Effects of A-site composition of perovskite (Sr$_{1-x}$Ba$_x$ZrO$_3$) oxides on H atoms adsorption, migration, and reaction

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1. Theoretical predictions for H atom adsorption energies by DFT calculations

For the evaluation of H atoms adsorption energies over Sr$_{1-x}$Ba$_x$ZrO$_3$, we carried out DFT calculations. The conditions and the procedures of the geometry optimizations were as mentioned in the main text. The constructed slab and bulk models are shown in Fig. S2 and Table S1. The obtained values of the H atom adsorption energies ($E$($H$ adsorption)) and the Bader charges of surface oxygen sites are summarized in Table S2.

2. Catalyst preparation

We prepared catalysts of 5 wt% ruthenium (Ru) loaded on Sr$_{1-x}$Ba$_x$ZrO$_3$ ($x$=0.000, 0.0625, 0.125, 0.250, 0.375, 0.500) supports. The Sr$_{1-x}$Ba$_x$ZrO$_3$ supports were synthesized using a complex polymerization method, which can circumvent the segregation of metal cations [s1]. In purified water, each metal cation was dispersed and complexed with citric acid, then the formed complexes were condensed and polyesterified with ethylene glycol. Here, the metal cations homogeneously existed
and were immobilized in the rigid polyester network. After that, the obtained products were calcined at low temperatures to decompose the network. We obtained blackish powder precursors with some carbons remaining. Finally, the carbonized blackish powders were calcined at high temperatures to decompose the residual carbon and to sinter the oxides.

Using the synthesized pure oxides, Ru was loaded using an impregnation method. Tris(acetylacetonato)ruthenium (III) (Ru(acac)\(_3\)) precursor and Sr\(_{1-x}\)Ba\(_x\)ZrO\(_3\) powders were added to acetone solvents, then the slurries were stirred and evaporated. To remove the ligands of the Ru(acac)\(_3\), the prepared powders were pre-treated at 723 K for 2 h in the stream of H\(_2\)/Ar=1/1 (total 100 SCCM).

3. **X-ray diffraction (XRD)**

XRD patterns were recorded to confirm the crystalline structures of Sr\(_{1-x}\)Ba\(_x\)ZrO\(_3\) and to decide whether Sr\(^{2+}\) and Ba\(^{2+}\) can completely be incorporated into the perovskite-A-site. Figure S3 presents the obtained XRD patterns, indicating that SrZrO\(_3\) can dissolve Ba\(^{2+}\) at any ratio (x). In addition, XRD measurements were also conducted for the fresh and the spent 5wt%Ru/Sr\(_{1-x}\)Ba\(_x\)ZrO\(_3\) catalysts to determine if the catalyst structure changed during activity tests. The recorded XRD patterns are shown in Fig. S4. The obtained XRD patterns exhibit that almost no peak shifts were observed between the fresh and the spent samples, which suggested that there are no significant changes in the catalyst structures during activity tests.

4. **Effects of the A-site composition in Sr\(_{1-x}\)Ba\(_x\)ZrO\(_3\) oxide on the electronic state of loaded Ru**

As explained in the main text, DFT calculations revealed the discontinuous change in the most stable exposed plane between the samples for x \(\leq 0.50\) and x \(\geq 0.75\). We presumed the difference in the exposed surface affected not only the H atom adsorption energies but also the electronic states of loaded Ru surface. We have previously reported that the high electron donating ability of the
catalyst supports made the Ru surface electron-rich, over which N$_2$H intermediate was stabilized [s2]. The stabilization of N$_2$H resulted in the enhancement of NH$_3$ synthesis activity in the electric field. In this investigation as well, the involvement of the Ru electronic state cannot be ignored. Thus, the impact of Sr$^{2+}$/Ba$^{2+}$ ratio on the Ru electronic state was evaluated with CO–DRIFTS measurements and CO$_2$–TPD measurements.

4.1 \textit{In-situ} DRIFTS measurements for adsorbed CO

To elucidate the effects of the A-site composition in Sr$_{1-x}$Ba$_x$ZrO$_3$ on the electronic state of loaded Ru surface, the behavior of CO adsorbed over Ru were evaluated using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements. IR study of adsorbed CO is well-known as an effective method for probing the electronic state of loaded active metal surfaces because the CO stretching vibration energy is affected by the back-donation of electrons from an active metal [s3-s4]. This measurement was carried out using Fourier transform infrared spectrometer (FT–IR6200; Jasco Corp.) with a MCT detector and a DRIFTS reactor cell (DR–600Ai; Jasco Corp.) equipped with the ZnSe window. In advance of the measurements, all Ru/Sr$_{1-x}$Ba$_x$ZrO$_3$ samples were pre-reduced at 723 K for 2 h under N$_2$/H$_2$=1/3 (total 60 SCCM) flow, then purged with Ar (60 SCCM) for 1 h to remove H species adsorbed on Ru surface. All the IR spectra were obtained at 303 K. First, the background-spectra were recorded under inert Ar (60 SCCM) atmosphere. Subsequently, 0.5%CO/Ar (60 SCCM) was supplied for 10 min. After the gas phase CO was purged with Ar, the \textit{in-situ} spectra of adsorbed CO were recorded. All recorded spectra were obtained with 4.0 cm$^{-1}$ resolution and 150 scans.

The results are shown in Fig. S5. The main peak was observed at around 2020–2050cm$^{-1}$, which derived from linearly adsorbed CO on Ru$^0$ surface [s5-s6]. Here, note that the behavior of adsorbed CO on Ru is too complicated owing to plenty of factors determining the peak position.
including the electronic state, the particle size, the morphology of adsorbed site, and the CO coverage. As for our measurement in this paper, Ru particle sizes were almost identical among all catalysts (Table 1). Also, the difference of the CO coverage is negligible because Ru surface would be sufficiently covered with CO at 303 K. Therefore, the electronic state of Ru surface can be evaluated using the peak at around 2020–2050 cm\(^{-1}\) shown in Fig. S5, which was assigned to linear CO adsorption on Ru\(^0\). The results show the discontinuous peak shift of linear CO vibration toward lower wavenumber region for \(x \geq 0.75\). This red-shift of the CO peak indicated that the electronic state of Ru became electron–rich. Based on this optical measurement and the most stable surface obtained by DFT calculations, it was assumed that the discontinuous shift of the CO peaks reflected the change in the exposed surface.

4.2 Basicity of Sr\(_{1-x}\)Ba\(_x\)ZrO\(_3\) supports evaluated by CO\(_2\)–TPD

As shown in the former section, the electronic state of Ru was discontinuously changed along with the increment in the Ba\(^{2+}\) content (\(x\)) in Sr\(_{1-x}\)Ba\(_x\)ZrO\(_3\). It is generally known the electron-donating ability is correlated to the basicity of an oxide surface \([s7-s11]\). Therefore, we conducted temperature–programmed desorption measurements of CO\(_2\) (CO\(_2\)–TPD) to evaluate the basic properties of Sr\(_{1-x}\)Ba\(_x\)ZrO\(_3\) surfaces.

Before the adsorption of CO\(_2\), each support 300 mg was pre–reduced at 723 K for 2 h in a stream of N\(_2\)/H\(_2\)=1/3 (240 SCCM), then purged with He (50 SCCM) for 1 h. After that, the sample was cooled down to 333 K, and 10%CO\(_2\)/He (50 SCCM) was fed for 1 h. The gas phase CO\(_2\) was purged with He (50 SCCM) for 0.5 h. Afterwards, the sample was heated at a ramping rate of 3 K min\(^{-1}\) to 1073 K under He (50 SCCM) flow, and the CO\(_2\) desorption profiles were detected. Quadrupole mass spectrometer (QGA; Hiden Analytical Ltd.) was used to monitor the desorbed CO\(_2\) (\(m/z=44\)) and inert He (\(m/z=4\)).
The results of CO$_2$–TPD are shown in Fig. S6. From the TPD profiles, two main peaks were identified at around 650 K and at above 900 K. They were derived from the weak and the strong base sites on oxide surfaces, respectively. Moreover, we confirmed a discontinuous change in the support basicity. Little change in the intensity and the amounts of base sites over Sr$_{1-x}$Ba$_x$ZrO$_3$ was observed for $x \leq 0.50$, whereas both of the two factors drastically increased for $x \geq 0.75$. In conclusion, it was clarified that the change in the basicity of catalyst supports caused the discontinuous trend in the electronic state of Ru for $x \geq 0.75$. Therefore, we performed other investigations using the samples in the range of $0.00 \leq x \leq 0.50$.

5. X–ray photoelectron spectroscopy (XPS)

XPS measurements were performed to evaluate the amount of hydroxy (OH) groups over Sr$_{1-x}$Ba$_x$ZrO$_3$ ($x=0.000$, 0.250, 0.500) oxides. The obtained C1s and O1s spectra are shown in Figs. S7 and S8, the calculated OH ratios are summarized in Fig. S9 and Table S3. Furthermore, we also analyzed the XPS spectra obtained with the fresh and the spent 5wt%Ru/SrZrO$_3$ samples in order to confirm the change in the catalyst surface structures during the activity tests. The recorded C1s, O1s, Ru3d, Zr3d, Sr3p, and Sr3d spectra are shown in Fig. S12. As there were no significant differences in the spectral shapes between the fresh and the spent samples, we concluded that the catalyst surface structure did not change during the catalysis.

6. Activity tests

Temperature dependence for NH$_3$ synthesis rates in the electric field was investigated using 5wt%Ru/Sr$_{1-x}$Ba$_x$ZrO$_3$ ($0.000 \leq x \leq 0.500$) catalysts. The experimental conditions are the same as the flow described in the main part. The results are represented in Fig. S10, the details in Tables S4 through S9. Furthermore, turn-over frequencies (TOF) were also calculated for the evaluation of catalytic
performances, summarized in Table 1 in the main part.

7. Distributions of the loaded Ru particle sizes (FE-TEM)

The loaded Ru particles over Sr_{1-x}Ba_xZrO_3 supports were analyzed with FE-TEM images. The obtained images and the histograms of the Ru particle size distributions are shown in Fig. S11.

8. Specific surface areas of catalysts

Among the most influential factors determining the particle size distributions of loaded Ru is a specific surface area (SSA) of catalyst supports. Therefore, we evaluated the SSA values of Sr_{1-x}Ba_xZrO_3 supports with BET method. The SSA values obtained with each support, summarized in Table 1 in the main text, tended to slightly increase in a higher Ba^{2+} content (x) region. Nevertheless, no correlation between the SSA values and the obtained Ru particle sizes was observed. In addition, the trend of TOFs was in close agreement with that of NH_3 synthesis rates. Therefore, we concluded that the small change in the SSA values had little effect on the catalytic performances. Moreover, we compared the SSA values of the fresh and the spent 5wt%Ru/Sr_{1-x}Ba_xZrO_3 catalysts, summarized in Table S10. The obtained SSA values were little altered after the activity tests, indicating the catalyst structures hardly changed during the NH_3 synthesis reaction in the electric field.

Notes and References

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Caption for Figures and Tables

**Figure S1** A schematic image of the activity test reactor.

**Figure S2** Atomic images of the optimized slab models of Sr$_{1-x}$Ba$_x$ZrO$_3$ for (a) $x=0.00$, (b) $x=0.25$, (c) $x=0.50$, (d) $x=0.75$, and (e) $x=1.00$. The images above are from the side, and the ones below are from the top. Sr atoms are shown in orange, Ba in blue, Zr in green, and O in red.

**Figure S3** XRD patterns (a) and the calculated lattice parameters (b) of the prepared Sr$_{1-x}$Ba$_x$ZrO$_3$ ($0.000 \leq x \leq 0.500$) samples. The focused peaks in (a) are diffracted from (112), (200), and (020) plane.

**Figure S4** XRD patterns (a) and the calculated cell volumes (b) for the fresh and the spent catalysts of 5wt%Ru/ Sr$_{1-x}$Ba$_x$ZrO$_3$ ($0.000 \leq x \leq 0.500$) catalysts.

**Figure S5** In-situ DRIFTS spectra obtained by the linear CO adsorbed on Ru/Sr$_{1-x}$Ba$_x$ZrO$_3$ surfaces for $x=0.00$, 0.25, 0.50, 0.75, and 1.00.

**Figure S6** Profiles for the temperature-programmed desorption of CO$_2$ over Sr$_{1-x}$Ba$_x$ZrO$_3$ oxide surfaces for $x=0.00$, 0.25, 0.50, 0.75, and 1.00.

**Figure S7** C1s X-ray photoelectron spectra with Sr$_{1-x}$Ba$_x$ZrO$_3$ oxides pre-reduced at 723 K for 2 h under N$_2$/H$_2$=1/3 (240 SCCM) flow, (a) $x=0.000$, (b) $x=0.250$, and (c) $x=0.500$.

**Figure S8** O1s X-ray photoelectron spectra with Sr$_{1-x}$Ba$_x$ZrO$_3$ oxides pre-reduced at 723 K for 2 h under N$_2$/H$_2$=1/3 (240 SCCM) flow, (a) $x=0.000$, (b) $x=0.250$, and (c) $x=0.500$.

**Figure S9** The hydroxy groups (OH) ratio over Sr$_{1-x}$Ba$_x$ZrO$_3$ oxides ($x=0.000$, 0.250, and 0.500) calculated by C1s and O1s X-ray photoelectron spectra.

**Figure S10** Temperature dependence for NH$_3$ synthesis rates in the electric field (0.1 MPa, 6.0 mA) using 5wt%Ru/Sr$_{1-x}$Ba$_x$ZrO$_3$ ($0.000 \leq x \leq 0.500$) catalysts.

**Figure S11** FE-TEM images and the obtained histograms of the 5wt%Ru/Sr$_{1-x}$Ba$_x$ZrO$_3$ catalysts for (a) $x=0.00$, (b) $x=0.063$, (c) $x=0.125$, (d) $x=0.250$ (e) $x=0.375$, and (f) $x=0.500$. 
**Figure S12** X-ray photoelectron spectra obtained with the fresh and the spent 5wt%Ru/SrZrO₃ samples, (a) O1s, (b) C1s, Ru3d, and Sr3p, (c) Zr3d, and (d) Sr3d.

**Table S1** The summary for the constructed bulk and slab models of Sr₁₋ₓBaₓZrO₃ (0.00≤x≤1.00). The lattice parameters of the BaZrO₃ cubic oxide (Pm-3m) were converted using the following equation, $a' = \sqrt{2}a$, $b' = \sqrt{2}b$, and $c' = 2c$.

**Table S2** The summary for the H atom adsorption energies ($E(\text{H adsorption})$) and the surface oxygen Bader charges over Sr₁₋ₓBaₓZrO₃ (x=0.00, 0.25, and 0.50) surfaces.

**Table S3** The summary for the quantitative analysis of OH groups with O1s XPS spectra.

**Table S4** NH₃ synthesis rate over 5wt%Ru/SrZrO₃ in the electric field (0.1 MPa, 6.0 mA).

**Table S5** NH₃ synthesis rate over 5wt%Ru/Sr₀.₉₃₇Ba₀.₀₆₃ZrO₃ in the electric field (0.1 MPa, 6.0 mA).

**Table S6** NH₃ synthesis rate over 5wt%Ru/Sr₀.₈₇₅Ba₀.₁₂₅ZrO₃ in the electric field (0.1 MPa, 6.0 mA).

**Table S7** NH₃ synthesis rate over 5wt%Ru/Sr₀.₇₅₀Ba₀.₂₅₀ZrO₃ in the electric field (0.1 MPa, 6.0 mA).

**Table S8** NH₃ synthesis rate over 5wt%Ru/Sr₀.₆₂₅Ba₀.₃₇₅ZrO₃ in the electric field (0.1 MPa, 6.0 mA).

**Table S9** NH₃ synthesis rate over 5wt%Ru/Sr₀.₅₀₀Ba₀.₅₀₀ZrO₃ in the electric field (0.1 MPa, 6.0 mA).

**Table S10** Specific surface areas of the fresh and the spent 5wt%Ru/Sr₁₋ₓBaₓZrO₃ (0.000≤x≤0.500) catalysts.
**Figure S1** A schematic image of the activity test reactor.
Figure S2 Atomic images of the optimized slab models of Sr$_{1-x}$Ba$_x$ZrO$_3$ for (a) $x=0.00$, (b) $x=0.25$, (c) $x=0.50$, (d) $x=0.75$, and (e) $x=1.00$. The images above are from the side, and the one below are from the top. Sr atoms are shown in orange, Ba in blue, Zr in green, and O in red.
Figure S3 XRD patterns (a) and the calculated lattice parameters (b) of the prepared $\text{Sr}_{1-x}\text{Ba}_x\text{ZrO}_3$ ($0.000 \leq x \leq 0.500$) samples. The focused peaks in (a) are diffracted from (112), (200), and (020) plane.
Figure S4 XRD patterns (a) and the calculated cell volumes (b) for the fresh and the spent catalysts of 5wt%Ru/Sr$_{1-x}$Ba$_x$ZrO$_3$ ($0.000 \leq x \leq 0.500$) catalysts.
**Figure S5** *In-situ* DRIFTS spectra obtained by the linear CO adsorbed on Ru/Sr$_{1-x}$Ba$_x$ZrO$_3$ surfaces for $x=0.00$, 0.25, 0.50, 0.75, and 1.00.
Figure S6 Profiles for the temperature-programmed desorption of CO$_2$ over Sr$_{1-x}$Ba$_x$ZrO$_3$ oxide surfaces for $x=0.00$, 0.25, 0.50, 0.75, and 1.00.
**Figure S7** C1s X-ray photoelectron spectra with Sr$_{1-x}$Ba$_x$ZrO$_3$ oxides pre-reduced at 723 K for 2 h under N$_2$/H$_2$=1/3 (240 SCCM) flow, (a) x=0.000, (b) x=0.250, and (c) x=0.500.
Figure S8 O1s X-ray photoelectron spectra with Sr_{1-x}Ba_xZrO_3 oxides pre-reduced at 723 K for 2 h under N_2/H_2=1/3 (240 SCCM) flow, (a) x=0.000, (b) x=0.250, and (c) x=0.500.
**Figure S9** The hydroxy groups (OH) ratio over Sr$_{1-x}$Ba$_x$ZrO$_3$ oxides ($x$=0.000, 0.250, and 0.500) calculated by C1s and O1s X-ray photoelectron spectra.
Figure S10 Temperature dependence for NH$_3$ synthesis rates in the electric field (0.1 MPa, 6.0 mA) using 5wt%Ru/Sr$_{1-x}$Ba$_x$ZrO$_3$ (0.000 ≤ x ≤ 0.500) catalysts.
Figure S11 FE-TEM images and the obtained histograms of the 5wt%Ru/Sr$_{1-x}$Ba$_x$ZrO$_3$ catalysts for (a) $x=0.000$, (b) $x=0.063$, (c) $x=0.125$, (d) $x=0.250$ (e) $x=0.375$, and (f) $x=0.500$. 
Figure S12 X-ray photoelectron spectra obtained with the fresh and the spent 5wt%Ru/SrZrO₃ samples, (a) O1s, (b) C1s, Ru3d, and Sr3p, (c) Zr3d, and (d) Sr3d.
Table S1 The summary for the constructed bulk and slab models of Sr$_{1-x}$Ba$_x$ZrO$_3$ (0.00 ≤ x ≤ 1.00). The lattice parameters of the BaZrO$_3$ cubic oxide (Pm-3m) were converted using the following equation, $a' = \sqrt{2}a$, $b' = \sqrt{2}b$, and $c' = 2c$.

| Sr/Ba ratio (x) in Sr$_{1-x}$Ba$_x$ZrO$_3$ | 0.00 | 0.25 | 0.50 | 0.75 | 1.00 |
|------------------------------------------|------|------|------|------|------|
| Space group                              | Pnma (62) | Pnma (62) | Ia/mma (74) | I4/mcm (139) | Pm-3m (221) |
| Crystal system                           | Orthorhombic | Orthorhombic | Orthorhombic | Tetragonal | Cubic |
| Tilt system                              | $a^*b^*b'$ | $a^*b^*b'$ | $a^*b^*b'$ | $a^*a^*c'$ | $a^*a^*a^*$ |
| Calculated lattice parameter             | $b$   | 5.78  | 5.80  | 5.83  | 5.85  | 5.92  |
|                                         | $c$   | 8.16  | 8.20  | 8.25  | 8.40  | 8.37  |
| Exposed surface for slabs                | $h$   | 1     | -1    | 1     | 2     | 1     |
|                                         | $k$   | 1     | 1     | 1     | 0     | 0     |
|                                         | $l$   | -2    | -2    | -2    | 0     | 1     |
Table S2 The summary for the H atom adsorption energies and the oxygen Bader charges over Sr$_{1.3}$Ba$_x$ZrO$_3$ ($x$=0.00, 0.25, and 0.50) surfaces

| site | Sr/Ba ratio ($x$) in Sr$_{1.3}$Ba$_x$ZrO$_3$ | 0.00 | 0.25 | 0.50 |
|------|--------------------------------------------|------|------|------|
|      | Bader charge | H atom adsorption energy | e | eV  | Bader charge | H atom adsorption energy | e | eV  | Bader charge | H atom adsorption energy | e | eV  |
| -    | -0.96        | -2.84 | -1.22 | -2.55 | -0.96         | -2.90 |
| 1    | -0.78        | -2.87 | -1.13 | -2.72 | -0.90         | -2.93 |
| 2    | -0.97        | -2.9  | -0.86 | -2.86 | -0.96         | -2.90 |
| 3    | -0.75        | -2.88 | -0.75 | -2.75 | -0.90         | -2.93 |
| 4    | -0.78        | -2.88 | -1.14 | -2.71 | -0.76         | -2.97 |
| 5    | -0.96        | -2.81 | -1.22 | -2.55 | -0.92         | -2.91 |
| 6    | -0.77        | -2.84 | -0.73 | -2.77 | -0.76         | -2.97 |
| 7    | -0.93        | -2.74 | -0.87 | -2.84 | -0.92         | -2.91 |
| 8    | -0.96        | -2.84 | -1.22 | -2.55 | -0.96         | -2.90 |
| 9    | -0.78        | -2.87 | -1.13 | -2.72 | -0.90         | -2.94 |
| 10   | -0.97        | -2.9  | -0.86 | -2.78 | -0.96         | -2.90 |
| 11   | -0.75        | -2.87 | -0.75 | -2.75 | -0.90         | -2.94 |
| 12   | -0.78        | -2.87 | -1.14 | -2.71 | -0.76         | -2.97 |
| 13   | -0.96        | -2.77 | -1.22 | -2.55 | -0.92         | -2.91 |
| 14   | -0.77        | -2.84 | -0.83 | -2.77 | -0.76         | -2.97 |
| 15   | -0.93        | -2.78 | -0.87 | -2.84 | -0.92         | -2.91 |
| 16   | -0.86        | -2.84 | -1.00 | -2.71 | -0.89         | -2.93 |

mean -0.86 -2.84 -1.00 -2.71 -0.89 -2.93
**Table S3** The summary for the quantitative OH group analysis with O1s XPS spectra

| Sr/Ba ratio (x) in Sr$_{1-x}$Ba$_x$ZrO$_3$ | OH ratio | Binding energy of O$_{\text{tot}}$ (eV) |
|------------------------------------------|----------|--------------------------------------|
| -                                        | -        | 528.27                               |
| 0.00                                     | 0.68     | 528.27                               |
| 0.25                                     | 0.48     | 528.27                               |
| 0.50                                     | 0.52     | 528.26                               |
Table S4 NH₃ synthesis rate over 5wt%Ru/SrZrO₃ in the electric field (0.1 MPa, 6.0 mA)

| Furnace temperature K | Catalyst bed temperature K | Imposed current mA | Response voltage kV | NH₃ synthesis rate μmol g⁻¹ h⁻¹ |
|-----------------------|-----------------------------|-------------------|--------------------|-----------------------------|
| R.T.                  | 496.2                       | 6.0               | 0.357              | 746.3                       |
| R.T.                  | 495.2                       | 6.0               | 0.383              | 676.8                       |
| R.T.                  | 498.3                       | 6.0               | 0.382              | 699.4                       |
| R.T.                  | 487.2                       | 6.0               | 0.377              | 652.4                       |
| R.T.                  | 483.7                       | 6.0               | 0.371              | 642.8                       |
| R.T.                  | 470.7                       | 6.0               | 0.337              | 825.2                       |
| R.T.                  | 467.8                       | 6.0               | 0.378              | 784.8                       |
| R.T.                  | 460.1                       | 6.0               | 0.348              | 759.1                       |
| 373                   | 515.2                       | 6.0               | 0.323              | 744.0                       |
| 423                   | 535.2                       | 6.0               | 0.344              | 686.4                       |
| 473                   | 570.5                       | 6.0               | 0.289              | 837.4                       |
| 573                   | 641.9                       | 6.0               | 0.245              | 1730.6                      |
Table S5 NH$_3$ synthesis rate over 5wt%Ru/Sr$_{0.937}$Ba$_{0.063}$ZrO$_3$ in the electric field (0.1 MPa, 6.0 mA)

| Furnace temperature K | Catalyst bed temperature K | Imposed current mA | Response voltage kV | NH$_3$ synthesis rate $\mu$mol g$^{-1}$ h$^{-1}$ |
|-----------------------|-----------------------------|-------------------|---------------------|---------------------------------|
| R.T.                  | 493.2                       | 6.0               | 0.405               | 1081.3                          |
| R.T.                  | 492.0                       | 6.0               | 0.391               | 1100.3                          |
| R.T.                  | 485.8                       | 6.0               | 0.403               | 1079.0                          |
| R.T.                  | 480.7                       | 6.0               | 0.360               | 1130.8                          |
| R.T.                  | 496.7                       | 6.0               | 0.440               | 1189.7                          |
| R.T.                  | 471.3                       | 6.0               | 0.370               | 1083.6                          |
| R.T.                  | 457.7                       | 6.0               | 0.391               | 1054.5                          |
| R.T.                  | 494.8                       | 6.0               | 0.429               | 1151.8                          |
| 373                   | 500.2                       | 6.0               | 0.359               | 1096.0                          |
| 423                   | 533.8                       | 6.0               | 0.333               | 1215.9                          |
| 473                   | 569.4                       | 6.0               | 0.319               | 1479.8                          |
| 573                   | 635.7                       | 6.0               | 0.235               | 3584.2                          |
Table S6 NH₃ synthesis rate over 5wt%Ru/Sr₀.₈₇₅Ba₀.₁₂₅ZrO₃ in the electric field (0.1 MPa, 6.0 mA)

| Furnace temperature K | Catalyst bed temperature K | Imposed current mA | Response voltage kV | NH₃ synthesis rate μmol g⁻¹ h⁻¹ |
|-----------------------|-----------------------------|--------------------|---------------------|-------------------------------|
| R.T.                  | 488.5                       | 6.0                | 0.391               | 1222.9                        |
| R.T.                  | 480.2                       | 6.0                | 0.365               | 1023.4                        |
| R.T.                  | 487.2                       | 6.0                | 0.402               | 1138.3                        |
| R.T.                  | 480.0                       | 6.0                | 0.351               | 1117.3                        |
| R.T.                  | 484.6                       | 6.0                | 0.400               | 1160.8                        |
| R.T.                  | 500.9                       | 6.0                | 0.401               | 1224.5                        |
| R.T.                  | 499.8                       | 6.0                | 0.389               | 1201.7                        |
| R.T.                  | 499.1                       | 6.0                | 0.399               | 1249.4                        |
| 373                   | 507.9                       | 6.0                | 0.368               | 1197.0                        |
| 423                   | 545.1                       | 6.0                | 0.346               | 1432.8                        |
| 473                   | 571.0                       | 6.0                | 0.326               | 1676.2                        |
| 573                   | 646.4                       | 6.0                | 0.284               | 3937.7                        |
**Table S7** NH₃ synthesis rate over 5wt%Ru/Sr₀.₇₅₀Ba₀.₂₅₀ZrO₃ in the electric field (0.1 MPa, 6.0 mA)

| Furnace temperature (K) | Catalyst bed temperature (K) | Imposed current (mA) | Response voltage (kV) | NH₃ synthesis rate (μmol g⁻¹ h⁻¹) |
|-------------------------|-------------------------------|----------------------|----------------------|----------------------------------|
| R.T. 498.9              | 6.0                           | 0.422                | 1009.8               |
| R.T. 497.4              | 6.0                           | 0.409                | 981.5                |
| R.T. 500.0              | 6.0                           | 0.439                | 999.5                |
| R.T. 505.1              | 6.0                           | 0.451                | 1070.5               |
| R.T. 506.0              | 6.0                           | 0.456                | 1106.4               |
| R.T. 490.6              | 6.0                           | 0.434                | 1094.9               |
| R.T. 482.6              | 6.0                           | 0.440                | 973.8                |
| R.T. 481.1              | 6.0                           | 0.410                | 935.4                |
| 373                     | 524.2                         | 6.0                  | 0.360                | 1035.6                           |
| 423                     | 545.2                         | 6.0                  | 0.344                | 1161.5                           |
| 473                     | 573.6                         | 6.0                  | 0.307                | 1336.9                           |
| 573                     | 633.7                         | 6.0                  | 0.205                | 2857.7                           |
**Table S8** NH₃ synthesis rate over 5wt%Ru/Sr₀.₆₂₅Ba₀.₃₇₅ZrO₃ in the electric field (0.1 MPa, 6.0 mA)

| Furnace temperature K | Catalyst bed temperature K | Imposed current mA | Response voltage kV | NH₃ synthesis rate μmol g⁻¹ h⁻¹ |
|-----------------------|----------------------------|-------------------|---------------------|-------------------------------|
| R.T.                  | 479.7                      | 6.0               | 0.403               | 967.7                         |
| R.T.                  | 478.3                      | 6.0               | 0.393               | 733.1                         |
| R.T.                  | 479.9                      | 6.0               | 0.393               | 708.6                         |
| R.T.                  | 481.0                      | 6.0               | 0.388               | 697.5                         |
| R.T.                  | 482.0                      | 6.0               | 0.405               | 866.9                         |
| R.T.                  | 484.4                      | 6.0               | 0.397               | 889.3                         |
| R.T.                  | 497.4                      | 6.0               | 0.388               | 692.9                         |
| R.T.                  | 498.3                      | 6.0               | 0.384               | 842.9                         |
| 373                   | 507.5                      | 6.0               | 0.365               | 670.9                         |
| 423                   | 531.4                      | 6.0               | 0.284               | 932.2                         |
| 473                   | 554.9                      | 6.0               | 0.278               | 1039.4                        |
| 573                   | 634.7                      | 6.0               | 0.244               | 2509.6                        |
Table S9 NH₃ synthesis rate over 5wt%Ru/Sr₀.₅Ba₀.₅ZrO₃ in the electric field (0.1 MPa, 6.0 mA)

| Furnace temperature K | Catalyst bed temperature K | Imposed current mA | Response voltage kV | NH₃ synthesis rate μmol g⁻¹ h⁻¹ |
|-----------------------|-----------------------------|--------------------|---------------------|-------------------------------|
| R.T.                  | 490.4                       | 6.0                | 0.391               | 819.1                         |
| R.T.                  | 484.8                       | 6.0                | 0.374               | 791.9                         |
| R.T.                  | 484.7                       | 6.0                | 0.368               | 750.0                         |
| R.T.                  | 488.2                       | 6.0                | 0.379               | 756.2                         |
| R.T.                  | 487.8                       | 6.0                | 0.382               | 762.8                         |
| R.T.                  | 467.1                       | 6.0                | 0.374               | 1044.7                        |
| R.T.                  | 452.9                       | 6.0                | 0.378               | 908.8                         |
| R.T.                  | 480.5                       | 6.0                | 0.444               | 1092.5                        |
| 373                   | 515.3                       | 6.0                | 0.378               | 942.3                         |
| 423                   | 523.4                       | 6.0                | 0.303               | 999.2                         |
| 473                   | 561.8                       | 6.0                | 0.287               | 1198.3                        |
| 573                   | 641.9                       | 6.0                | 0.245               | 3480.4                        |
Table S10 Specific surface areas of the fresh and the spent 5wt%Ru/Sr$_{1-x}$Ba$_x$ZrO$_3$ (0.000 ≤ x ≤ 0.500) catalysts

| Sr/Ba ratio (x) in 5wt%Ru/Sr$_{1-x}$Ba$_x$ZrO$_3$ | Specific surface area (BET method) |   |   |
|-----------------------------------------------|-----------------------------------|---|---|
|                                               | fresh                            | m$^2$ g$^{-1}$ | spent | m$^2$ g$^{-1}$ |
| -                                             |                                  |              |       |               |
| 0.000                                         | 6.11                             | 6.67         |       |               |
| 0.063                                         | 6.46                             | 7.11         |       |               |
| 0.125                                         | 7.21                             | 7.59         |       |               |
| 0.250                                         | 7.31                             | 6.79         |       |               |
| 0.375                                         | 7.88                             | 7.87         |       |               |
| 0.500                                         | 8.05                             | 9.36         |       |               |