## Electro-catalytic synthesis of ammonia by surface proton hopping

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### **ESI (Electronic Supplementary Information)**

#### Methods

**Preparation for catalyst supports.** Various oxides (CeO<sub>2</sub>, ZrO<sub>2</sub>, Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>, SrZrO<sub>3</sub>, and SrCeO<sub>3</sub>) are used as catalyst supports. Catalyst supports were prepared using a complex polymerization method. First, ethylene glycol and citric acid were measured in an amount of 3 mol of metallic amount, and dissolved in distilled water. Then, metal nitrate (Ce(NO<sub>3</sub>)<sub>2</sub> (6H<sub>2</sub>O), ZrO(NO<sub>3</sub>)<sub>2</sub> (2H<sub>2</sub>O), and/or Sr(NO<sub>3</sub>)<sub>2</sub>) were dissolved in the solution and stirred. Then the obtained solution was heated and stirred at 343 K. The obtained sample was pre-calcined at 673 K for 2 h. Subsequently, it was calcined under air flow at 1123 K for 10 h.

**Preparation for catalysts.** Using prepared supports, Ru-loaded catalysts (Ru/Oxide) were prepared for this work using an impregnation method for this work. RuCl<sub>3</sub> (3H<sub>2</sub>O) or Ru(acac)<sub>3</sub> was used as the metal precursor. First the distilled water solvent with prepared support oxide was evaporated *in vacuo* at room temperature for 2 h. Then the solvent with Ru precursor was added and stirred for another 2 h. The obtained solution was heated and stirred at 343 K, and dried at 393 K for 20 h. The dried sample was treated under H<sub>2</sub> (50 SCCM) and Ar (50 SCCM) flow at 723 K for 2 h. The Ru content was fixed at 5.0 wt%. Cesium-promoted Ru catalysts were prepared using the sequential impregnation method. The solvent of Ru-loaded catalyst was evaporated at room temperature *in vacuo* for 2 h. Then CsNO<sub>3</sub> aqueous solution was added to the impregnated sample and stirred for another 2 h. The solvent was heated and stirred at 343 K and then dried at 393 K for 20 h. The amount of Cs was 0, 3.3, 6.6, 9.9, and 13.2 wt%. The prepared catalyst was crushed into 355–500  $\mu$ m diameter particles.

**Catalytic activity tests.** In all activity tests, a quartz tube (6.0 mm i. d.) was used for a fixedbed flow-type reactor as shown in supplementary materials figure S8. Two stainless steel rods (6 or 2 mm o. d.) were inserted into the reactors as electrodes. The upper electrode was set on the top of the catalyst bed. The ground electrode was set on the bottom of the catalyst bed. The catalyst bed temperature can be measured using a thermocouple. The imposed current and response voltage waves were observed using a digital phosphor oscilloscope (TCP A 300, and TDS 2001C; Tektronix Inc.). Before the reaction, the catalyst was pre-reduced for activation under N<sub>2</sub> (60 SCCM) and H<sub>2</sub> (180 SCCM) flow at 723 K for 2 h. Activity tests were conducted basically with 200 mg catalyst under N<sub>2</sub> (60 SCCM) and H<sub>2</sub> (180 SCCM) flow at various furnace temperatures, 6 mA (D.C.). Product gases were analyzed by using a gas chromatograph-TCD. The trapped ammonia was analyzed using an ion chromatograph (IC-2001, Tosoh Corp.). When using isotopes, <sup>30</sup>N<sub>2</sub> (6 SCCM) was introduced with <sup>28</sup>N<sub>2</sub> (6 SCCM), H<sub>2</sub> (36 SCCM), and Ar (12 SCCM). To detect <sup>28</sup>N<sub>2</sub>, <sup>29</sup>N<sub>2</sub>, and <sup>30</sup>N<sub>2</sub>, Q-Mass (QGA; Hiden Analytical Ltd.) was used for qualitative and quantitative analyses.

*In-situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) measurements. To elucidate the adsorbed species on catalysts with and without the electric field, *in-situ* DRIFTS measurements were conducted using FT-IR (FT-IR6200; Jasco Corp.) with an MCT detector and a diffuse reflectance infrared Fourier transform spectroscopy reactor cell (DR-600Ai; Jasco Corp.) with the ZnSe window. For IR measurements with application of the electric field, two DRIFTS cells were used. They were made of SUS304 for catalytic reaction (for tolerance of high temperatures) and of Teflon for catalytic reaction in the electric field (to avoid short circuits in the cell), as presented in supplementary materials figure S2. The sample was 9.9 wt%Cs / 5.0 wt%Ru / SrZrO<sub>3</sub>. First, the sample was pre-reduced under N<sub>2</sub> (15 SCCM) and H<sub>2</sub> (45 SCCM) flow at 473 or 723 K for 2 h. Then, the reducing gas was purged for 30 min with Ar (60 SCCM). Then background (BKG) measurements were taken under Ar gas at 473 K or 648 K. Subsequently, the reactant gas (N<sub>2</sub> : H<sub>2</sub> = 15 : 45 SCCM or N<sub>2</sub> : Ar = 15 : 45 SCCM or 10%NH<sub>3</sub>/He : Ar = 1 : 59 SCCM, or H<sub>2</sub>/D<sub>2</sub> = 15 SCCM) was supplied for 30 min at most. Subsequently, the electric field was applied for about 10 min. Each spectrum was recorded at resolution of 4.0 cm<sup>-1</sup>, over 50 scans. The imposed current was 6 or 10 mA.

**Characterization of catalyst.** The crystalline structure was characterized using powder X-ray diffraction (XRD, SmartLab3; Rigaku Corp.) operating at 40 kV and 40 mA with Cu- $K\alpha$  radiation. The XRD measurement results are presented in supplementary materials figure S9. The dispersion

ratio and particle diameter of Ru catalysts are characterized using CO pulse (BEL CAT II; Bel Japan, Inc.). Before measurements, the catalyst sample was pre-treated under  $H_2$  (50 SCCM) flow at 723 K for 30 min. After the treatment, the temperature was decreased to 323 K with He, and 10% CO was pulsed. Results of the CO pulse are presented in supplementary materials table S3. The structure of supported Ru was observed using a TEM (JEM-2100F, 200kV).

Theoretical calculations for ammonia synthesis on Ru with/without the electric field. All the calculations were conducted using the Vienna *ab initio* simulation package (VASP) 5.4. A corevalence effect was included with the projector-augmented wave (PAW) method [43, 44]. The valence part wave functions were expanded using plane-wave basis sets with kinetic energy lower than 400 eV. For the calculation of energetics, i.e. adsorption energy, reaction energy, and activation barriers, re-parameterized Perdew-Burke-Ernzerhof (RPBE) was used as the exchange-correlation functional for spin-polarized DFT calculation [45, 46]. For vibrational frequency calculations, PW91 exchangecorrelation functional was used [47]. The DFT calculations were done in a spin-polarized manner. For k-space, integration was conducted by taking  $3 \times 3 \times 1$  points. For the smearing method in the electronic state, the first-order Methfessel-Paxton method with  $\sigma = 0.2$  and tetrahedron method were used, respectively, for catalyst system and free-molecules (N<sub>2</sub>, H<sub>2</sub>, etc.). Both Ru(0001) and Ru(101) surfaces were modeled by four Ru atomic layers. During geometry optimization, the lower and upper two layers of Ru were fixed and relaxed, respectively. The geometry of adsorbates was fully relaxed. The catalytic system was represented by repeated slabs, which were separated by an approximately 20 Å vacuum layer. The definitions of adsorption sites on Ru(0001) and Ru(101) are presented in supplementary materials figure S10. For a transition state search, nudged elastic band (NEB) method was used. The electric field effect was considered by adding or removing electrons from the model system. Monopole and dipole corrections were included. Vibrational frequencies of CO were obtained by diagonalizing the Hessian matrix, which was computed from a finite-difference method. The C-O stretching frequencies perpendicular to the surface were calculated.

Apparatus and IR cell for applying electric field to catalyst bed. We prepared original reactor for application of the electric field to a catalyst bed. Schematic images of reactor are portrayed in figure S6. We inserted a thermocouple into the reactor to measure the catalyst bed temperature. In addition, a hand-made Teflon cell was used to conduct DRIFTS measurements during application of the electric field to the catalyst bed. A schematic image of the Teflon cell for *in-situ* DRIFTS measurements is presented in figure S2.

Screening tests and activities for ammonia synthesis over 9.9wt%Cs/5.0wt%Ru/SrZrO<sub>3</sub> catalyst in the electric field. We chose 9.9wt%Cs/5.0wt%Ru/SrZrO<sub>3</sub> catalyst for detailed investigation because that catalyst showed the highest performance in our screening tests, as presented in table S4. These screening tests were conducted under the same conditions, at 473 K, 0.1 MPa, 200 mg catalyst, 6 mA current, and gas flow (N<sub>2</sub> = 60 SCCM, and H<sub>2</sub> = 180 SCCM). As Figure S13 shows, 9.9wt%Cs/5.0wt%Ru/SrZrO<sub>3</sub> catalyst showed a stable activity for 5 h. We conducted screening tests for catalyst support in terms of the ability of proton conduction [48-50]. Also, the property of not only protonic but also mixed ionic and electronic conductor is considered to be significant because electron should run through the catalyst support during the electric field application, proton hopping at the surface of the catalyst. According to the numerous researches, SrZrO<sub>3</sub>-based oxides show a mixed conductivity with its defect chemistry, even under dry and low temperature conditions [51-53]. Therefore, SrZrO<sub>3</sub>-based catalyst is considered to show the stable and high activity among these catalysts.

XRD patterns for each support are presented in figure S9. The crystalline structure was almost identical before and after reactions in the electric field. Using Ru catalyst, Cs is known as a promoter, which shows the electron donor effects [5]. Our tests showed that the best amount of Cs is 9.9wt% for 5.0wt%Ru-loaded catalyst. Cs dopant is positively effective to some extent because both the associative reaction and the dissociative one would proceed even when the electric field is applied to catalyst bed at low temperatures. Also, H<sup>+</sup> is partially removed from NH<sub>4</sub><sup>+</sup>, which results in producing ammonia thanks to the ability of electron donor for Cs. Furthermore, the activities for ammonia synthesis with or without the electric field at various reaction temperatures, are presented in table S5.

Isotope exchange tests and the calculation for  $N_2$  dissociative rate in the electric field. To avoid the influence of hydrogen poisoning on isotope exchange tests, we conducted isotope exchange tests without the electric field and only supplying  $N_2$  species. Before experiments, hydrogen was purged at 723 K with Ar = 48 SCCM for 30 min. Then  ${}^{28}N_2$  and  ${}^{30}N_2$  were supplied. These results are presented in figure S1.  ${}^{29}N_2$  was not detected even without hydrogen supply, indicating that the N<sub>2</sub> dissociative rate without the electric field is very low: under the limit of detection.

However, we can calculate the N<sub>2</sub> dissociative rate from the detected outflow rate of  $^{29}N_2$ . Estimating the reaction mechanism as Langmuir-Hinshelwood mechanism, steady state, and the same zero-point motion energy for  $^{14}N$  and  $^{15}N$  [34, 35], the following equations (1) - (3) are obtained. Balance equation for N species flow;

$$V_{\rm in} - V_{\rm out} - r_{\rm NH3} / 2 = 0 \tag{1}$$

Equation for N<sub>2</sub> outflow;

$$F_{28} = (F_{28})_0 + V_{\text{out}} \cdot (f_{s14}f_{s14}) - V_{\text{in}} \cdot (f_{28})_0 \tag{2}$$

$$F_{29} = V_{\text{out}} \cdot (2f_{s14}f_{s15}) = V_{\text{out}} \cdot \{2f_{s14} \cdot (1 - f_{s14})\}$$
(3)

In those equations, V stands for the total flow rate, F signifies flow of each species, and f represents the molar fraction of isotopic species. Subscripts <sub>28</sub>, <sub>29</sub>, <sub>14</sub>, <sub>15</sub> respectively denote <sup>28</sup>N<sub>2</sub>, <sup>29</sup>N<sub>2</sub>, <sup>14</sup>N, and <sup>15</sup>N. Also <sub>s</sub> signifies the Ru surface. Subscript <sub>0</sub> denotes an input value (see also figure S11). From the experiment, we obtained  $r_{\text{NH3}}$ ,  $F_{28}$ ,  $(F_{28})_0$ ,  $(f_{28})_0$ , and  $F_{29}$ . Then  $V_{\text{in}}$ ,  $V_{\text{out}}$ , and  $f_{\text{s14}}$  were calculated. Results of analyses showed that the N<sub>2</sub> dissociative rate,  $V_{\text{in}}$  or  $V_{\text{out}}$ , can be calculated as about 36,000 µmol g<sub>-cat</sub><sup>-1</sup> h<sup>-1</sup> and show  $f_{\text{s14}}$  as presented in tables S6 and S7.

Influence of metal precursor on ammonia synthesis in the electric field. Our analysis of IR measurements revealed that  $NH_4^+Cl^-$  was produced in the electric field. Actually, Cl is regarded as derived from the metal precursor: RuCl<sub>3</sub> (3H<sub>2</sub>O). Therefore, to investigate the influence of Cl on activity, we prepared Cl-free catalyst using metal precursor Ru(acac)<sub>3</sub>. Table S8 presents activities for both catalysts: Cl precursor and acac precursor. The ammonia synthesis rate, TOF (using CO pulse results, shown in table S3), and the apparent activation energy were nearly equal for the two catalysts. Table S9 and figure S12 present results for isotope exchange tests. The N<sub>2</sub> dissociative rate was calculated using the same procedure for Cl precursor catalyst (table S10). These results demonstrate that both catalysts exhibited almost identical performance, and also that N<sub>2</sub> dissociative rate per unit of electric power was the same value. Therefore, the mechanisms for ammonia synthesis in the electric field.

#### Theoretical calculations for ammonia synthesis with/without the electric field on Ru.

From experimental results on the ammonia synthesis on Ru, we considered that two reaction mechanisms are plausible for ammonia synthesis: One is well known as a multistep reaction that is expressed as following elementary steps (10) - (15) in the main text [54], which is named a dissociative mechanism. The other one is designated as an associative mechanism because the association of N<sub>2</sub> and surface H atom takes place before N<sub>2</sub> dissociation, which is expressed as the following elementary steps (16) - (21). Here, the N-N bond dissociation process was assumed to take place from N<sub>2</sub>H species.

The difference between two mechanisms was investigated using results of theoretical calculations. First, we consider the main reaction sites for ammonia synthesis. Figure 4 and figure S14 show TEM images of Ru particle supported on SrZrO<sub>3</sub>, and the proposed models of for Ru particle. The figures show that the Ru particle surface consists mainly of Ru(0001), Ru(101) and Ru(100) facets. Among them, Ru(0001), Ru(101) are exposed to the particle surface. Based on this experimentally obtained result, we inferred that the mainly exposed facets of Ru particle are Ru(0001) and Ru(101). The theoretical calculations on these surfaces were considered. The definitions of adsorption sites on Ru(0001) and Ru(101) are presented in figure S10.

Before the investigation on NH<sub>3</sub> synthesis, the effects of electric fields on the catalyst system were examined by making comparison between experimental and theoretical results on *in-situ* IR spectroscopy using CO as probe molecules. The experimental results are presented in figures S3 and S4. As shown in figures S3 and S4, the appearance of the obtained peaks changed into broad ones with the electric field application. If we use each background spectrum (BKG) which was recorded at 523, 573, and 623 K against the obtained spectrum at 473 K in an electric field, then almost the same spectra with the original one (background at 473 K) were obtained, as presented in figure S5. Also as figure S6 shows, the obtained spectra at high temperature around 673 K without an electric field demonstrate that only gas phase of CO peaks were observed due to high temperature. These two results indicate that the change of peak appearance (broad peaks) by the electric field application is not derived from the catalyst bed heating, but from various CO adsorbates. One research group elucidated the polarization effect of catalyst for ammonia synthesis with DC current supply [22]. There might be an analogy, indicating that our Ru catalyst is polarized to some extent during the electric field application, resulting in producing various CO adsorbates (broad peaks). So we estimated the electron state of Ru surface via the peaks of CO adsorbate with/without the electric field. When using Cs-Ru catalyst, the

peak assigned to linear CO around 1986 cm<sup>-1</sup> [55, 56] shifted to around 2000 cm<sup>-1</sup>, as shown in figure S3. Moreover, when using Ru catalyst without Cs, the peaks assigned to adsorbed CO on a hollow site around 1750 and 1890 cm<sup>-1</sup> [57-59] show a clear blue-shift of about 20 - 30 cm<sup>-1</sup>, as shown in figure S4. This blue-shift with Ru catalyst was more clearly and larger than that with Cs-Ru catalyst. These results implied the effect of Cs addition, which is regarded as an electron donor toward Ru [6-11]. However, the blue-shift of peaks derived from CO vibrational frequency was observed in both cases with/without Cs addition, especially without Cs addition only when the electric field was applied to the catalyst bed. The blue-shift of peaks assigned to adsorbed CO reflected that the electron state of Ru changed by application of the electric field. Previous studies revealed that the peaks assigned to adsorbed CO showed blue shift when Ru was oxidized to some degree [55,56]: this blue-shift was observed when the electron state of Ru became positive.

This blue-shift observed experimentally was confirmed by our theoretical calculations. Table S2 presents the influence of Ru charges on CO adsorbed onto Ru(0001) and Ru(101) by calculations. On Ru(0001), it is widely known that CO preferentially adsorbs on either on-top of hcp three-fold hollow sites [57-59]. Thus, we considered CO adsorptions on these sites. Here, the electric field was expressed by introducing positive and negative charges on the system. Introduction of negative and positive charges on the system induces the elongation and contraction of C-O bond from that of neutral system. For example, the addition of one electrons on the system elongates the C-O bond by 0.008 Å while removing two electron shortens the C-O bond by 0.005 Å. Our calculation have shown that the C-O stretching frequency is also affected by the positive and negative charges. As shown in the Table, the addition and removing of electron in the system induces the decrease and increase of C-O stretching frequency, respectively. For example, ~33 and 35 cm<sup>-1</sup> decrease and increase of C-O stretching frequency shifts are in accordance with the C-O bond length dependence on positive and negative charges i.e. positive charge induces the contraction on the C-O bond and blue-shift in the spectrum, while negative charge does the CO elongation and red-shift.

Again, the increase in the C-O stretching frequency when removing electrons from Ru-CO system corresponds to the experimentally observed blue shift observed around 1750 - 2000 cm<sup>-1</sup>. Therefore, we can conclude that the Ru surface under electric field can be expressed by introducing positive charges on or removing electrons from the system.

Next, to elucidate the detailed reaction mechanism of ammonia synthesis under electric field,

we investigated the detailed energetic change of elementary reactions along the reaction path. We consider the ammonia synthesis reaction proceeds via dissociative or associative mechanism. Previous theoretical study by Garden el al. have suggested that the rate-determining step of the dissociative and associative mechanism is the  $N_2$  dissociation and  $N_2$ H formation steps, respectively [42].

Based on this model, we carried out geometry optimization of transition state for  $N_2$  dissociation and  $N_2H$  formation reactions on Ru. Both (0001) and (101) facets were examined since these facets mainly compose the Ru particle, as observed by the TEM experiment in figure 4. In figure 5, structures of reactant state, transition state, and product state for these reactions were shown. The structures in figure are those of the neutral charge system i.e. without the electric field. We observed no significant change in the structures of reactant state, transition state, and product state between neutral and charged systems. That is, the effect of electric field on the kinetics is mainly via the stability of the surface species and not via the structural factor.

The formation energy ( $\Delta E$ ) and activation barrier ( $E_a$ ) of these steps are summarized in figures 5 and S7. The effect of electric field was expressed by the positive charge in the system, since our calculation on the CO vibrational frequency have shown that electric field applied to the Ru catalyst bed is well expressed by the positive charge.  $\Delta E$  in figure 5 indicates that, irrespective of the facets, application of the electric field prevents the N<sub>2</sub> dissociation but promotes the N<sub>2</sub>H formation. Without electric field, the N<sub>2</sub>H formation was endothermic process. In this case, the reverse reaction i.e. N<sub>2</sub>H decomposition becomes faster than the formation. When electric field was applied, on the other hand, N<sub>2</sub>H species stably exists on the surface. The  $E_a$  plot in figure S7(B) shows similar tendency: the N<sub>2</sub> dissociation becomes slower but the N<sub>2</sub>H formation becomes faster under electric field. The amount of the positive charge was changed up to fifteen; this state corresponds to removing ~2 % of valence electron from the whole system since our model system contains ~760 electrons. The decrease of N<sub>2</sub>H formation  $E_a$  is notable, since it becomes from 1.23 eV to 0.56 eV by the application of electric field. References for supplementary material

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Supplementary Figure S1. Isotope exchange tests using  ${}^{30}N_2$  without an electric field at various furnace temperatures. After pre-reduction at 723 K, hydrogen was purged with Ar for 30 min. Then the temperature was set for each test: catalyst, 9.9wt%Cs/5.0wt%Ru/SrZrO<sub>3</sub>, 200mg; flow,  ${}^{28}N_2$  :  ${}^{30}N_2$  : H<sub>2</sub> : Ar = 6 : 6: 0: 48 SCCM.



Supplementary Figure S2. Schematic image of Teflon cell for *in-situ* DRIFTS measurements.



Supplementary Figure S3. *In-situ* IR spectra with CO: (a) before applying EF (b) with EF (6 mA, 0.58 – 0.61 kV): (c) after stopping EF; temperature, 473 K; catalyst, 9.9wt%Cs/5.0wt%Ru/SrZrO<sub>3</sub>; flow,  $N_2 : H_2 : CO = 15 : 45 : 1$  SCCM; current, 0 or 6 mA.)



Supplementary Figure S4. *In-situ* IR spectra with CO: (a) before applying EF; (b) with EF 5 min (6 mA, 0.49 - 0.52 kV); (c) with EF 10 min (6 mA, 0.50 - 0.60 kV); (d) after stopping EF; temperature, 473 K; catalyst, 5.0wt%Ru/SrZrO<sub>3</sub>; flow, N<sub>2</sub> : H<sub>2</sub> : CO = 15 : 45 : 1 SCCM; current, 0 or 6 mA.



Supplementary Figure S5. *In-situ* IR spectra with various background (BKG) temperature; catalyst, 9.9wt%Cs/5.0wt%Ru/SrZrO<sub>3</sub>; furnace temperature, 473 K; flow,  $N_2 : H_2 : CO = 15 : 45 : 1$  SCCM; current, 6 mA.



Supplementary Figure S6. *In-situ* IR spectra under various conditions; catalyst,  $9.9wt\%Cs/5.0wt\%Ru/SrZrO_3$ ; flow, N<sub>2</sub> : H<sub>2</sub> : CO = 15 : 45 or 0 : 1 SCCM; current, 0 or 6 mA.



Supplementary Figure S7. Theoretical calculations for ammonia synthesis with/without an electric field. (A) Activation energy of  $N_2$  dissociation and  $N_2H$  formation reactions on Ru(0001) and Ru(1011), and its dependence on the electric field expressed by the positive charge. Nudged elastic band method was employed. (B) Arrhenius plot of ammonia synthesis reaction with and without electric field, estimated both experimentally and theoretically. Pre-exponential factor of experimental Arrhenius plot was estimated from Eqs.(19) and (20) for with/without electric field reactions, respectively. Activation energy of fifteen positive charges was used in the computational Arrhenius plot with electric field. Values for Ru(1011) was taken.



Supplementary Figure S8. Schematic image of the reactor for ammonia synthesis in an electric field.



Supplementary Figure S9. XRD patterns for respective catalysts (support only, Ru-load catalyst and after reaction in an electric field): (A) CeO<sub>2</sub> (B) ZrO<sub>2</sub> (C) Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> (D) SrCeO<sub>3</sub> (E) SrZrO<sub>3</sub>

(A)



Supplementary Figure S10. Surface model and definition of adsorption sites on Ru: (A) Ru(0001) and (B) Ru(1011).



Supplementary Figure S11. Schematic image of the  $N_2$  dissociation process for calculation of the  $N_2$  dissociative rate in an electric field.



Supplementary Figure S12. Isotope exchange tests using  ${}^{30}N_2$ , furnace temperature 473 K, catalyst, 9.9wt%Cs/5.0wt%Ru(acac)/SrZrO<sub>3</sub>, 200mg; flow,  ${}^{28}N_2 : {}^{30}N_2 : H_2 : Ar = 6 : 6: 36: 12$  SCCM; current, 0 or 6 mA.



Figure S13. The activity test over 9.9wt%Cs/5.0wt%Ru/SrZrO<sub>3</sub> catalyst; catalyst weight, 200 mg; furnace temperature, 473 K; catalyst bed temperature, 624 K; flow,  $N_2 : H_2 : CO = 60 : 180$  SCCM; current, 6 mA.



Figure S14. Various TEM images of Ru particle supported on  $\mbox{SrZrO}_3$  .

Table S1. Kinetic data for analyzing N<sub>2</sub>, H<sub>2</sub>, and NH<sub>3</sub> pressure dependency of ammonia synthesis rate: catalyst, 9.9wt%Cs/5.0%Ru/SrZrO<sub>3</sub>, 200 mg; flow, 220 - 280 SCCM, H<sub>2</sub>/N<sub>2</sub> = 3 for NH<sub>3</sub> pressure; 240 SCCM with He as a balance gas for N<sub>2</sub> and H<sub>2</sub> pressure; current, 0 or 6 mA.

Condition	1/q	$P_{\rm N2}$ or $P_{\rm H2}$	Furnace Temperature	$T_{\text{thermocouple}}$	Ammonia synthesis rate	Voltage	<i>y</i> 0	С	Orders
condition	h mol <sup>-1</sup>	/ atm	/ K	/ K	/ $\mu mol g_{-cat}^{-1} h^{-1}$	/ kV	10-4 /-	$10^{-4}$ / mol h <sup>-1</sup>	$r = k P_{\text{N2}}{}^{\alpha} P_{\text{H2}}{}^{\beta} P_{\text{NH3}}{}^{\gamma}$
	1.45			634	2163		6.29		
Without	1.58		(22	637	2250		7.07		0.1(w)
(NH <sub>2</sub> )	1.78	Const	025	636	2220	-	7.91	-	-0.1 (y)
(1113)	1.93	-(P = 0.25  otm)		634	2109		8.13		
	1.44	$P_{\rm N2} = 0.25$ atml,		547	575	-0.22	1.67		
With alastria field	1.66	$r_{\rm H2} = 0.75 \text{ aum}$	172	542	567	-0.21	1.89		0.26()
(NH <sub>2</sub> )	1.81		4/5	545	543	-0.22	1.95	-	-0.26 (y)
(1113)	2.00			545	541	-0.22	2.17		
	1.74	0.20		635	1922		6.68	2.04	
Without	1.72	0.24	622	634	2129		7.30	2.28	0.68(a)
(N <sub>2</sub> )	1.72	0.30	023	633	2484	-	8.55	2.70	0.08(a)
(**2)	1.73	0.35		635	2738		9.47	3.01	
With	1.72	0.24		532	599	-0.20	2.06	0.167	
electric field	1.72	0.27	473	533	601	-0.18	2.07	0.168	0.24 (α)
(N <sub>2</sub> )	1.71	0.37		530	647	-0.20	2.21	0.184	
117.4	1.73	0.58		635	2173		7.39	2.33	
Without	1.74	0.62	623	634	2075		7.20	2.29	0.21(R)
(H <sub>2</sub> )	1.74	0.69	023	635	2131	-	7.20	2.22	-0.21(p)
(112)	1.74	0.77		635	2052		7.14	2.19	
117.41	1.74	0.58		544	698	-0.23	2.46	0.204	
With alastria field	1.75	0.63	472	543	690	-0.23	2.40	0.200	O(R)
(H <sub>2</sub> )	1.74	0.70	4/3	544	706	-0.23	2.46	0.206	$(\psi)$
(**2)	1.76	0.79		545	683	-0.23	2.37	0.197	

Table S2. C-O bond length ( $d_{CO}$ , in Å), and C-O stretching frequency ( $v_{CO}$ , in cm<sup>-1</sup>) of CO adsorbed on Ru(0001) and Ru(1011).

Surface	Droporty	A dependion site				Charge			
Surface	Property	Adsorption site	-3	-2	-1	0	1	2	3
		on-top	1.183	1.180	1.173	1.165	1.161	1.156	1.152
	$d_{\rm CO}({ m \AA})$	hcp	1.218	1.215	1.208	1.202	1.195	1.189	1.184
$P_{11}(0001) =$		fcc	1.212	1.208	1.200	1.194	1.189	1.182	1.177
Ku(0001)		on-top	1855.8	1877.0	1919.5	1953.4	1988.6	2018.1	2048.2
	$v_{\rm CO}  ({\rm cm}^{-1})$	hcp	1608.3	1630.8	1668.6	1699.9	1734.0	1765.5	1790.3
		fcc	1645.7	1666.4	1711.3	1742.4	1772.9	1812.3	1840.4
		on-top	1.183	1.179	1.174	1.170	1.166	1.162	1.159
		bridge1	1.186	1.182	1.178	1.174	1.170	1.165	1.162
	$d_{\rm CO}({\rm \AA})$	hcp	1.213	1.208	1.203	1.198	1.194	1.189	1.185
		fcc	1.200	1.194	1.189	1.185	1.180	1.176	1.171
$\mathbf{D}_{11}(1011)$		4-fold	1.232	1.227	1.224	1.217	1.214	1.210	1.206
Ku(1011) -		on-top	1845.1	1872.5	1905.6	1927.2	1949.5	1967.7	1991.4
	( -1)	bridge1	1798.7	1812.8	1831.6	1848.1	1869.5	1899.3	1925.5
	$v_{\rm CO} ({\rm cm}^{-1})$	hcp	1633.2	1660.3	1688.1	1715.9	1741.3	1766.9	1789.3
		fcc	1626.3	1662.7	1686.5	1710.9	1736.9	1759.4	1785.5
		4-fold	1526.9	1544.5	1566.3	1602.5	1615.7	1634.5	1650.5

Table S3. Dispersion ratio and particle diameter of Ru catalysts analyzed by CO pulse. Loaded Ru,

3	.0wt%.	
Catalyst	Dispersion ratio	Average particle diameter
Catalyst	/ %	/ nm
9.9wt%Cs/Ru (Cl precursor) /SrZrO <sub>3</sub>	8.13	16.4
9.9wt%Cs/Ru (acac precursor) /SrZrO <sub>3</sub>	5.56	24.1

 $\label{eq:s4} Table S4. \ Activities \ for \ ammonia \ synthesis \ over \ various \ catalysts \ in \ an \ electric \ field: \ preset \ reaction \ temperature, \ 473 \ K; \ catalyst \ weight, \ 200 mg; \ flow, \ N_2: \ H_2 = 60: \ 180 \ SCCM; \ current, \ 6 \ mA; \ loaded \ Ru, \ 5.0 wt\%.$ 

Catalyst	T <sub>thermocouple</sub> / K	Voltage / kV	Ammonia synthesis rate per consumption electrical power $/ \mu mol g_{-cat}^{-1} J^{-1}$
Ru/CeO <sub>2</sub>	513	-0.12	0.016
Ru/ZrO <sub>2</sub>	613	-0.45	0.032
Ru/Ce <sub>0.5</sub> Zr <sub>0.5</sub> O <sub>2</sub>	594	-0.40	0.062
Ru/SrCeO <sub>3</sub>	563	-0.29	0.032
Ru/SrZrO <sub>3</sub>	578	-0.30	0.078
3.3wt%Cs/Ru/SrZrO3	545	-0.24	0.082
6.6wt%Cs/Ru/SrZrO3	549	-0.27	0.074
9.9wt%Cs/Ru/SrZrO3	532	-0.22	0.20
13.2wt%Cs/Ru/SrZrO <sub>3</sub>	527	-0.22	0.16

Pressure	T <sub>thermocouple</sub>	Voltage	Ammonia synthesis rate	Apparent activation energy Ea
/ MPa	/ K	/ kV	/ $\mu$ mol g <sub>-cat</sub> <sup>-1</sup> h <sup>-1</sup>	/ kJ mol <sup>-1</sup>
	524		38	
	574		266	
0.1	599	-	778	110
	624		2331	
	633		2737	
	599		1247	
0.2	612		2074	100
0.3	624	-	3211	109
	633		4077	
	523		38	
0.5	573	-	519	129
	623		4282	
	573		567	
	598		1232	
0.9	614	-	3025	121
	624		4699	
	634		5537	
	524	-0.44	1415	
0.1	574	-0.35	4672	53
	614	-0.49	8339	
	463	-0.46	2617	
0.5	527	-0.44	5309	22
0.5	574	-0.37	10494	52
	627	-0.31	23664	
	474	-0.28	3208	
0.9	523	-0.35	6453	37
0.9	576	-0.43	14614	10
	624	-0.47	30099	

Table S5. Activities for ammonia synthesis with or without an electric field: catalyst,  $9.9wt\%Cs/5.0\%Ru/SrZrO_3$ , 200mg; flow,  $N_2 : H_2 = 60 : 180$  SCCM; current, 6 mA.

Table S6. Isotope exchange tests with or without an electric field.

\*The  $N_2$  dissociative rate was calculated from equations (7) - (9).

Condition		Furnace Temperature	$T_{\text{thermocouple}}$	C <sub>thermocouple</sub> Voltage		low rate	/ µmol min <sup>-1</sup>	Ammonia synthesis rate	N <sub>2</sub> dissociative rate <sup>*</sup>	
		) K	/ K	/ kV	$^{28}N_{2}$	$^{30}N_{2}$	<sup>29</sup> N <sub>2</sub>	/ µmol g <sub>-cat</sub> <sup>-1</sup> h <sup>-1</sup>	/ µmol g <sub>-cat</sub> <sup>-1</sup> h <sup>-1</sup>	
With										
Electric Field	17 min	473	597	-0.70	251	224	59.2	1742	36000	
Wales	10 min	573	574		227	237		155		
Flastria	8 min	623	625		217	248	Limit of	432		
Electric	7 min	648	649	-	215	248	Detection	1003	-	
Tielu	8 min	673	673		214	248		1521		

Table S7. Calculation results of  $N_2$  dissociative rate

V <sub>in1</sub>	V <sub>out1</sub>	$f_{14}$
/ 10 <sup>4</sup> µmol	g-cat <sup>-1</sup> h <sup>-1</sup>	/ -
3.65	3.57	0.53

Precursor	Furnace Temperature	Furnace $T_{\text{thermocouple}}$		Ammonia synthesis rate	Apparent activation energy Ea	Turn Over Frequency		
	/ K	/ K	/ kV	/ µmol g <sub>-cat</sub> <sup>-1</sup> h <sup>-1</sup>	/ kJ mol <sup>-1</sup>	10 <sup>-3</sup> / s <sup>-1</sup>	10 <sup>-3</sup> / J <sup>-1</sup>	
	423	505	-0.24	566		5.7	4.0	
	473	542	-0.23	769		7.8	5.6	
acac	523	591	-0.26	1314	31.2	13.3	8.5	
	573	630	-0.20	1985		20.0	16.7	
	598	654	-0.22	3380		34.1	25.9	
	373	491	-0.30	306		2.1	1.2	
	473	544	-0.21	537		3.7	3.0	
Cl	523	588	-0.22	1001	38.2	6.9	5.3	
	573	630	-0.21	1865		12.9	10.2	
	603	662	-0.21	3621		25.0	20.1	

Table S8. Activities for ammonia synthesis with an electric field: catalyst,  $9.9wt\%Cs/5.0\%Ru/SrZrO_3$ , 200mg; flow, N<sub>2</sub> : H<sub>2</sub> = 60 : 180 SCCM; current, 6 mA.

Table S9. Isotope exchange tests with or without an electric field.

*The N <sub>2</sub> dissociative	rate was c	alculated from	equations	(7)	- (	(9)	).
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Precursor	Time	Furnace Temperature	$T_{\text{thermocouple}}$	Voltage	Out fl	Out flow rate / µmol min <sup>-1</sup>		Out flow rate / $\mu$ mol min <sup>-1</sup>		Out flow rate / $\mu$ mol min <sup>-1</sup>		Dut flow rate / µmol min <sup>-1</sup> Ar synt		Ammonia synthesis rate	N <sub>2</sub> dissociative rate*	N <sub>2</sub> dissociative rate per electric power
	/ min	/ K	/ K	/ kV	$^{28}N_{2}$	$^{30}N_{2}$	<sup>29</sup> N <sub>2</sub>	/ $\mu mol g_{-cat}^{-1} h^{-1}$	/ $\mu mol g_{-cat}^{-1} h^{-1}$	/ µmol J <sup>-1</sup>						
Cl	17	473	597	-0.70	251	224	59.2	1742	36000	0.48						
acac	9	473	604	-0.56	242	213	43.1	1574	26000	0.43						

# Table S10. Calculation results of $N_{\rm 2}$ dissociative rate: for acac precursor

V <sub>in1</sub>	V <sub>out1</sub>	$f_{14}$
/ 10 <sup>4</sup> µmol g	$-cat^{-1} h^{-1}$	/ -
2.67	2.59	0.53