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Three-Dimensional Ordered Macroporous Ru-Substituted $BaZrO_3$ Perovskite: Active Catalysts for Ammonia Synthesis under Mild Conditions

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1. Methods

1.1 Sample preparation

In a typical synthesis, 1.440 g of $Ba(NO_3)_3$, 1.614 g of $ZrOCl_2•8H_2O$ and 0.055 g of $RuCl_3•nH_2O$ were dissolved in 10 mL of aqueous ethanol solution (40%). Then the solution was stirred at room temperature (RT) for 3 h. 2.0 g of the well-arrayed hard template PMMA (ca. 300 nm, reported in the literature[1]) was soaked in the above precursor solution for 4 h. After being filtered, the obtained solid powder was dried at RT overnight. Then the product was transferred to a tubular furnace, first calcined in N_2 atmosphere at 300 ℃ for 3 h, and then calcined in air atmosphere at 700 ℃ for 6 h. Finally, three-dimensional ordered macroporous $BaZr_{0.95}Ru_{0.05}O_3$ was obtained. The synthetic procedures for $BaZrO_3$ and $BaZr_{0.9}Ru_{0.1}O_3$ were similar to that for $BaZr_{0.95}Ru_{0.05}O_3$ except for different Zr/Ru molar ratios.

For comparison purposes, the traditional $BaZrO_3$ was prepared by sol-gel method described elsewhere[2] (S-G $BaZrO_3$). Stoichiometry amounts of $Ba(NO_3)_2$ and $Zr(NO_3)_4·5H_2O$ were dissolved in 100 mL deionized water. The obtained mixture was homogenized by stirring at 80 ℃ for 1 h. The solution was slowly evaporated at 80 ℃ to get a clear yellow gel and then a white foam sample was formed. The sample was dried at 100 ℃ overnight and calcined at 300 ℃ for 3 h and 700 ℃ for 6 h in air atmosphere. The resulting white powder was S-G $BaZrO_3$ catalyst. Besides, we also prepared S-G Ru/$BaZrO_3$ by incipient wetness imprecation method.

1.2 Sample characterization

Powder X-ray diffraction (XRD) was conducted on a Panalytical X'Pert Pro diffractometer using Co-K_α radiation. Raman spectra of catalysts were recorded under ambient conditions on a Renishaw spectrometer, and a laser beam (λ= 532 nm) was used for excitation. N_2 physisorption measurements were carried out at 77 K on an ASAP 2020 apparatus. Scanning Electron Microscope (SEM) was performed on a JSM6700-F instrument. High-resolution transmission electron microscopy (HR-TEM) measurement were measured on a JEM-2010 microscope. The pore-size distributions of the 3DOM $BaZr_{(1-x)}RuxO_3$ samples were determined by mercury intrusion porosimetry (Micromeritics, Autopore IV 9500). Before measurement, 0.5 g of the sample was pretreated in a vacuum drying oven at 150 °C for 1 h. N_2 (or H_2) Temperature-programmed desorption (N_2-TPD or H_2-TPD) was carried out on an Autochem 2920 instrument. After being treated in hydrogen at 450 °C for 60 min, purged with Ar, and cooled down to 50 °C, the catalyst (100 mg) was exposed to nitrogen (or hydrogen) at 50 °C for 1 h. The sample was flushed with Ar for 1 h before being heated to 600 °C at a rate of 10 °C/min, and held at 600 °C for 20 min, with the desorption of nitrogen or hydrogen monitored by a thermal conductivity detector. Ru dispersions were determined from CO-pulse chemisorption on an Autochem 2920 instrument at 50 °C using a He flow of 30 ml/min and pulse of 0.49 mL CO. One CO molecule was assumed to be absorbed in one Ru atoms. X-ray photoelectron spectroscopy (XPS) analysis was performed on Physical Electronics Quantum 2000, equipped with monochromatic Al-K_α source (K_α= 1,486.6 eV) and a charge neutralizer. The catalysts were first treated in H_2 atmosphere at 450 ℃ for 4 h. The X-ray absorption find structure spectra (XAFS) measurements (Cu K-edge) were collected at 1W1B station in Beijing Synchrotron Radiation Facility (BSRF). The storage rings of BSRF was operated at 2.5 GeV with a maximum current of 250 mA. Using Si (111) double-crystal monochromator, the data collection were carried out in transmission mode using ionization chamber. All spectra were collected in ambient conditions. Before measured, the catalysts were also treated in 10% H_2/Ar atmosphere at 450 °C for 4 h. Moreover, the acquired EXAFS data were processed according to the standard procedures using the ATHENA module implemented in the IFEFFIT software packages. The k3-weighted EXAFS spectra were obtained by subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge-jump step. Subsequently, k3-weighted χ(k) data of Cu K-edge were Fourier transformed to real (R) space using a hanning windows (dk=1.0 $Å^{-1}$) to separate the EXAFS contributions from different coordination shells. To obtain the quantitative structural parameters around central atoms, least-squares curve parameter fitting was performed using the ARTEMIS module of IFEFFIT software packages.

1.3 Catalytic reaction

The catalytic reaction was conducted in a fixed bed flow system. Before the activity test for ammonia synthesis, the catalysts (0.30 g, diluted with quartz powder in a 1:10 volumetric ratio) were reduced in 10% H_2/Ar at 450 °C for 4 h. In the evaluation of catalytic activity under the condition of 0.2-5 MPa at a WHSV of 50 000 h^{-1}, the produced ammonia was trapped in a known amount of diluted H_2SO_4 solution (5 mmol), and then ammonia concentration was determined by ion chromatography (Thermo Scientific, DIONEX, ICS-600). Finally, the rates of ammonia synthesis were calculated based on the outlet ammonia concentration.

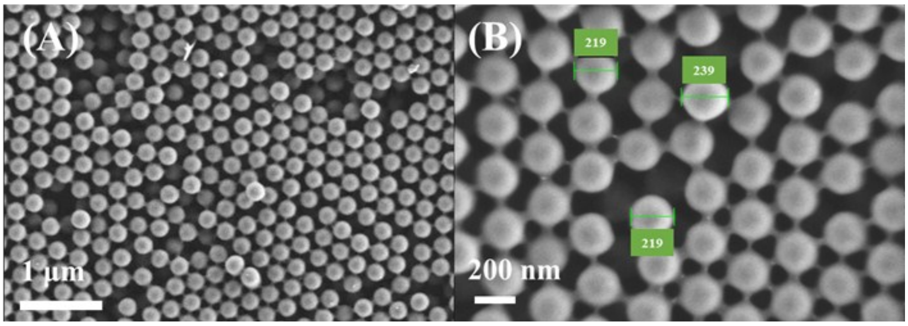

Figure S1 SEM images of PMMA.

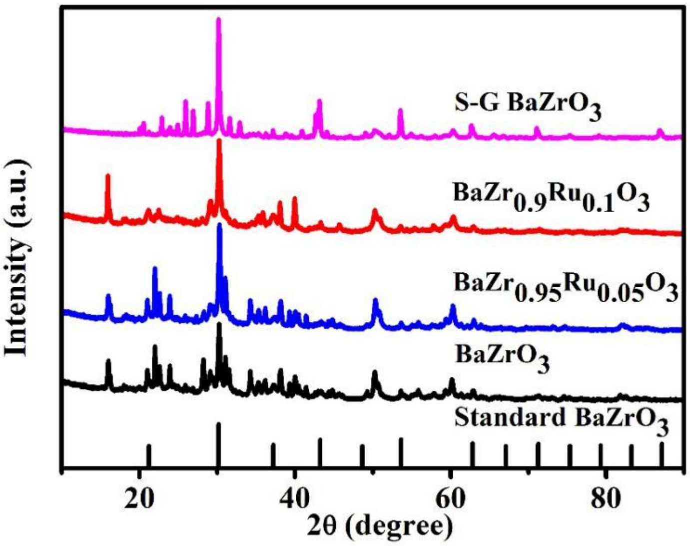

Figure S2 XRD patterns of S-G BaZrO$_3$, 3DOM BaZrO$_3$, 3DOM BaZr$_{0.95}$Ru$_{0.05}$O$_3$ and 3DOM BaZr$_{0.9}$Ru$_{0.1}$O$_3$.

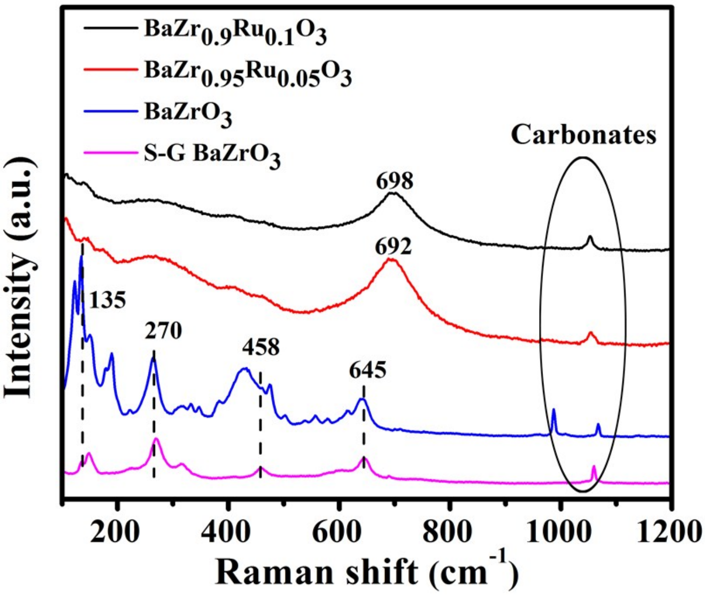

Figure S3 Raman spectra of S-G BaZrO$_3$, 3DOM BaZrO$_3$, 3DOM BaZr$_{0.95}$Ru$_{0.05}$O$_3$ and 3DOM BaZr$_{0.9}$Ru$_{0.1}$O$_3$.

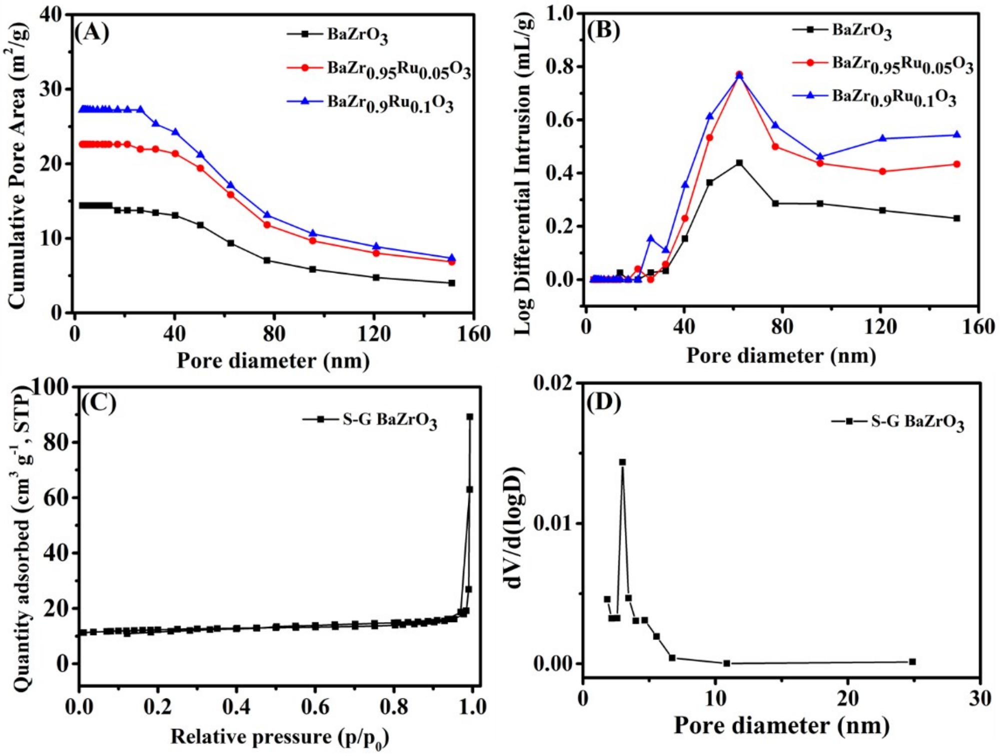

Figure S4 (A) Total pore area and (B) pore-size distribution of 3DOM $BaZrO_3$, 3DOM $BaZr_{0.95}Ru_{0.05}O_3$ and 3DOM $BaZr_{0.9}Ru_{0.1}O_3$ measured by pressurized mercury method (C) Nitrogen adsorption–desorption isotherms and (D) pore-size distributions of S-G $BaZrO_3$.

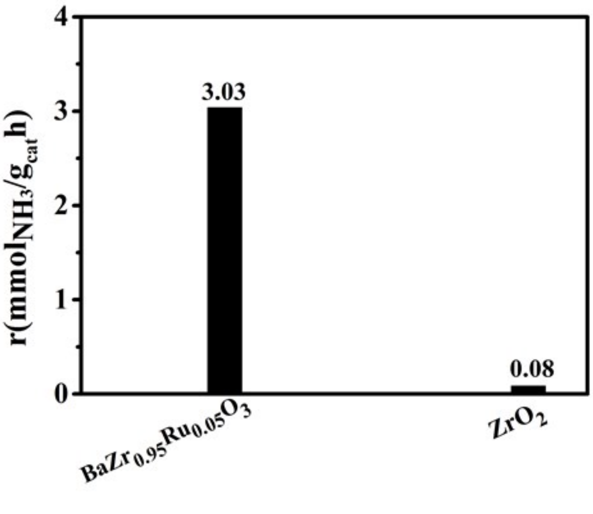

Figure S5 Ammonia synthesis rates over 3DOM $BaZr_{0.95}Ru_{0.05}O_3$ and ZrO_2 at 350 °C and 1 MPa. (Reaction conditions: N_{2Vol}: H_{2Vol} = 1:3, WHSV: 50 000 h^{-1}).

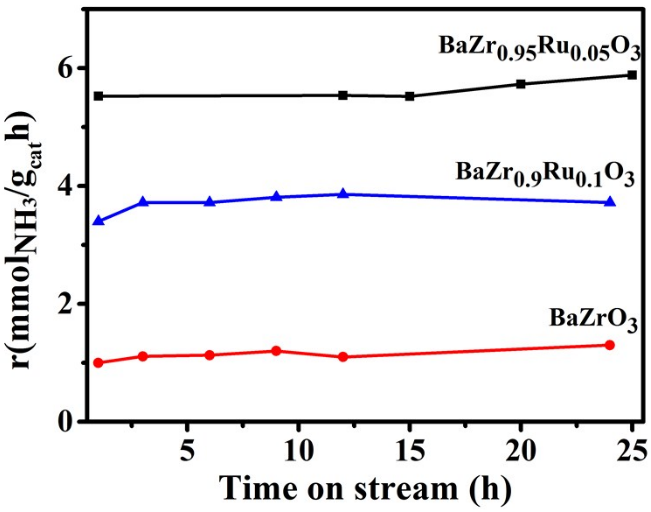

Figure S6 Time course of the ammonia synthesis rate over 3DOM $BaZrO_3$, $BaZr_{0.95}Ru_{0.05}O_3$ and $BaZr_{0.9}Ru_{0.1}O_3$ at 1 MPa and 400 °C. (Reaction conditions: N_{2Vol}: H_{2Vol} = 1:3, WHSV: 50 000 h^{-1}).

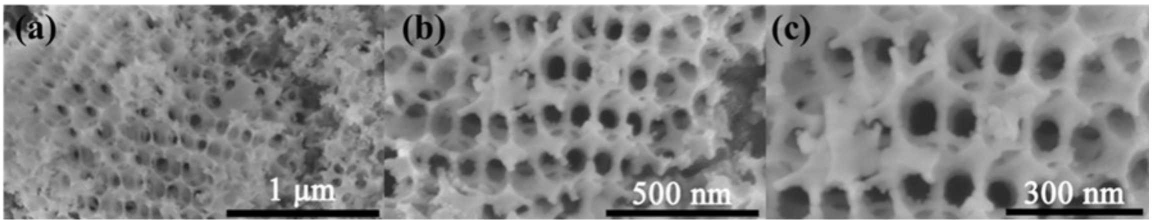

Figure S7 SEM images of the used 3DOM $BaZr_{0.95}Ru_{0.05}O_3$.

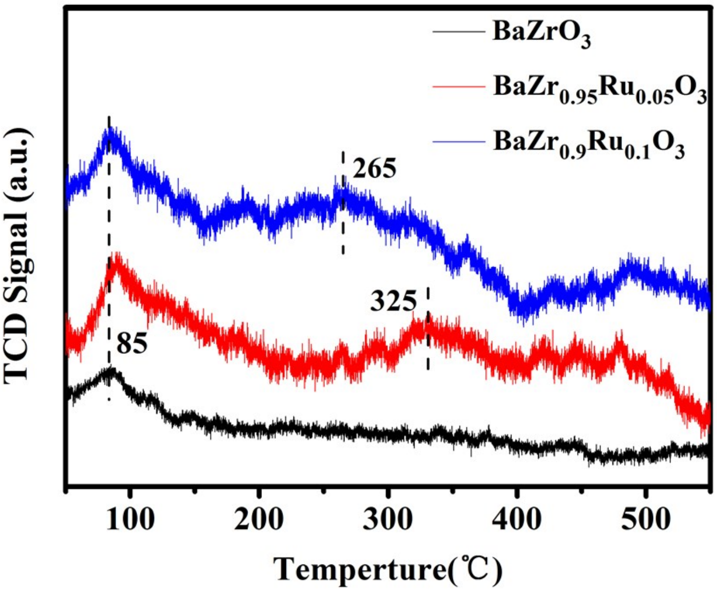

Figure S8 H_2-TPD profiles of 3DOM $BaZrO_3$, 3DOM $BaZr_{0.95}Ru_{0.05}O_3$ and 3DOM $BaZr_{0.9}Ru_{0.1}O_3$.

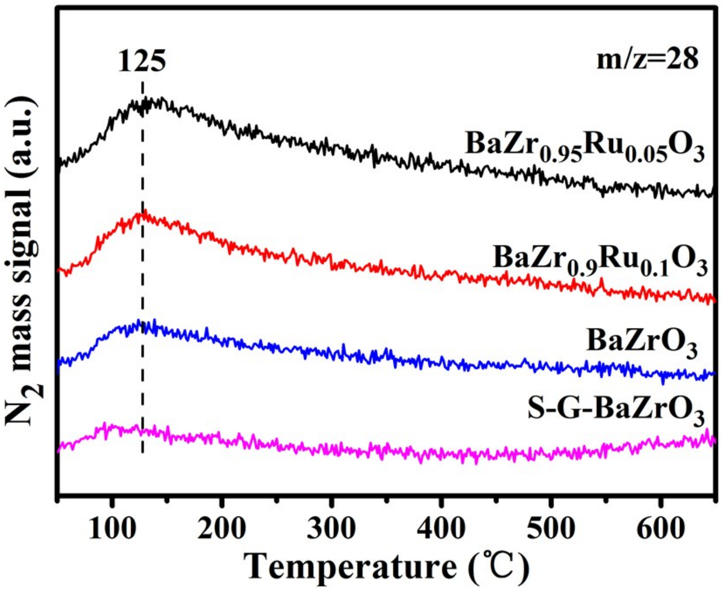

Figure S9 N_2-TPD-MS profiles of S-G $BaZrO_3$, 3DOM $BaZrO_3$, 3DOM $BaZr_{0.95}Ru_{0.05}O_3$ and 3DOM $BaZr_{0.9}Ru_{0.1}O_3$.

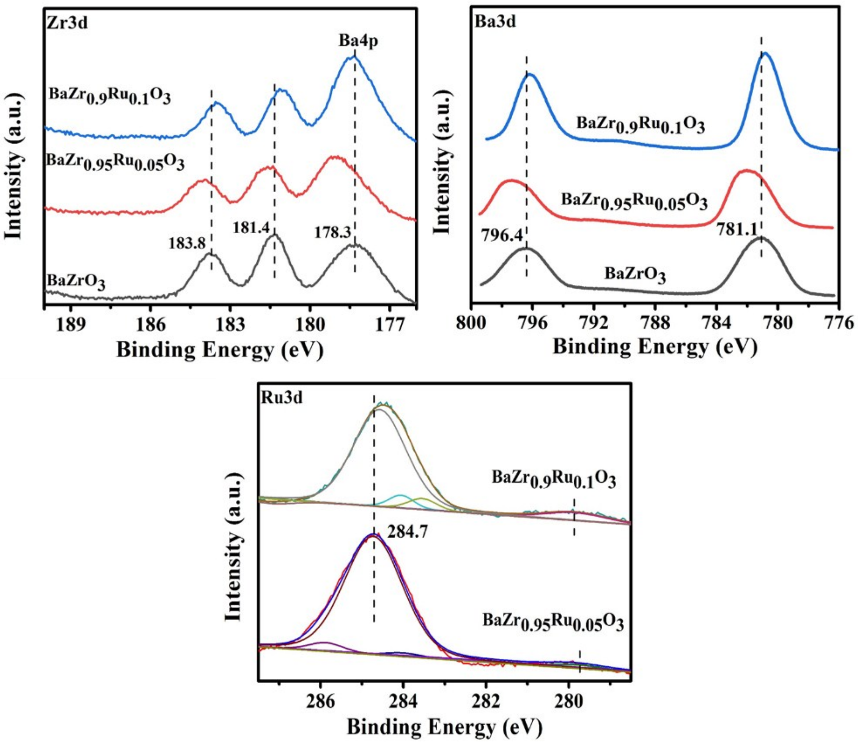

Figure S10 XPS Zr3d, Ba3d, O1s, and Ru3d spectra over 3DOM $BaZrO_3$, 3DOM $BaZr_{0.95}Ru_{0.05}O_3$ and 3DOM $BaZr_{0.9}Ru_{0.1}O_3$.

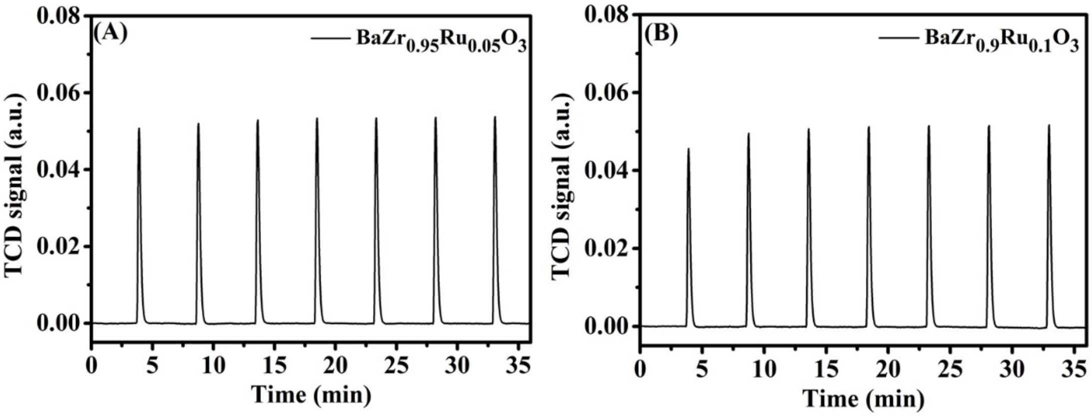

Figure S11 CO-plus chemisorption profiles of (A) 3DOM $BaZr_{0.95}Ru_{0.05}O_3$ and (B) 3DOM $BaZr_{0.9}Ru_{0.1}O_3$.

Table S1 Ru content (wt.%), Crystallize size, pore parameters, Dispersion (D_m), turnover frequency (TOF) and N_2 desorption amounts of as-prepared catalysts.

Catalyst	Ru content (wt.%)	Crystallite size[a] (nm)	Pore diameter (nm)[b]	Total pore area (m^2/g)[c]	Pore diameter (nm)[c]	D_m[d] (%)	TOF_{Ru}[e] (10^{-3} s^{-1})	N_2 desorption amounts[f] (μmol/g)
3DOM-$BaZrO_3$	-	31	74	14	75	-	-	19.4
3DOM-$BaZr_{0.95}Ru_{0.05}O_3$	1.8	29	95	23	80	1.9	4.5	32.1
3DOM-$BaZr_{0.9}Ru_{0.1}O_3$	3.6	25	85	27	75	2.3	2.6	23.1
S-G $BaZrO_3$	-	47	-	-	-	-	-	18.0

[a] Data calculated according to the full width at half-maximum of the (110) line.

[b] Estimated according to SEM and TEM images.

[c] Estimated according to the result measured by pressurized mercury method.

[d] Data calculated on the basis of CO chemisorption values

[e] TOF_{Ru} values based on the number of surface Ru atoms at 350 °C.

[f] Based on the area of N_2-TPD-MS peak around 125 °C.

Table S2 Ammonia synthesis rates of various Ru-based catalysts reported in this work and previous literature under the given conditions.

catalyst	Ru content (wt.%)	WHSV (h^{-1})	Pressure (MPa)	Temperature (°C)	Ammonia synthesis rate ($mmol_{NH3}/(g_{cat}·h)$)	Ref.
3DOM $BaZr_{0.95}Ru_{0.05}O_3$	1.8	50 000	1	350	3.0	This work
				400	5.5	This work
Ru/$BaZrO_3$	4.0	10 000	1	400	2.5	6
Ru/$BaTiO_3$	0.89	66 000	5	400	4.1	17
Ru/CeO_2	2.42	60 000	1	350	2.2	18
Cs−Ru/MgO	-	66 000	5	400	2.7	19

Table S3 Surface Ba content, Surface Zr content, Surface Ru content and $O_{ads}/(O_{ads}+O_{latt})$ ratio.

Sample	Surface Ba content (%)	Surface Zr content (%)	Surface Ru content (%)	$O_{ads}/(O_{ads}+O_{latt})$
3DOM-$BaZrO_3$	16	21	-	0.50
3DOM-$BaZr_{0.95}Ru_{0.05}O_3$	17	21	6	0.49
3DOM-$BaZr_{0.9}Ru_{0.1}O_3$	12	21	2	0.44

Table S4 EXAFS fitting parameters at the Ru K-edge.

Sample	Shell	*CN* [a]	*R* (Å) [b]	σ^2 (Å^2·10^3) [c]	ΔE_0 (eV)[d]	*R* factor (%)
$BaZr_{0.95}Ru_{0.05}O_3$	Ru-O	2.6	1.99	4.0	2.0	0.8
	Ru-Ru	4.2	2.67	4.4	-3.1	
$BaZr_{0.90}Ru_{0.1}O_3$	Ru-O	0.9	2.08	2.5	7.24	0.4
	Ru-Ru	6.3	2.67	5.1	-2.4	

[a] *CN*: coordination numbers;

[b] *R*: bond distance;

[c] σ^2: Debye-Waller factors;

[d] ΔE_0: the inner potential correction.

R factor: goodness of fit.

References

1. H. Li, L. Zhang, H. Dai and H. He, *Inorg. Chem.*, 2009, **48,** 4421–4434.

2. Z. Wang, B Liu and J. Lin. *Appl. Catal. A: Gen.*, 2013, **458**, 130–136.