Supplemental Information

Acid-durable Electride with Layered Ruthenium for Ammonia Synthesis: Boosting the Activity via Selective Etching

Jiang Li,[a,*] Jiazhen Wu,[a,*] Haiyun Wang,[b] Yangfan Lu,[a] Tiannan Ye,[a] Masato Sasase,[a] Xiaojun Wu,[#,b] Masaaki Kitano,[#,a] Takeshi Inoshita,[a] and Hideo Hosono[#,a]

[a] Materials Research Center for Element Strategy, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

[b]Hefei National Laboratory for Physical Sciences at the Microscale, Synergetic Innovation of Quantum Information & Quantum Technology, School of Chemistry and Materials Science, CAS Key Laboratory of Materials for Energy Conversion, and CAS Center for Excellence in Nanoscience, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

[*] These authors contributed equally.

[#]To whom correspondence should be addressed.

E-mail: hosono@msl.titech.ac.jp; kitano.m.aa@m.titech.ac.jp; xjwu@ustc.edu.cn

Experimental Details

Sample Preparation. LnRuSi, $LaRu_2Si_2$, LaSi and La_5Si_3 were synthesized by arc-melting the corresponding rare-earth, ruthenium and silicon ingots with corresponding stoichiometric ratios under an argon atmosphere. The melting process was repeated 5 times to ensure homogeneity, and the weight loss was less than 0.1% for each sample after the melting process. The ingots obtained were silver colored and were ground using an agate motor in an Ar-filled glove box. As-melted LnRuSi and La_5Si_3 were not single phase and were purified by annealing at 1000 °C for two weeks.

Selective Chemical Etching. Disodium dihydrogen ethylenediaminetetraacetate (EDTA-2Na), HCl, HNO_3 and HCOOH aqueous solutions were used for the selective etching of LnRuSi. Typically, 0.2 g of catalyst was placed into 10 mL of acid solution, and stirred for 0.5–24 hours. The catalyst was then separated by centrifugation, washed once with distilled water, 3 times with ethanol, and dried in a vacuum at room temperature for 1 h.

Ammonia Synthesis Reactions. Ammonia synthesis reactions were conducted in a silica tube reactor supplied with an ultrapure mixture of $N_2/H_2 = 1/3$ (purity >99.99995% for both gases).[1] The concentration of ammonia in the stream that left the catalyst bed (0.1 g catalyst) was monitored under steady-state conditions of temperature (260 to 400 °C), gas flow rate (60 $mL{\cdot}min^{-1}$) and pressure (0.1 to 0.9 MPa). All kinetic experiments were conducted far from equilibrium conditions (for example, the conversion level was less than 20% of that at equilibrium). The reaction orders with respect to N_2 and H_2 were obtained at a constant flow rate (60 $mL{\cdot}min^{-1}$) using Ar gas (purity >99.99999%) as a diluent, and that for NH_3 was determined with a $3H_2+N_2$ mixture by changing the synthesis gas flow rate. The produced ammonia was trapped in 5 M sulfuric acid solution and the amount of NH_4^+ generated in the solution was determined using ion chromatography (Prominence, Shimadzu, Japan) with a conductivity detector.

TOF was calculated from the reaction rate derived by the number of Ru atoms exposed to the catalyst surface. CO/H_2 cannot be well adsorbed on the bulk catalysts; therefore, the estimation was performed using the surface area (S_{BET}) and Wigner-Seitz radii (r_{ws}) as the averaged radii for the bulk compounds. Here r_{ws} is given by $(3V/4N\pi)^{1/3}$, where V and N are the unit cell volume and the number of atoms involved, respectively. The estimated numbers of active sites for various bulk catalysts are given in Table S1.

Characterization. The crystal structure and crystal quality were confirmed by powder X-ray diffraction (XRD) measurements using an X-ray diffractometer (D8 Advance, Bruker) with monochromatic Cu Kα radiation ($\lambda = 0.15418$ nm). The Brunauer-Emmett-Teller (BET) surface areas of the catalysts were determined from nitrogen adsorption/desorption isotherm measurements at –196 °C using a gas-adsorption instrument (BELSORP-mini II, MicrotracBEL, Japan) after evacuation of the samples at 200 °C. The amounts of dissolved La, Ru and Si species during the etching process were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES; ICPS-8100, Shimadzu). X-ray photoelectron spectroscopy (XPS; ESCA-3200, Shimadzu, Japan) measurements were performed using Mg K α radiation at $<10^{-6}$ Pa (8 kV bias voltage applied to the X-ray source). The as-prepared and used catalysts were pressed into pellets with a diameter of 10 mm (ca. 0.1 g) in a glove box, and then transferred into the XPS chamber without exposure to the ambient atmosphere. The binding energy of each spectrum was corrected according to the C 1s peak (284.6 eV). The surface morphologies of the catalyst samples were investigated using scanning electron microscopy (SEM; JEOL JSM-7600F) and high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM; JEOL ARM200F) with an operate voltage of 200 kV. For SEM measurements, powder samples were fixed on carbon tape on a sample stage, while for STEM measurements, the samples were dispersed in hexane, and the suspension was dropped on a carbon-coated copper TEM grid in an Ar-filled glove box.

DFT Calculations. All calculations were performed using the DFT method with the generalized gradient approximation (GGA) expressed by the Perdew, Burke, and Ernzerhof (PBE) functional, which is implemented in the Vienna ab initio simulation package (VASP).[2-5] The energy cutoff was set to be 500 eV. The energy and force convergence criterions were set to 10^{-4} eV and 0.05 eV/Å, respectively. The first Brillouin zone was sampled with a 3×3×1 *k*-point mesh. Dipole corrections were adopted to take account of the asymmetric layer arrangement in the process of slab calculations. The climbing-image nudged elastic band (CI-NEB) method was employed to search the energy barriers for N_2 dissociation on the surface of LaRuSi (001) with a force convergence criterion of 0.05 $\mathrm{eV \cdot Å^{-1}}$.[6]

The adsorption energy of nitrogen species on the LaRuSi (001) surface is defined as $E_{\mathrm{ad}}(X) = E_{\mathrm{tot}}(X/\mathrm{surface}) - E_{\mathrm{tot}}(\mathrm{X}) - E_{\mathrm{tot}}(\mathrm{surface})$, where $E_{\mathrm{tot}}(\mathrm{X/surface})$, $E_{\mathrm{tot}}(\mathrm{X})$ and $E_{\mathrm{tot}}(\mathrm{surface})$ are the total energies of the X (i.e. N or N_2)-adsorbed surface, the X species, and the surface, respectively. To reveal the charge transfer between nitrogen and the surface, the charge density difference between pure and nitrogen-adsorbed LaRuSi(001) surfaces was calculated, which is defined as $\Delta\rho = \rho(X/\mathrm{surface}) - \rho(X) - \rho(\mathrm{surface})$, where $\rho(X/\mathrm{surface})$, $\rho(X)$ and $\rho(\mathrm{surface})$ are the calculated charge densities of the adsorption configuration, an X molecule or atom and the LaRuSi(001) surface, respectively.

The LaRuSi(001) surface was described with a slab mode having a vacuum gap of 20 Å. During the geometric optimization, the forces on the atoms were less than 0.02 eV/Å. The energy cutoff was selected to be 600 eV, and 11×11×7 and 11×11×1 *k*-point meshes were set for the bulk and slabs, respectively. The cleavage energy E_c, of the surface is defined as $E_c = E_{slab} - E_{bulk}$, where E_{bulk} is the total energy of a 1×1×10 bulk supercell after structural optimization, and E_{slab} is the total energy of a slab with 10 layers of bulk.

Table S1. Estimation of the number of active sites for selected bulk catalysts. Since CO cannot be well adsorbed on the bulk catalysts, the estimation was made by using surface area (S_{BET}) and the covalent radii of active atoms and Wigner-Seitz radii (r_{ws}) as the averaged radii for the bulk compounds.

Catalyst	r_{ws} [a] (Å)	Active sites (sites·cm^{-2})	S_{BET} (m^2·g^{-1})	Active sites (sites·g^{-1})
LaRuSi before EDTA	1.71	3.61×10^{14}	1.4	5.06×10^{18}
LaRuSi after EDTA	1.71	3.61×10^{14}	4.2	1.52×10^{19}
CeRuSi before EDTA	1.69	3.71×10^{14}	1.6	5.94×10^{18}
CeRuSi after EDTA	1.69	3.71×10^{14}	4.0	1.48×10^{19}
PrRuSi before EDTA	1.69	3.72×10^{14}	1.5	5.59×10^{18}
PrRuSi after EDTA	1.69	3.72×10^{14}	2.0	7.45×10^{18}
NdRuSi before EDTA	1.68	3.74×10^{14}	1.5	5.62×10^{18}
NdRuSi after EDTA	1.68	3.74×10^{14}	2.2	8.24×10^{18}
Ru powder	1.48	1.45×10^{15}	3.1	4.48×10^{19}
YRu_2 [b]	1.61	8.19×10^{14}	0.7	5.89×10^{18}
YRu_2 [b]	1.61	8.19×10^{14}	6.4	5.24×10^{19}
LaCoSi [c]	1.68	3.76×10^{14}	1.8	6.77×10^{18}
Co_3Mo_3N [c]	1.42	1.35×10^{15}	8.5	1.15×10^{20}

a: r_{ws} is given by $(3V/4N\pi)^{1/3}$, where V and N are the unit cell volume and the number of atoms involved, respectively.

b: Ref. 26.

c: Ref. 21.

Table S2. Catalytic activities for LnRuSi catalysts milled with different time and other reported catalysts. The activity is measured at 400 °C for 0.1 g catalysts at 0.1 MPa with $H_2/N_2 = 45/15$ $\mathrm{ml \cdot min^{-1}}$ flow.

Catalyst	S_{BET} ($\mathrm{m^2 \cdot g^{-1}}$) [c]	Activity ($\mathrm{\mu mol \cdot g^{-1} \cdot h^{-1}}$) [d]	Specific activity ($\mathrm{\mu mol \cdot m^{-2} \cdot h^{-1}}$)	NH_3 yield (%) [e]	Ref.
LaRuSi-0.5h	1.4	1750	1250	0.218	This work
LaRuSi-1.0h	1.8	1810	1010	0.225	This work
LaRuSi-1.0h [a]	1.8	990	550	0.492	This work
LaRuSi-2.0h	2.2	1800	820	0.224	This work
CeRuSi-0.5h	1.6	1680	1050	0.209	This work
PrRuSi-0.5h	1.5	1180	780	0.146	This work
NdRuSi-0.5h	1.5	670	450	0.083	This work
Ru powder	3.1	23	7.4	0.0028	This work
YRu_2 [b]	0.7	490	680	0.121	26
YRu_2	6.4	3320	520	0.413	26
LaCoSi	1.8	1250	690	0.156	21
Co_3Mo_3N	8.5	800	90	0.099	21
Cs-Ru/MgO [b]	12	3400	280	0.846	14
$Fe\text{-}K_2O\text{-}Al_2O_3$ [a]	14	330	24	0.164	31

a: Catalyst amount is 0.4 g.
b: Catalyst amount is 0.2 g.
c: Measured after ammonia synthesis.
d: Measured after keeping at 400 °C for 24 h.
e: NH_3 yield = Produced NH_3/theoretical NH_3 production of full conversion.

Table S3. Catalytic activities for various catalysts. The activity is measured at 400 ^{o}C for 0.1 g catalysts at 0.1 MPa with H_2/N_2 = 45/15 ml·min^{-1} flow.

Catalyst	S_{BET} ($m^2 \cdot g^{-1}$)	Ammonia formation rate ($\mu mol \cdot g^{-1} \cdot h^{-1}$)
La_5Si_3	1.5	0
LaSi	1.6	0
$LaRu_2Si_2$	1.5	0
LaScSi	2.0	0

Table S4. Catalytic activities for LaRuSi catalysts. The activity is measured for 0.1 g catalysts at 0.1 MPa with H_2/N_2 = 45/15 ml·min^{-1} flow after holding at 400 °C for 24 h.

Entry	Catalyst	Ammonia formation rate (μmol·g^{-1}·h^{-1})
1	As prepared LaRuSi	1810
2	LaRuSi in air for 6 months	1800
3	LaRuSi in H_2O for 24 h [a]	1760
4	Used catalyst in air for 1 year	1780

a: after stirred in water for 24 h, the catalyst was separated by centrifugation and dried in vacuum.

Table S5. Catalytic activities for LaRuSi catalysts with EDTA treatment. The activity is measured at 400 °C for 0.1 g catalysts at 0.1 MPa with H_2/N_2 = 45/15 ml·min^{-1} flow.

Entry	Catalyst	Ammonia formation rate (μmol·g^{-1}·h^{-1})
1	LaRuSi after EDTA [a]	5100
2	LaRuSi after EDTA without wash [b]	3160
3	LaRuSi mixed with 5wt% EDTA-2Na [c]	0

a: EDTA treated for 3.5 h, then washed with water and ethanol.
b: EDTA treated for 3.5 h, without any further wash process.
c: LaRuSi and EDTA-2Na were mixed and milled in an agate mortar for 0.5 h.

The residual EDTA-2Na has a negative influence on the catalytic performance of LaRuSi.

Table S6. Reaction orders for various catalysts.

Catalyst	α (N_2)	β (H_2)	γ (NH_3)	Reference
LaRuSi before EDTA	0.98	0.66	−1.05	27
LaRuSi after EDTA	0.93	0.62	−0.85	This work
YRu_2	0.94	0.81	−0.73	26
Ru	1.11	−0.54	−0.19	26
Co_3Mo_3N	0.99	0.80	−1.34	31
$Fe\text{-}K_2O\text{-}Al_2O_3$ (KM1)	0.96	1.41	−0.80	31
$Ru/Ba/Ca(NH_2)_2$	0.96	0.75	−0.92	S7
Ru-Cs/MgO	1.10	−0.50	−0.35	S7

Table S7. Dissolved species in the centrifugal solution after EDTA treatment of LaRuSi measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Sample	Concentration (mM)		
	La	Ru	Si
5 mM EDTA-2Na	0	0	0.006
LaRuSi-EDTA	4.611	0.145	3.633

Table S8. The distance of neighboring ruthenium in different intermetallic compounds and Ru metal.

Catalyst	$d_{\text{Ru-Ru}}$ (nm)
LaRuSi	0.298
CeRuSi	0.297
PrRuSi	0.296
NdRuSi	0.297
YRu_2	0.264
Ru	0.265

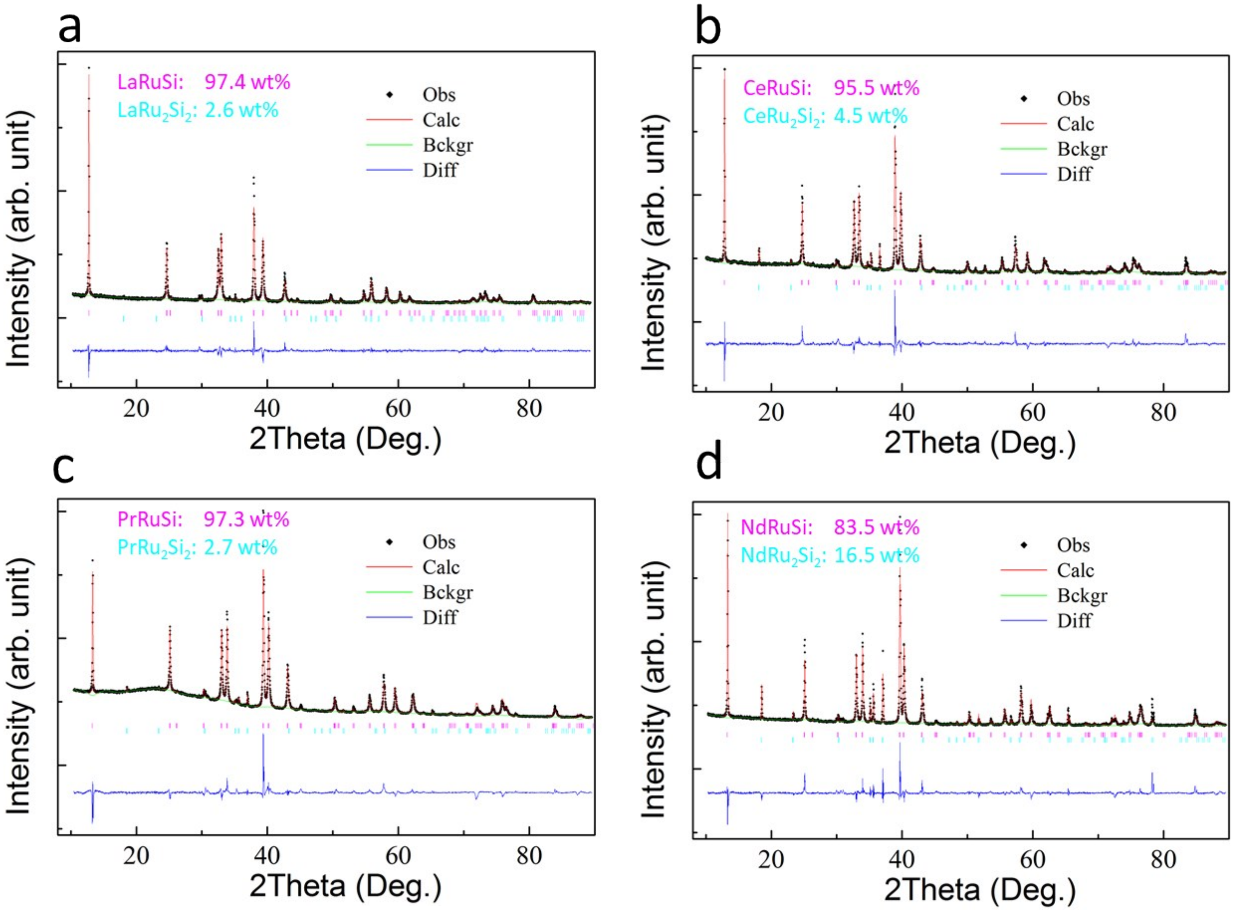


Figure S1. Powder XRD patterns with Rietveld refinement for (a) LaRuSi, (b) CeRuSi, (c) PrRuSi and (d) NdRuSi.

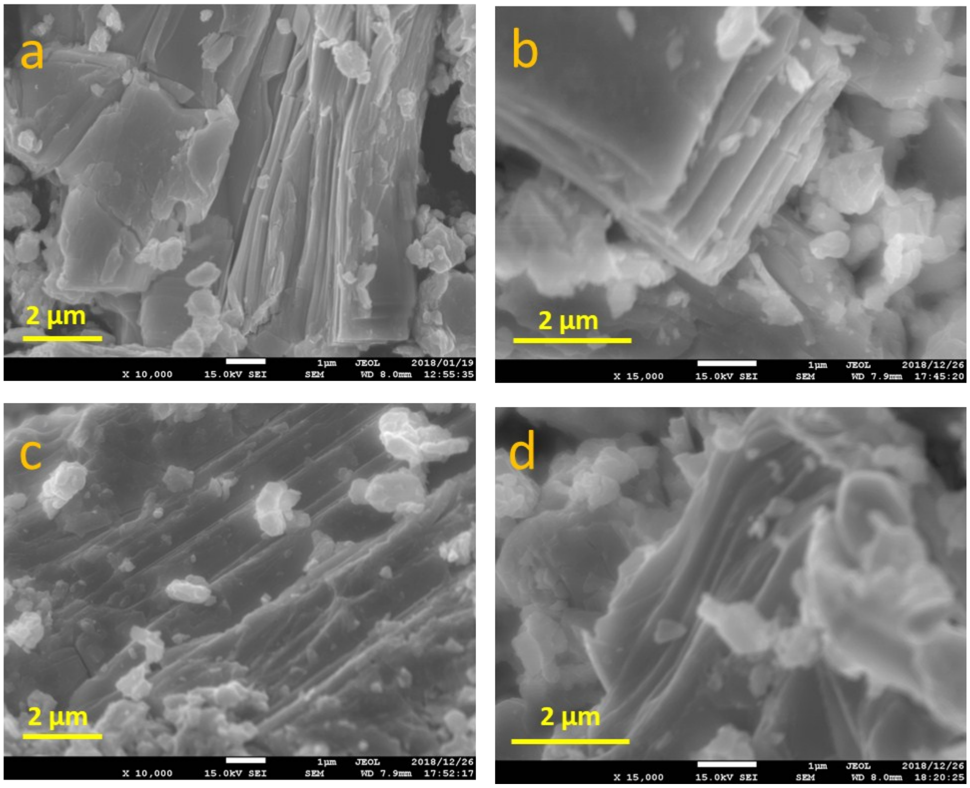


Figure S2. SEM pictures for (a) LaRuSi, (b) CeRuSi, (d) PrRuSi and (d) NdRuSi catalysts.

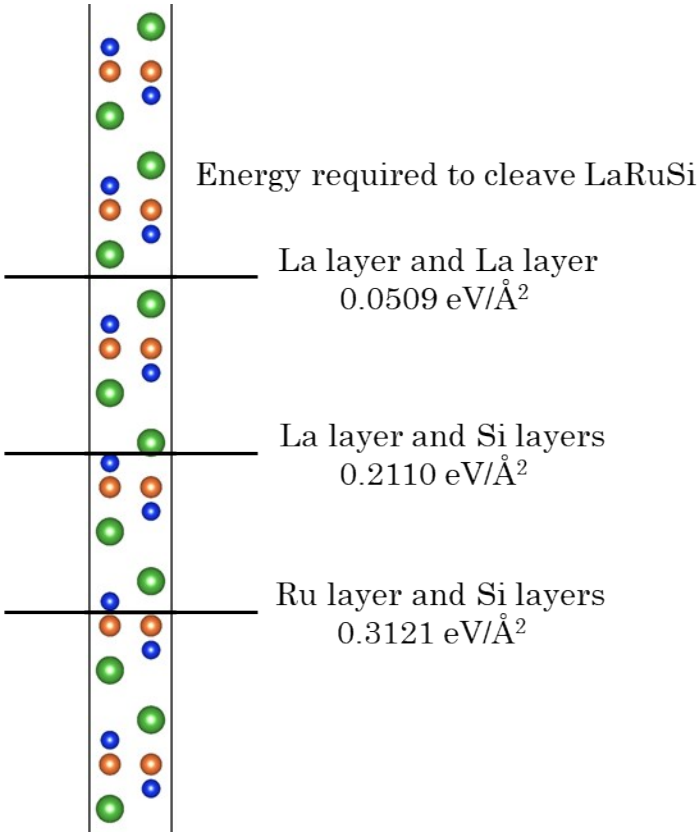


Figure S3. Cleavage energy between different layers of LaRuSi by DFT calculations.

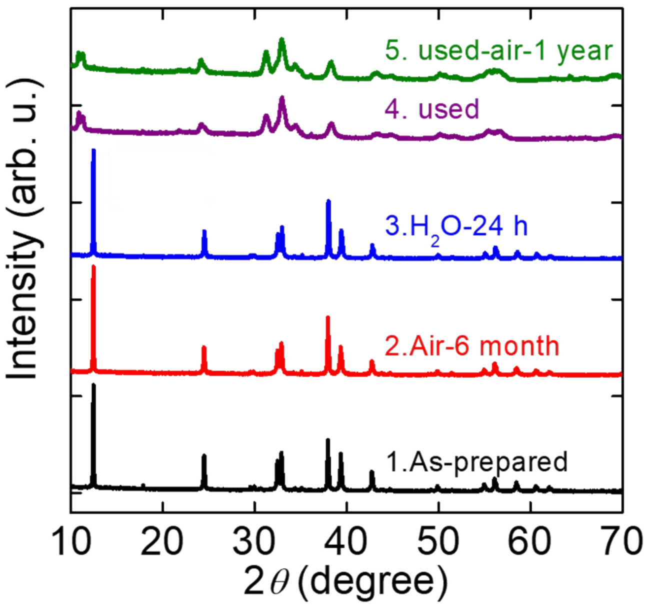


Figure S4. XRD patterns for LaRuSi catalysts. (1) As-prepared, (2) stored in the air for 6 months, (3) treated with water for 24 hours, (4) LaRuSi used for ammonia synthesis and (5) the used sample stored in the air for 1 year.

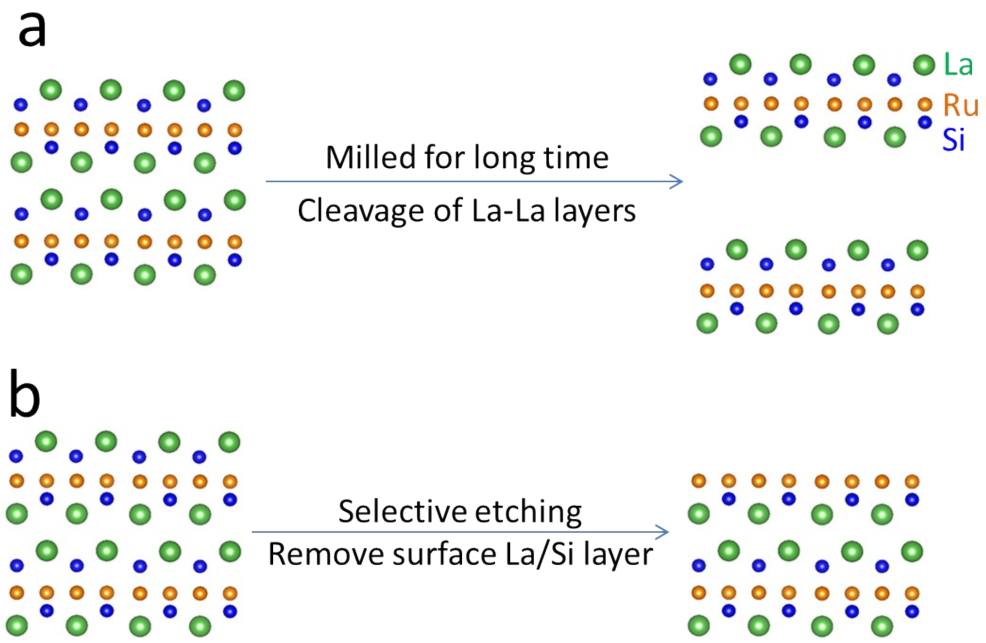


Figure S5. Schematic diagram for (a) cleavage process by milling and (b) selective etching process.

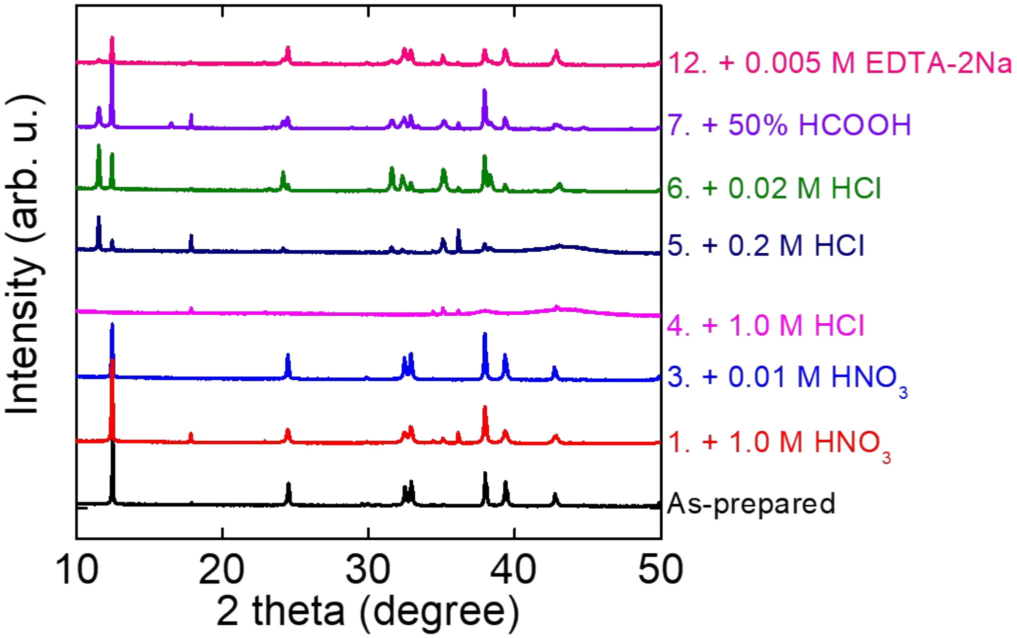


Figure S6. XRD patterns for LaRuSi after chemical etching with different acid solutions. The numbers are the entries shown in Table 1.

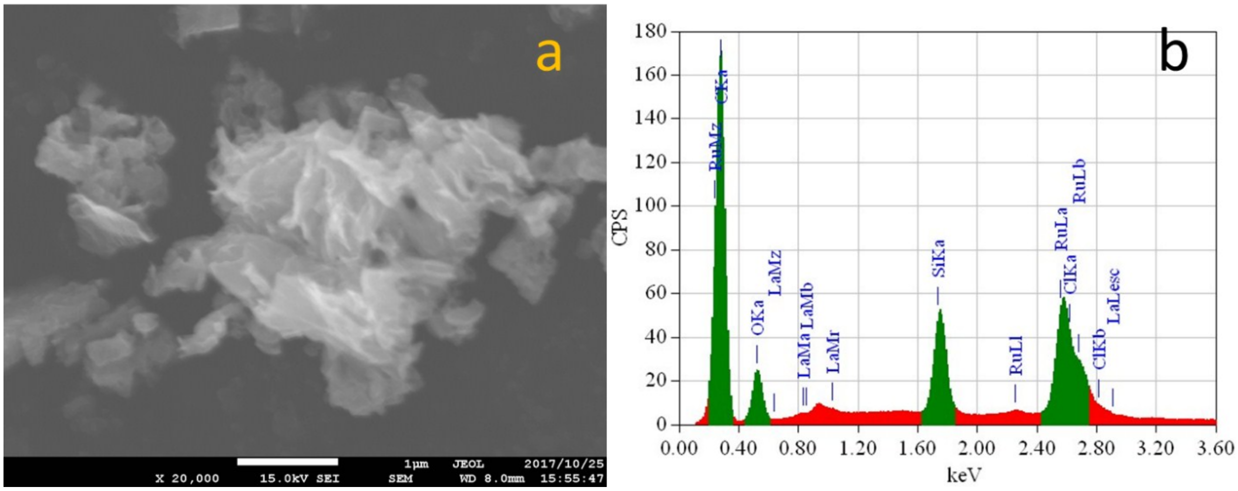


Figure S7. (a) SEM and (b) EDS measurements for LaRuSi treated with 1 M HCl acid for 5 h. Most of La were removed and high surface area Ru-Si compound was formed.

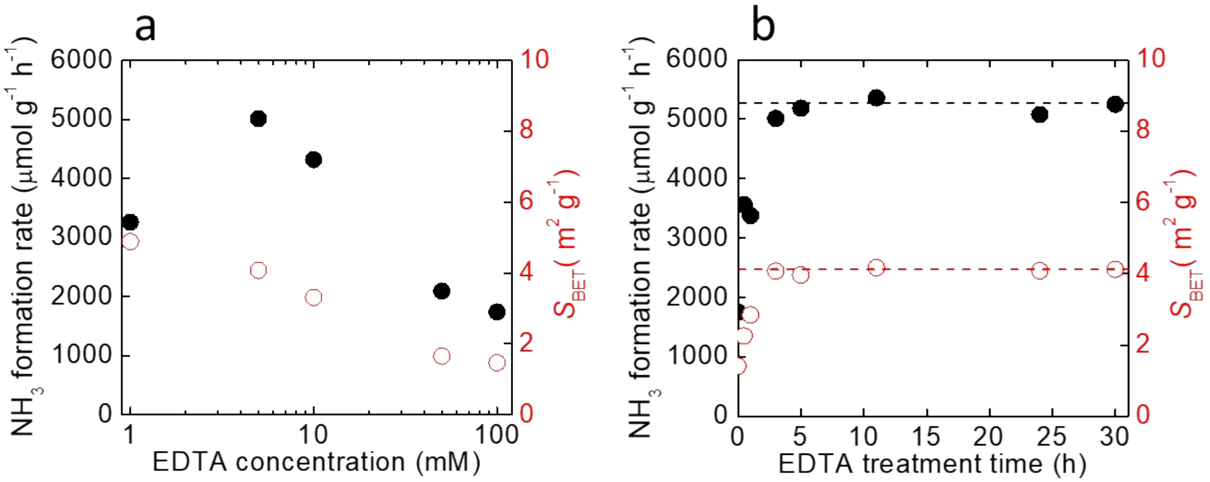


Figure S8. Catalytic performance and surface area for the EDTA-2Na treated LaRuSi. LaRuSi treated with (a) different concentration solution for 3 h, and (b) 5 mM EDTA-2Na solution for different time. The activity is measured at 400 °C for 0.1 g catalysts at 0.1 MPa with $H_2/N_2 = 45/15$ ml min^{-1}.

We found that 5mM EDTA-2Na was the best solution for selective etching. When the LaRuSi was treated in 5 mM EDTA-2Na solution, both the surface area and ammonia formation rate of the resultant catalyst increased dramatically at initial 3 hours, and reached constant values. The optimum values were determined to be around 4.1 m^2·g^{-1} and 5200 μmol·g^{-1}·h^{-1}, respectively.

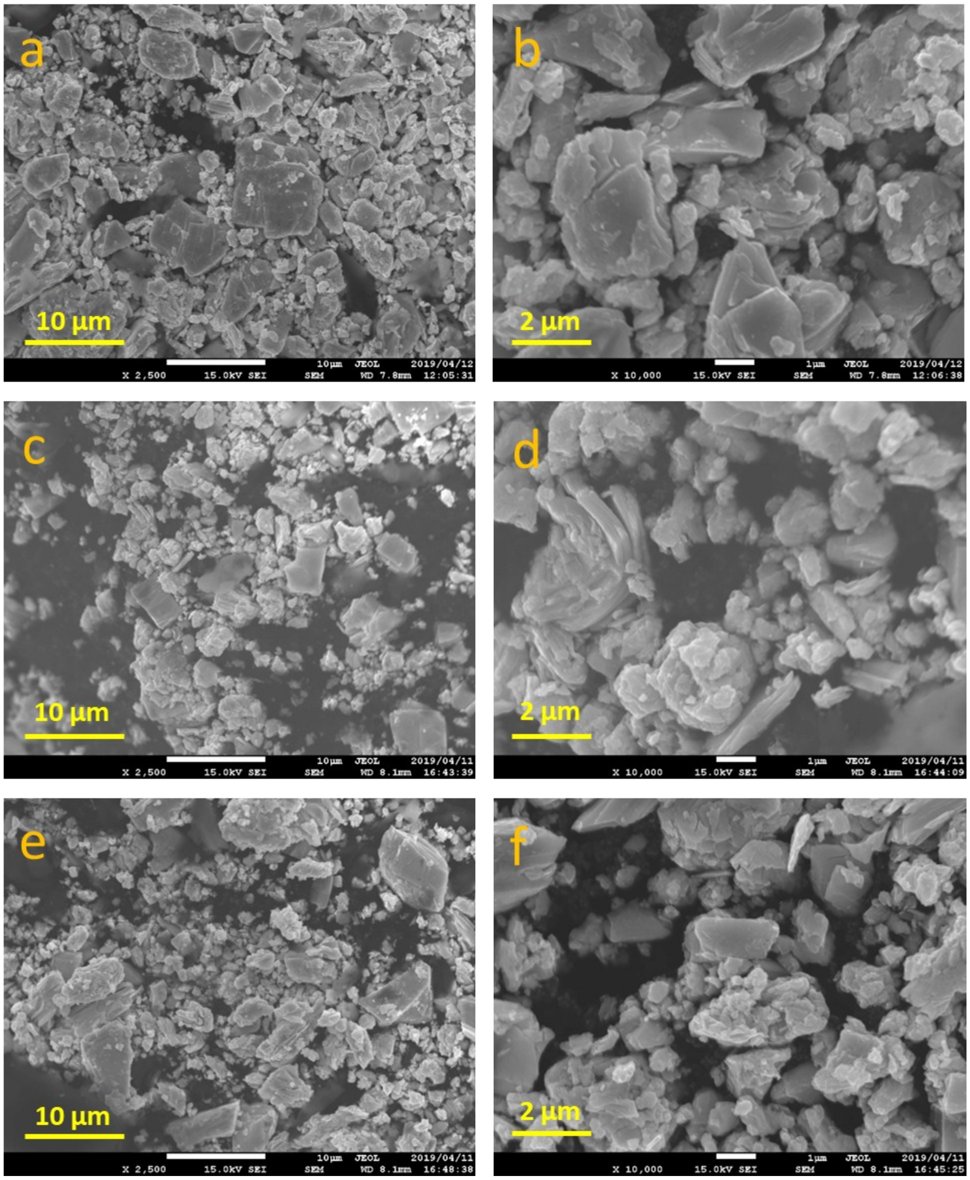


Figure S9. SEM pictures for LaRuSi catalyst. (a) and (b) for as prepared catalyst, (c) and (d) for the catalyst after EDTA treatment, (e) and (f) for the EDTA treated catalyst after ammonia synthesis.

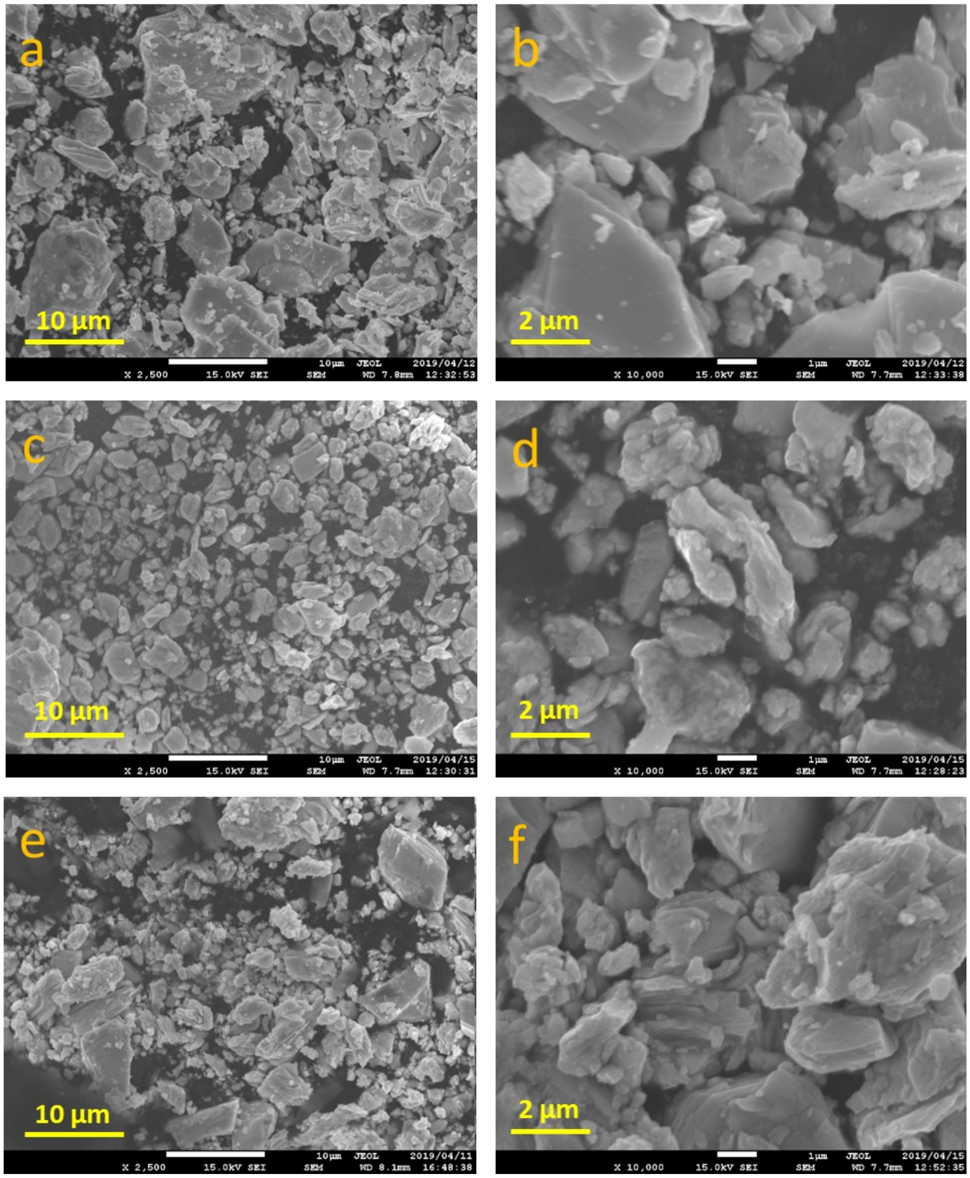


Figure S10. SEM pictures for CeRuSi catalyst. (a) and (b) for as prepared catalyst, (c) and (d) for the catalyst after EDTA treatment, (e) and (f) for the EDTA treated catalyst after ammonia synthesis.

Figure S11. SEM pictures for PrRuSi catalyst. (a) and (b) for as prepared catalyst, (c) and (d) for the catalyst after EDTA treatment, (e) and (f) for the EDTA treated catalyst after ammonia synthesis.

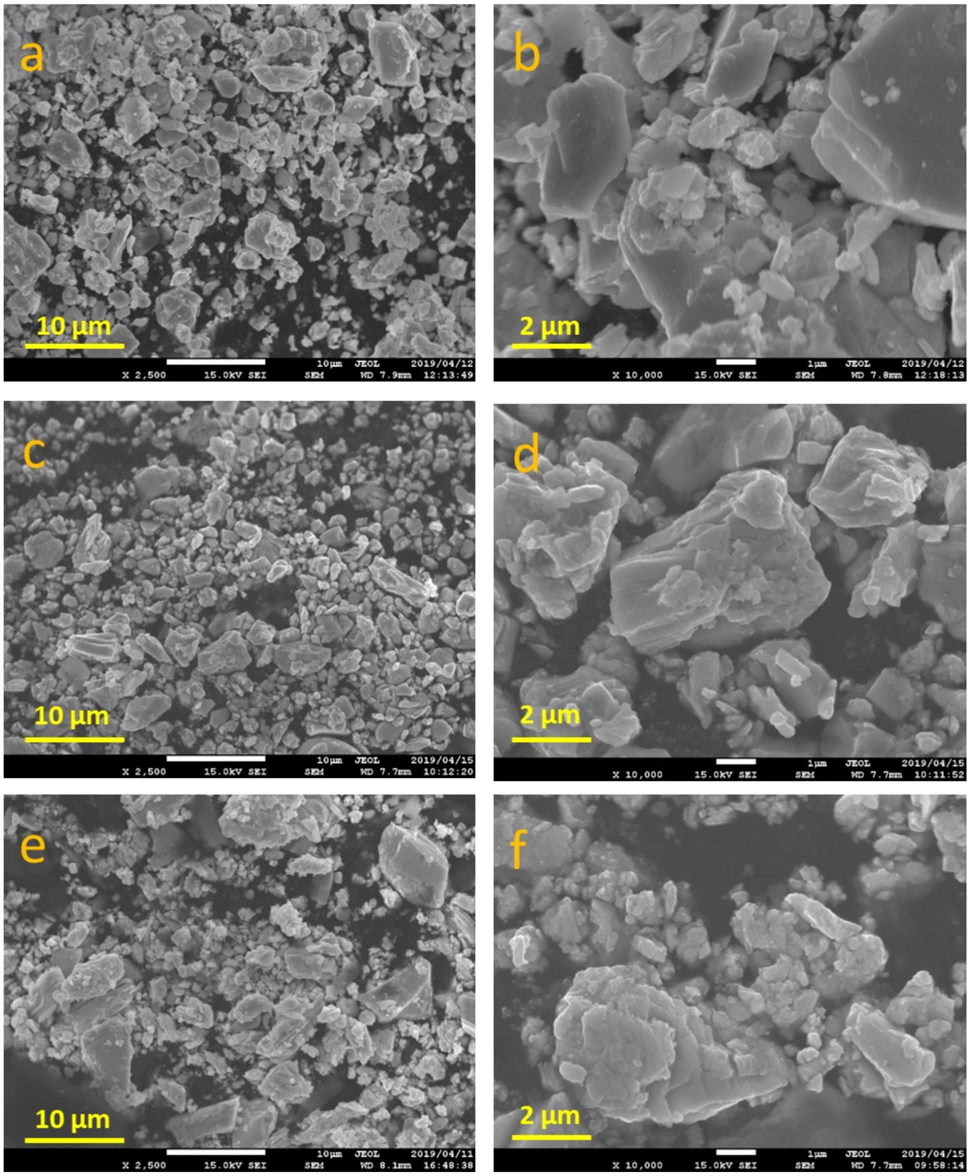


Figure S12. SEM pictures for NdRuSi catalyst. (a) and (b) for as prepared catalyst, (c) and (d) for the catalyst after EDTA treatment, (e) and (f) for the EDTA treated catalyst after ammonia synthesis.

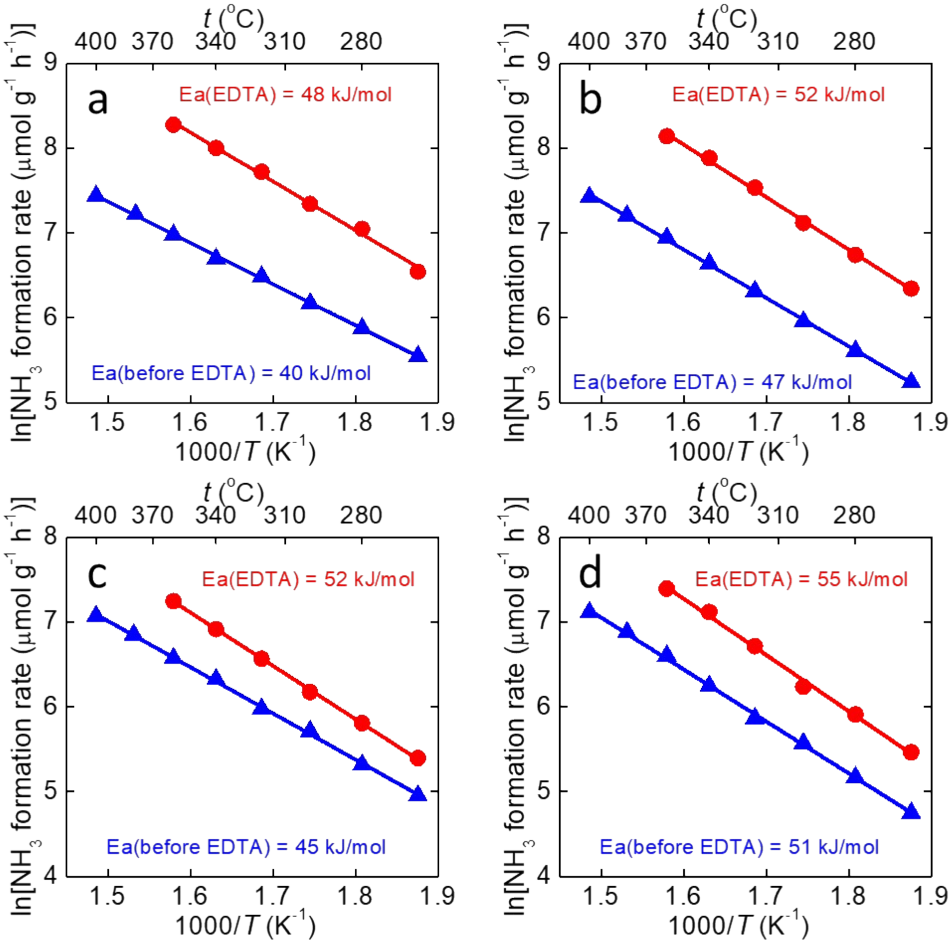


Figure S13. Arrhenius plots for the ammonia synthesis over (a) LaRuSi, (b) CeRuSi, (c) PrRuSi and (d) NdRuSi before and after EDTA treatment at 0.1 MPa.

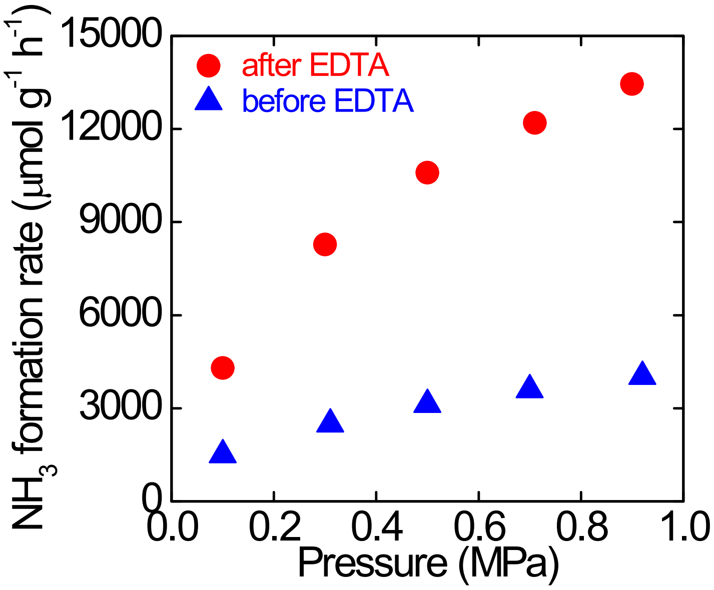


Figure S14. Pressure effects for the ammonia synthesis over LaRuSi before and after EDTA treatment at 400 ^{o}C.

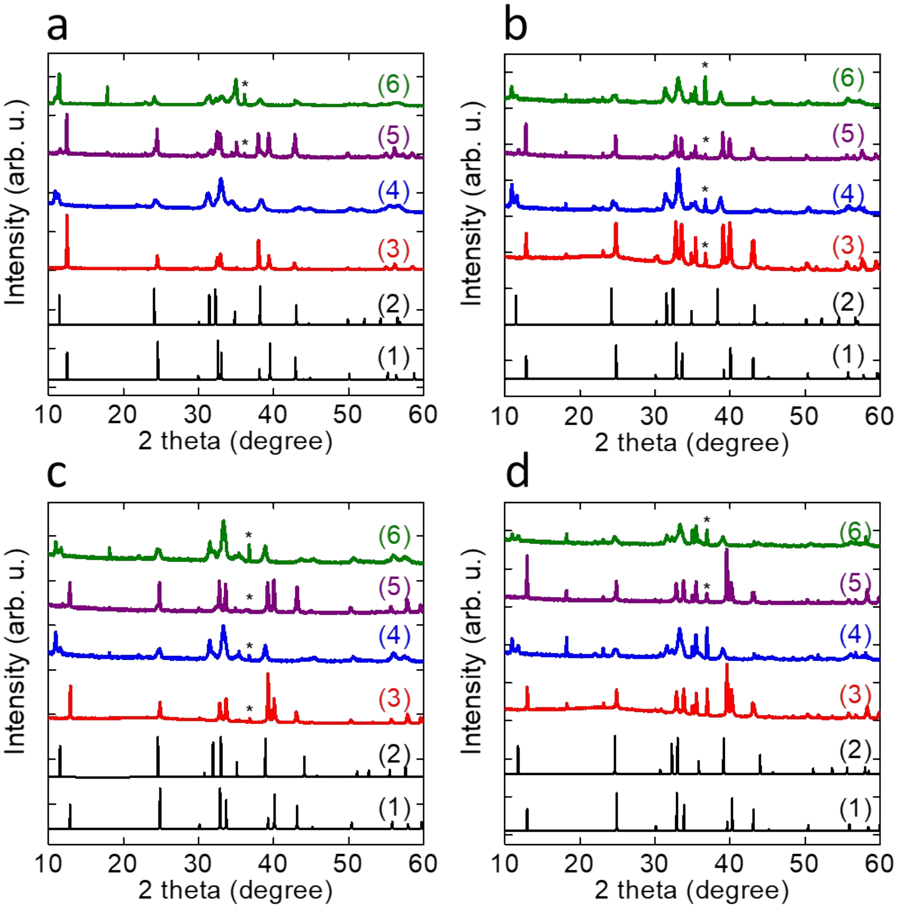


Figure S15. XRD patterns for (a) LaRuSi, (b) CeRuSi, (c) PrRuSi and (d) NdRuSi catalysts. (1) and (2) are simulated LnRuSi and LnRuSiH$_x$ XRD patterns, respectively; (3) and (4) are catalysts without EDTA treatment before and after ammonia synthesis, respectively; (5) and (6) are catalysts with EDTA treatment before and after ammonia synthesis, respectively. All catalysts were operated for ammonia synthesis more than 80 hours. The peak mark with a star at 36° –37° indicates the 122 impurity phase.

Although LnRuSi and LnRu$_2$Si$_2$ belong to different space group, the packing of the atoms is quite similar.[27] By removing one Ln layer, LnRuSi can convert into LaRu$_2$Si$_2$. Present ICP measurement confirmed that the amount of removed La was higher than Si during EDTA treatment. Therefore, LaRu$_2$Si$_2$ could be formed at silicon rich sites during ammonia synthesis for the EDTA treated LaRuSi.

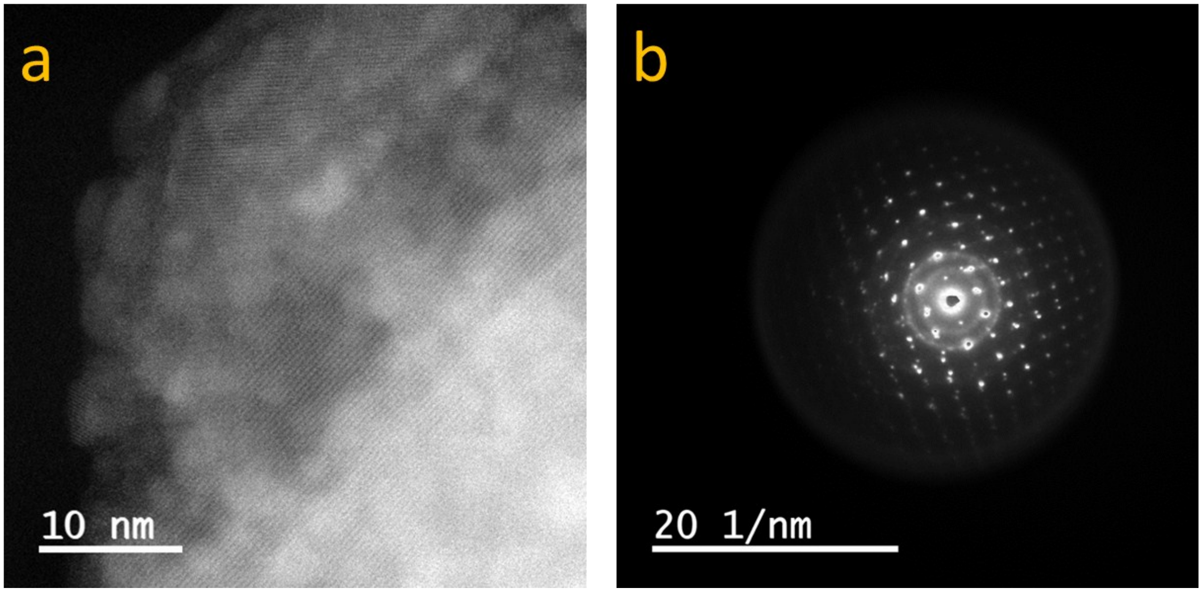


Figure S16. (a) HAADF-STEM images and (b) its corresponding diffraction pattern for the EDTA treated LaRuSi catalyst after ammonia synthesis.

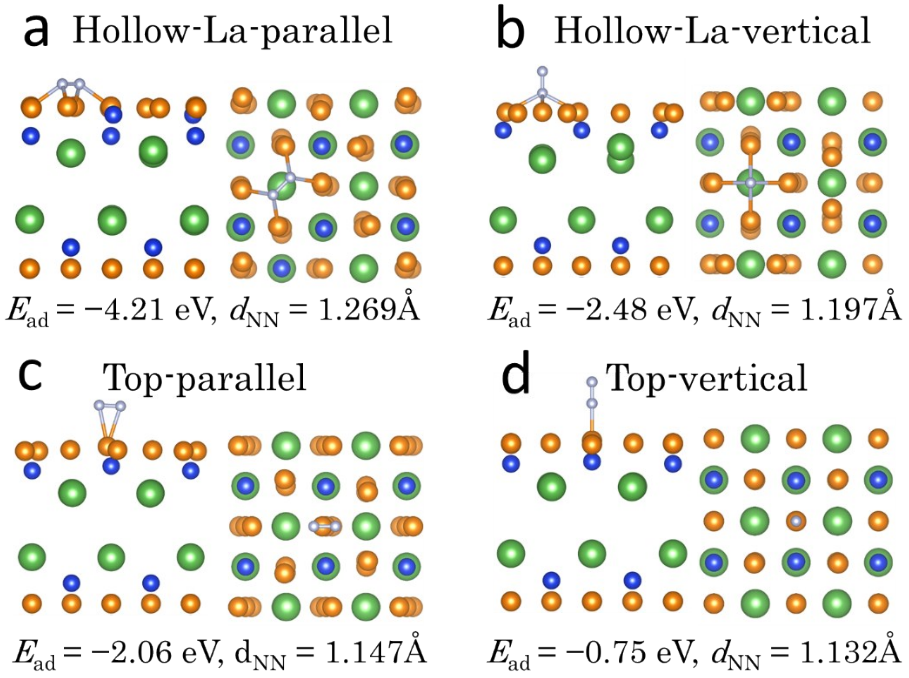


Figure S17. The optimized adsorption configurations of N_2 molecule on the LaRuSi (001)-Ru surface. Parallel (a, c) and vertical (b, d) adsorption configurations are presented. The calculated adsorption energies and the N-N bond lengths are indicated in the figures. (Green: La, Orange: Ru, Blue: Si, gray: N).

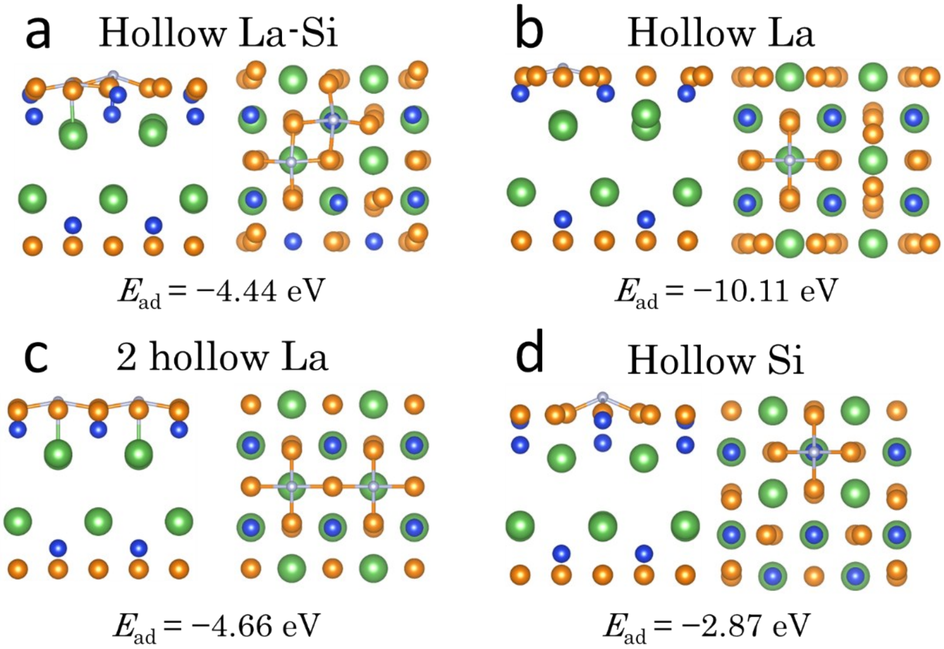
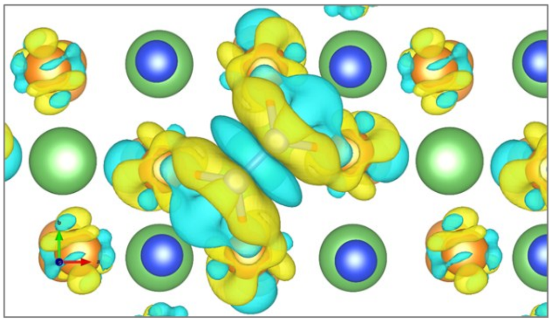


Figure S18. The optimized adsorption configurations of N atoms on the LaRuSi (001)-Ru surface. The calculated adsorption energies are indicated in the figures. (Green: La, Orange: Ru, Blue: Si, gray: N).

a. Hol-La-para



b. Hol-La-Si

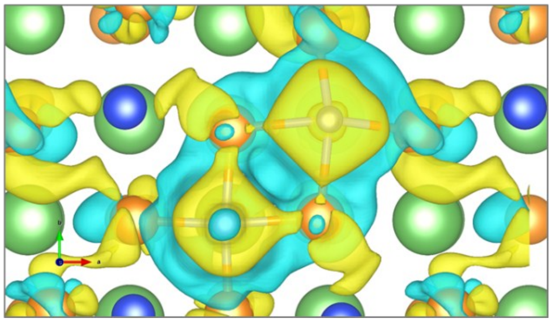


Figure S19. The deformation charge density of (a) parallel N_2 adsorption at the hollow La site and (b) N atom adsorption at the hollow La and Si sites on the LaRuSi (001)-Ru surface. Yellow indicates the increase in charge density, while light blue indicates the decrease in charge density.

Reference S

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