

*Supporting Information*

Improved ammonia synthesis activity of Ce doped barium tantalate supported  
Ru catalysts

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Table: 5

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## 1. Experimental

### 1.1 Catalyst preparation

The Ce/BTO samples were prepared via a hydrothermal process.<sup>1</sup> All reagents are analytical grade and used without further purification. The 6.300 g Ba(OH)<sub>2</sub>·8H<sub>2</sub>O (20.0 mmol) and 0.550 g Ta<sub>2</sub>O<sub>5</sub> (1.25 mmol) were added into 45 mL of pure water and stirred for 1 h. Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was dissolved in 15 mL of pure water and dropped into the above solution and stirred for 30 min. Then, the mixture was transferred into a Teflon-lined autoclave (100 mL) and treated at 200 °C for 7 days. The light yellow product was recovered by filtering and washed repeatedly with pure water until the pH of the filtrate was nearly neutral. Finally the sample was dried at 60 °C in an oven for 12 h. The weights of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O are 0.077g, 0.154g, 0.231g and 0.308g, respectively, and they are named 1Ce/BTO, 2Ce/BTO, 3Ce/BTO and 4Ce/BTO according to the weight from small to large. The Ce was used to replace Ta element to prepare the sample of BCO and the other processes were kept consistent.

Ru catalysts were prepared according to the previously reported method.<sup>2</sup> The 0.500 g Ce/BTO support and 0.0315 g Ru<sub>3</sub>(CO)<sub>12</sub> added in 10 mL of tetrahydrofuran (THF) solution and stirred at 25 °C for 5 h. The rotary evaporator was used to remove THF solvent. Then, the obtained powder was heated at 250 °C for 3 h in the flow of Ar (99.999%, 5 mL min<sup>-1</sup>) to decompose Ru<sub>3</sub>(CO)<sub>12</sub>. The Cs-promoted catalysts also were prepared according to the previously reported. Based on the molar ratio of Cs to Ru (2, 3 and 4), the produced catalysts were named as 2Cs-Ru/2Ce/BTO, 3Cs-Ru/2Ce/BTO and 4Cs-Ru/2Ce/BTO.

### 1.2 Catalyst characterizations

XRD profiles of samples performed on a PANalytical X'Pert Pro diffractometer with a Cu-K $\alpha$  radiation. Electron paramagnetic resonance (EPR) spectrometer (Bruker, EMXnano) was used to detect oxygen vacancies operated at X-band at 25 °C. X-ray photoelectron spectra (XPS) were performed on an ESCALAB 250Xi (Thermo Fisher Scientific Inc., USA). The content of Ru and Ce in the catalysts was detected by ICP-AES (IRIS Intrepid II XSP, Thermo Fisher Scientific Inc., USA). Nitrogen adsorption-desorption isotherm evaluated the surface area of the prepared sample on BELSORPmini II (BEL, Japan) at -196 °C. Scanning electron microscopy (SEM, Zeiss Sigma) was used to observe the morphology of Ce/BTO samples. Transmission electron microscope (TEM, JEM-2100, JEOL, Japan) was used to recorded the microstructures of Ru/2Ce/BTO.

The Altamira AMI-300 instrument with a thermal conductivity detector was used for Temperature-programmed reduction (H<sub>2</sub>-TPR) experiments. Before the test, the samples (0.100 g) were pretreated under the flow of Ar (30 mL min<sup>-1</sup>) at 400 °C for 1 h. After cooling down to 25 °C in Ar (30 mL min<sup>-1</sup>), the temperature was raised up to 800 °C at 10 °C min<sup>-1</sup> in 30 mL min<sup>-1</sup> of 10 vol% H<sub>2</sub>/Ar and kept 30 min.

The kinetic measurements of Ru/2Ce/BTO catalyst was conducted based on method developed previously.<sup>2</sup> 0.100 g catalyst was loaded in a quartz tubular reactor (I.D. = 7 mm) in a flow rate of 60 mL min<sup>-1</sup>, and Ar gas was used as a diluent. The Ru/2Ce/BTO was reduced at 400 °C or 500 °C for 3 h at 0.1 MPa before the tests. The constituent gases of the reactant (N<sub>2</sub>, H<sub>2</sub>, Ar) were as follows in mL min<sup>-1</sup>: (5, 45, 10), (8, 45, 7), (10, 45, 5), (12, 45, 3) and (15, 45, 0) for N<sub>2</sub> order, (15, 5, 40), (15, 15, 30), (15, 25, 20), (15, 35, 10) and (15, 45, 0) for H<sub>2</sub> order.

In situ DRIFTS of adsorbed N<sub>2</sub> were collected on a Nicolet IS50 FTIR spectrometer in the range of 650-4000 cm<sup>-1</sup>. Prior to tests, catalysts were pretreated at 400 °C or 500 °C for 3 h in 45

mL min<sup>-1</sup> of H<sub>2</sub> and then purged at the same temperature for 60 min with He flow (15 mL min<sup>-1</sup>). The samples were cooled to 25 °C to obtain a background spectrum. The samples were exposed to 15 mL min<sup>-1</sup> of N<sub>2</sub> and the FTIR spectra for N<sub>2</sub> adsorbed on the catalyst were recorded.

### 1.3 Activity measurements

Ammonia synthesis was measured in a fixed bed plug flow system. Prior to measurement, the catalysts (0.100 g, 220 – 450 μm) were pretreated in synthesis gas (H<sub>2</sub>/N<sub>2</sub> = 3/1, 60 mL min<sup>-1</sup>) at 400 °C for 3 h to reduce Ru cations to metallic state and decompose CsNO<sub>3</sub>. The reaction temperature was from 300 to 400 °C at 0.1 MPa. The produced ammonia was trapped by a dilute sulfuric acid solution (1 mmol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>) solution. The rate of ammonia formation was calculated based on the rate of decrease in the conductivity of the H<sub>2</sub>SO<sub>4</sub> solution. It was necessary to stabilize for 20 minutes under each reaction condition before the measurement.

Table S1. The BET specific surface area ( $S_{\text{BET}}$ ) of Ce doped BTO.

| catalysts                                       | BTO  | 1Ce/BTO | 2Ce/BTO | 3Ce/BTO | 4Ce/BTO |
|-------------------------------------------------|------|---------|---------|---------|---------|
| $S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ ) | 10.8 | 29.3    | 35.6    | 39.3    | 42.6    |

Table S2. The content of Ce and Ru in support by ICP-AES

| catalysts | Ru/BTO | Ru/1Ce/BTO | Ru/2Ce/BTO | Ru/3Ce/BTO | Ru/4Ce/BTO |
|-----------|--------|------------|------------|------------|------------|
| Ru (wt%)  | 1.96   | 2.35       | 2.62       | 2.42       | 2.48       |
| Ce (wt%)  | -      | 2.06       | 3.57       | 4.51       | 6.59       |

Table S3. Comparison of ammonia synthesis activity over Ru catalyst on BTO, 2Ce/BTO and BCO supports

| catalysts  | $\text{NH}_0$ synthesis rates ( $\mu\text{mol g}^{-1}\text{cat h}^{-1}$ ) |        |        |        | $E_a$ (kJ mol $^{-1}$ ) |
|------------|---------------------------------------------------------------------------|--------|--------|--------|-------------------------|
|            | 325 °C                                                                    | 350 °C | 375 °C | 400 °C |                         |
| Ru/BTO     | 370                                                                       | 529    | 806    | 1508   | 62                      |
| Ru/2Ce/BTO | 554                                                                       | 954    | 1775   | 3251   | 79                      |
| Ru/BCO     | 356                                                                       | 832    | 1426   | 2235   | 81                      |

Table S4. XPS spectra results of Ce 3d on 2Ce/BTO and Ru/2Ce/BTO catalysts at various activated temperature.

|                                   | Area     |                       |                        |                        |                        |                        |                        |                        |                        |                        |
|-----------------------------------|----------|-----------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
|                                   | 2Ce/BTO  | Ru/2Ce/BTO<br>(fresh) | Ru/2Ce/BTO<br>(400 °C) | Ru/2Ce/BTO<br>(450 °C) | Ru/2Ce/BTO<br>(500 °C) | Ru/2Ce/BTO<br>(550 °C) | Ru/2Ce/BTO<br>(600 °C) | Ru/2Ce/BTO<br>(650 °C) | Ru/2Ce/BTO<br>(700 °C) | Ru/2Ce/BTO<br>(750 °C) |
| 916.0                             | 10824.63 | 5890.769              | 5945.58                | 11290.82               | 5906.766               | 8458.456               | 5926.049               | 3612.979               | 8400.356               | 3431.513               |
| 901.0                             | 52086.45 | 39860.72              | 45591.45               | 46199.76               | 45326.22               | 70310.52               | 58485.13               | 33512.32               | 49927.68               | 50331.42               |
| 898.0                             | 74770.48 | 53213.7               | 61122.31               | 67288.34               | 66460.69               | 99709.66               | 84759.61               | 46764.07               | 10925.13               | 66032.91               |
| 888.6                             | 46076.01 | 33726.63              | 42918.14               | 46957.82               | 46725.7                | 69784.41               | 59856.4                | 31679.33               | 66753.66               | 46857.21               |
| 882.2                             | 30244.32 | 21009.5               | 18185.57               | 24874.31               | 18674.07               | 30934.72               | 27503.54               | 13063.29               | 21555.98               | 22901.82               |
| Total area<br>of Ce <sup>4+</sup> | 21401.89 | 153701.31<br>9        | 173763.05              | 196611.05              | 183093.446             | 279197.766             | 236530.72<br>9         | 128631.989             | 157562.806             | 189554.873             |
| 903.7                             | 19403.71 | 9441.6                | 18720.34               | 28860.14               | 25762.21               | 39313.06               | 35880.63               | 18805.39               | 36086.55               | 38282.69               |
| 899.3                             | 0.22     | 6088.649              | 6507.059               | 5608.325               | 7491.358               | 7193.872               | 13123.72               | 7726.825               | 9641.424               | 22080.42               |
| 885.6                             | 10824.63 | 38767.3               | 43724.29               | 41041.5                | 43076.55               | 65302.49               | 61472.91               | 36253.2                | 51236.51               | 68669.29               |
| 880.6                             | 3295.437 | 3677.36               | 1574.772               | 4521                   | 5577.44                | 8221.598               | 8150.503               | 3298.341               | 6165.702               | 10428.08               |

|                                                            |           |           |           |           |           |           |           |           |            |           |
|------------------------------------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|------------|-----------|
| Total area<br>of Ce <sup>3+</sup>                          | 33523.997 | 57974.909 | 70526.461 | 80030.965 | 81907.558 | 120031.02 | 118627.76 | 66083.756 | 103130.186 | 139460.48 |
| Ce <sup>3+</sup> /(Ce <sup>3+</sup><br>+Ce <sup>4+</sup> ) | 13.5 %    | 27.4 %    | 28.9 %    | 28.9 %    | 30.9 %    | 30.1 %    | 33.4 %    | 33.9 %    | 39.6 %     | 42.4 %    |

Table S5. Comparison of ammonia synthesis activity over various Ru catalysts at 0.1 MPa

| Catalysts                                             | Ru loading (wt%) | T (°C) | NH <sub>3</sub> synthesis rate                        |                                                    | Ref.      |
|-------------------------------------------------------|------------------|--------|-------------------------------------------------------|----------------------------------------------------|-----------|
|                                                       |                  |        | ( $\mu\text{mol g}^{-1}_{\text{cat}} \text{h}^{-1}$ ) | ( $\text{mmol g}^{-1}_{\text{Ru}} \text{h}^{-1}$ ) |           |
| 3Cs-Ru/2Ce/BTO                                        | 2.62             | 350    | 4390                                                  | 167.6                                              | This work |
| 8Cs-Ru/Sr <sub>2</sub> Nb <sub>2</sub> O <sub>7</sub> | 2.0              | 350    | 1060                                                  | 53.0                                               | 3         |
| Ru/C12A7:e <sup>-</sup>                               | 1.2              | 400    | 2757                                                  | 229.8                                              | 4         |
| Ru/Pr <sub>2</sub> O <sub>3</sub>                     | 5                | 400    | 3600                                                  | 72                                                 | 5         |
| Ru/BaO–CaH <sub>2</sub>                               | 10               | 340    | 10500                                                 | 105.0                                              | 6         |
| Ru/CaH <sub>2</sub>                                   | 10               | 340    | 7400                                                  | 74.0                                               | 6         |
| Ru/Ca <sub>2</sub> N:e <sup>-</sup>                   | 1.8              | 340    | 3386                                                  | 188.1                                              | 7         |
| Ru/CaNH                                               | 1.8              | 340    | 308                                                   | 17.1                                               | 7         |
| Ru–Cs/MgO                                             | 2.0              | 340    | 3200                                                  | 160.0                                              | 7         |
| LaRuSi                                                | -                | 340    | 3020                                                  | -                                                  | 8         |

Fig. S1 The SEM images of BTO and Ce/BTO: (a) BTO, (b) 1Ce/BTO, (c) 2Ce/BTO, (d) 3Ce/BTO, (e) 4Ce/BTO.



Fig. S2 The SEM-mapping images of BTO and Ce/BTO: (a) BTO, (b) 2Ce/BTO and (c) 4Ce/BTO

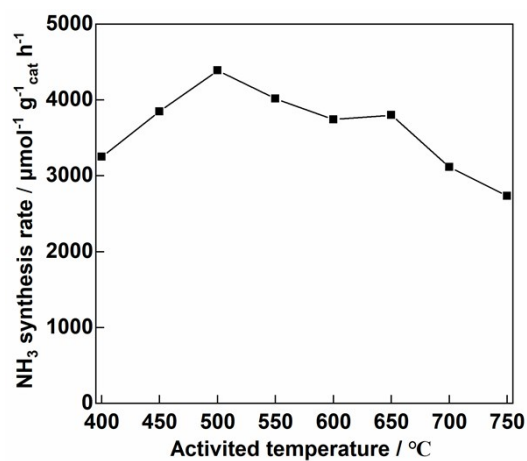


Fig S3. The ammonia synthesis over Ru/2Ce/BTO at 400  $^\circ\text{C}$  with different activated temperature.

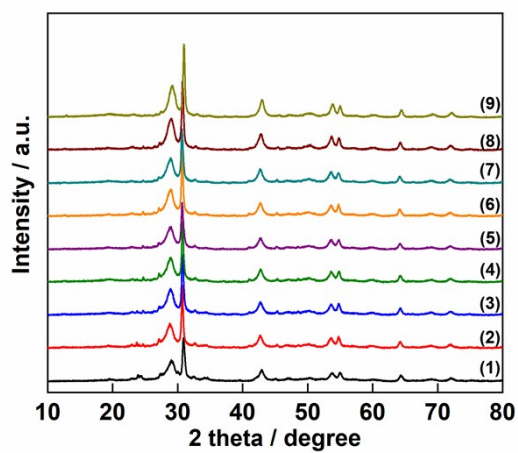


Fig. S4. The XRD profiles of used Ru/2Ce/BTO activated at different temperatures: (1) as-prepared (fresh), (2) 400 °C, (3) 450 °C, (4) 500 °C, (5) 550 °C, (6) 600 °C, (7) 650 °C, (8) 700 °C, (9) 750 °C.

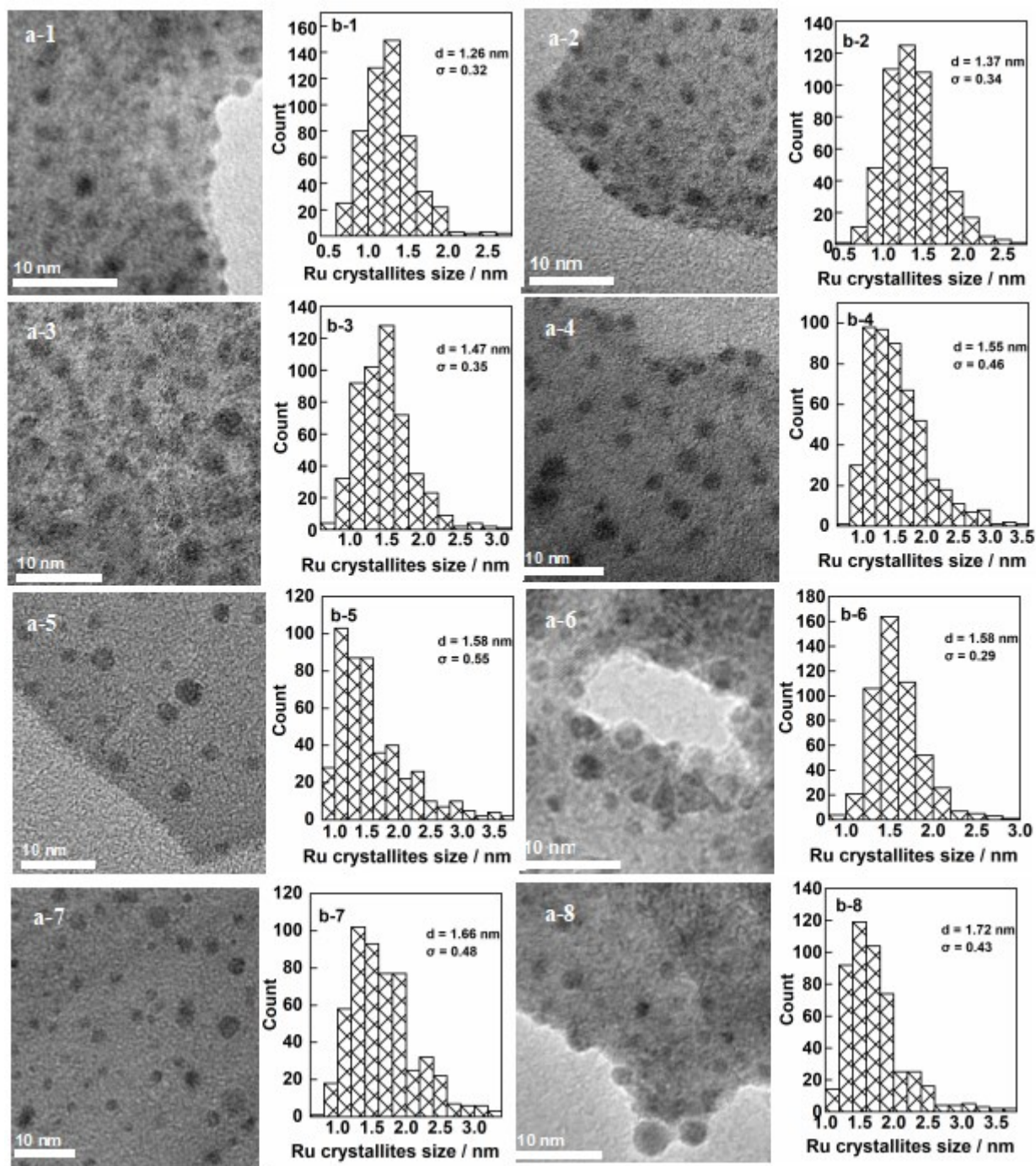


Fig. S5 (a) TEM images and (b) size distribution of Ru particles on Ru/2Ce/BTO catalyst after reaction at different temperature; (1) 400 °C, (2) 450 °C, (3) 500 °C, (4) 550 °C, (5) 600 °C, (6) 650 °C, (7) 700 °C, and (8) 750 °C.

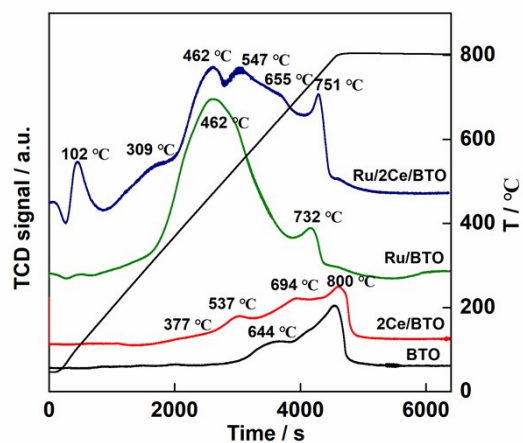


Fig. S6 The H<sub>2</sub>-TPR profiles of BTO, 2Ce/BTO, Ru/BTO and Ru/2Ce/BTO.

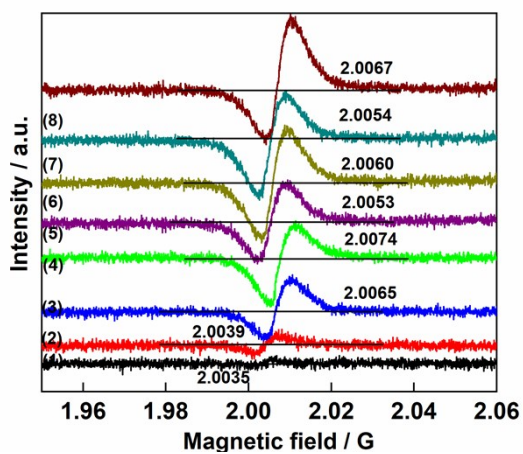


Fig. S7 EPR spectra of Ru/2Ce/BTO catalyst after reaction at different temperature; (1) 400 °C, (2) 450 °C, (3) 500 °C, (4) 550 °C, (5) 600 °C, (6) 650 °C, (7) 700 °C, (8) 750 °C.

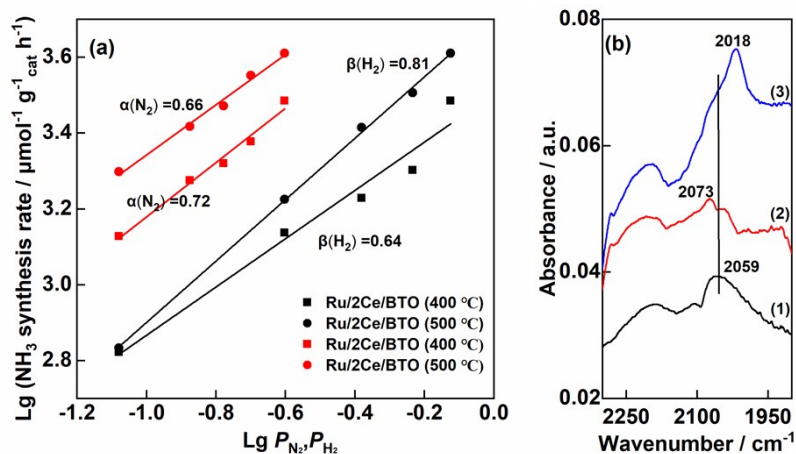


Fig. S8 (a) Effect of the partial pressures of  $N_2$  and  $H_2$  on  $NH_3$  synthesis rate on Ru/2Ce/BTO activated at 400 °C or 500 °C. Reaction conditions: catalyst 0.100 g; pressure 0.1 MPa; temperature 400 °C. (b) In situ FTIR spectra of adsorbed  $N_2$  at 25 °C on different catalysts: (1) Ce/BTO (2) Ru/2Ce/BTO activated at 400 °C, and (3) Ru/2Ce/BTO activated at 500 °C.

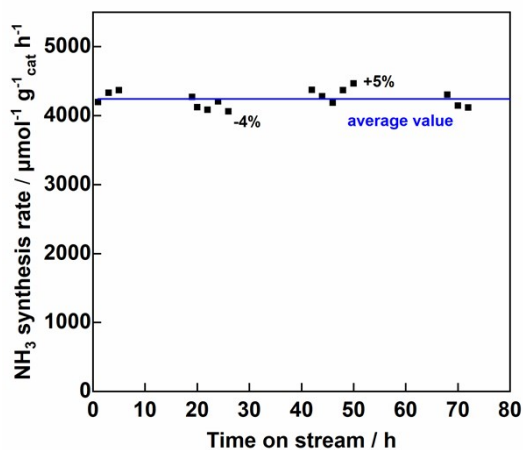


Fig. S9 The time dependence of catalytic rates of Ru/2Ce/BTO catalyst. Reaction conditions: catalyst, 0.100 g, synthesis gas, H<sub>2</sub>/N<sub>2</sub>=3 60 mL min<sup>-1</sup>, at 400 °C and 0.1 MPa.

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