH-NH_2 coupling. The values in parentheses are the calculated energies for the Ru-doped Li_2NH surface. We did not simulate the NH_2-NH_2 coupling because of the less chance of occurrence. (b) The models of the transition state and final state of NH-NH coupling simulated from DFT calculations. (c) The models of Ru-doped Li_2NH, and NH_3 adsorption, H transfer, NH-NH coupling, NH_2-NH_2 coupling over Ru-doped Li_2NH (110) surface. Li, N, H and Ru atoms are represented as purple, light blue, grey and dark green spheres, respectively.

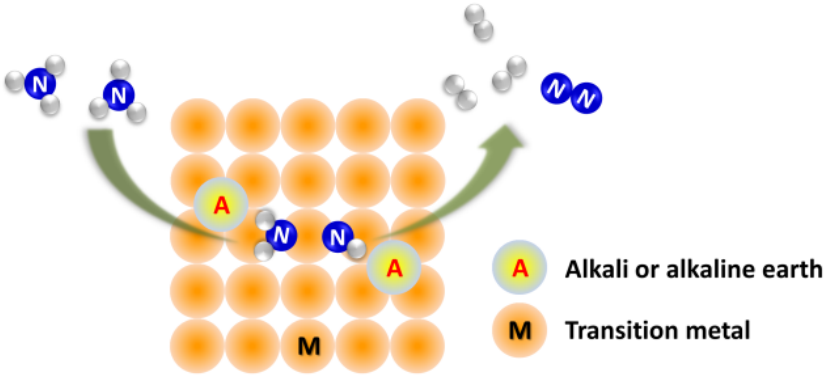


Figure S12. Scheme of NH_3 decomposition on alkali or alkaline earth metal amide – transition metal composites.

Reference

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