Supplementary Information

Synergistic effect of coordinating interface and promoter for enhancing ammonia synthesis activity of Ru@N-C catalyst

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1. Ru/AC(450) catalyst:

The activated carbon particles treated with nitric acid were placed in an ark and roasted in a tube furnace under argon atmosphere at 450 °C for one hour of a heating rate of 5 °C/min. Then $Ru_3(CO)_{12}$ was dissolved in tetrahydrofuran solution, roasted activated carbon was added, impregnated and stirred at room temperature for 24 hours, and then the sample was placed on a rotary evaporator to remove the solvent, and the obtained sample was dried in a drying oven at 60 °C. The dried sample is also roasted in the tube furnace under argon gas for one hour, the temperature is 450 °C, and the heating rate is 5 °C /min. After the roasting is completed, the sample is removed by the furnace after natural cooling to room temperature, which is donated as Ru/AC(450). The load capacity of Ru is 3%.

2. The analysis of ammonia synthesis rate

A). Chemical titration: The rate of ammonia synthesis was determined with Congo red as an indicator when the amount of H_2SO_4 was known. The concentration of H_2SO_4 used is 0.05 mol/L. Determination is to take 25 μL of H_2SO_4 and add 50 μL of Congo red indicator to the sample tube, and then add 2 mL of deionized water, the sample tube is connected to the fixed bed reactor, record the time of indicator color change, and convert to the export ammonia rate.

B). Nessler's reagent spectrophotometry: The outlet ammonia is absorbed by 0.05 mol/L H_2SO_4 solution, and the NH_4^+ generated in the solution reacts with the Nessler's reagent to form a yellow brown complex. The absorbance of the complex is directly proportional to the content of NH_4^+. The absorbance of the complex is measured at 420 nm wavelength, and the NH_4^+ content in the solution can be calculated according to the absorbance. The outlet ammonia rate is obtained.

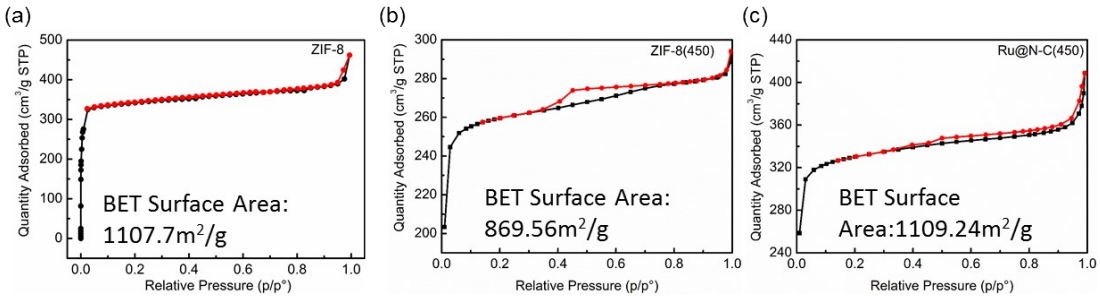

Figure S1. Nitrogen adsorption–desorption isotherms of ZIF-8, ZIF-8(450) and Ru@N-C(450) samples.

Table S1. Textural parameters of calcined ZIF-8(450) and Ru@N-C(450) samples.

Sample	*S* (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
ZIF-8	1107.7	2.163	0.63
ZIF-8(450)	869.56	0.45	2.05
Ru@N-C(450)	1109.24	0.60	2.17

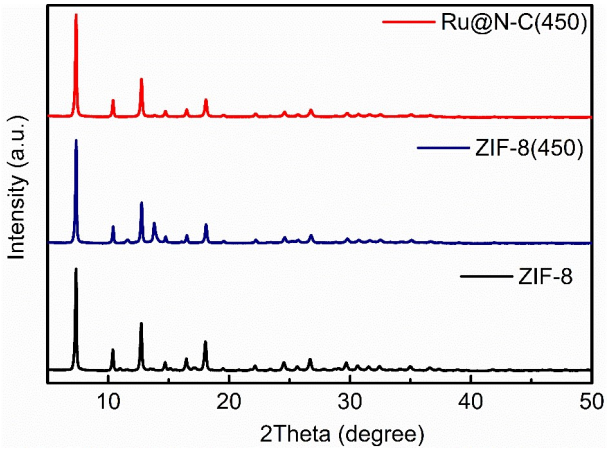

Figure S2. XRD patterns of ZIF-8, ZIF-8(450), and Ru@N-C(450).

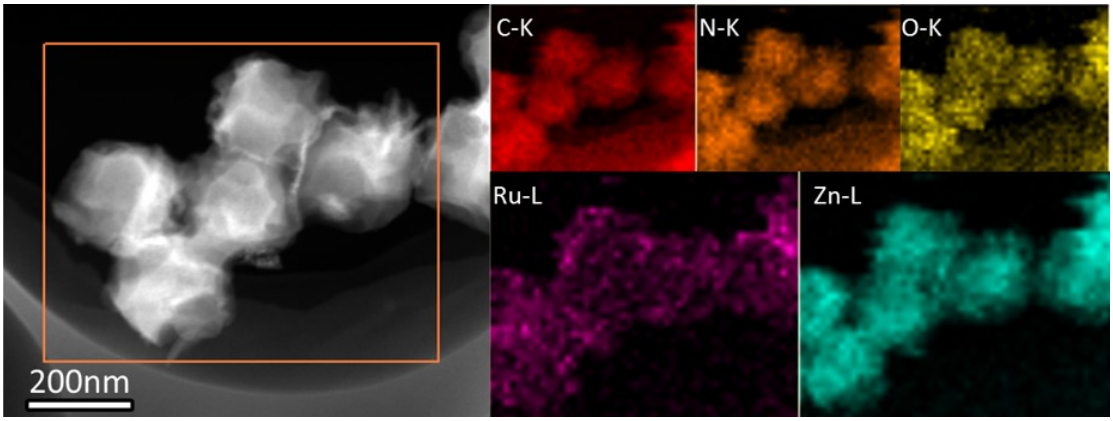

Figure S3. The elemental mapping of Ru@N-C(450) catalyst before reaction.

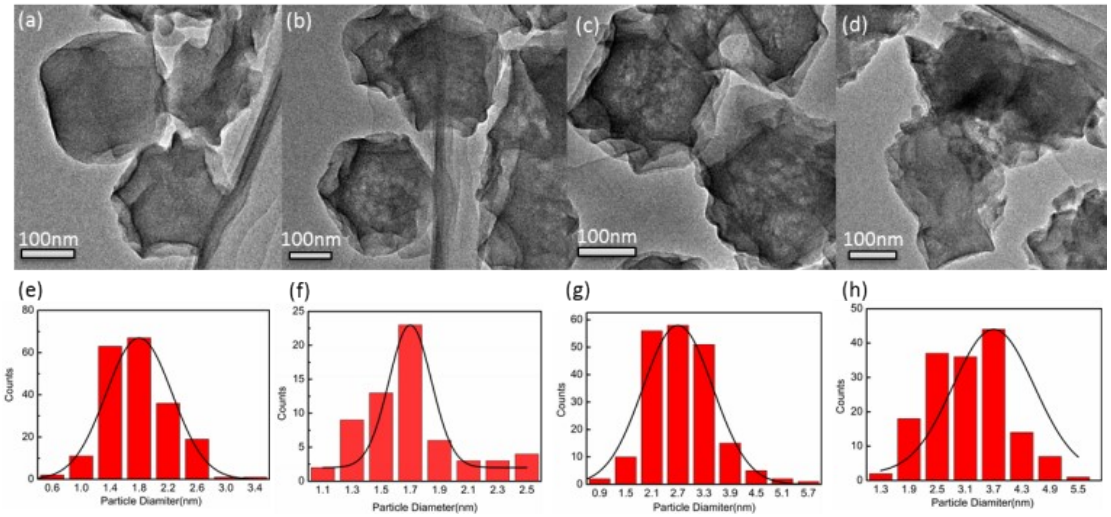

Figure S4. TEM images of (a) Ru@N-C(400), (b) Ru@N-C(450), (c) Ru@N-C(500), (d) Ru@N-C(900) and their corresponding Ru particle distribution histograms(e-h).

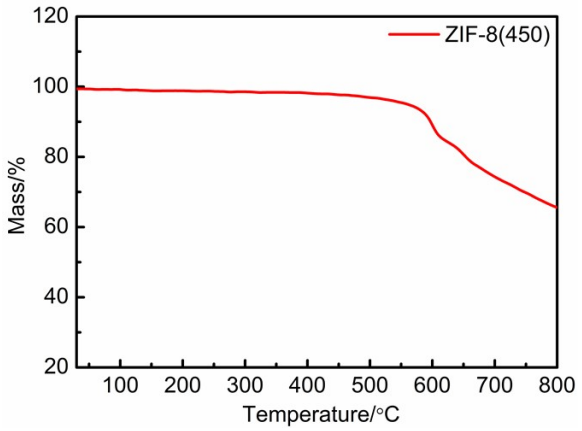

Figure S5. TG analysis plot of ZIF-8(450) support**.**

ZIF-8(450) catalyst:

The prepared ZIF-8 was placed in an ark and calcined in a tubular furnace at 450°C for one hour of a heating rate of 5°C /min. After the calcination, the sample was naturally cool to room temperature and then taken out and recorded as ZIF-8(450).

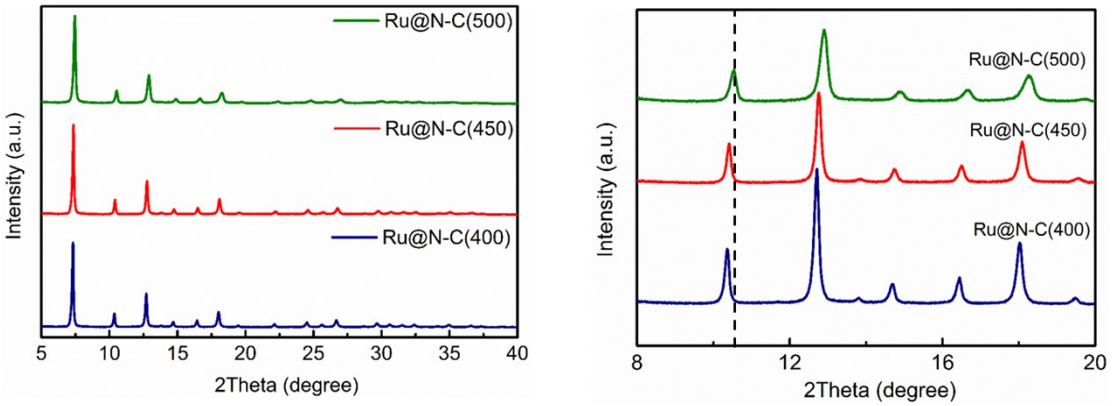

Figure S6. XRD patterns of Ru@N-C(400), Ru@N-C(450), and Ru@N-C(500).

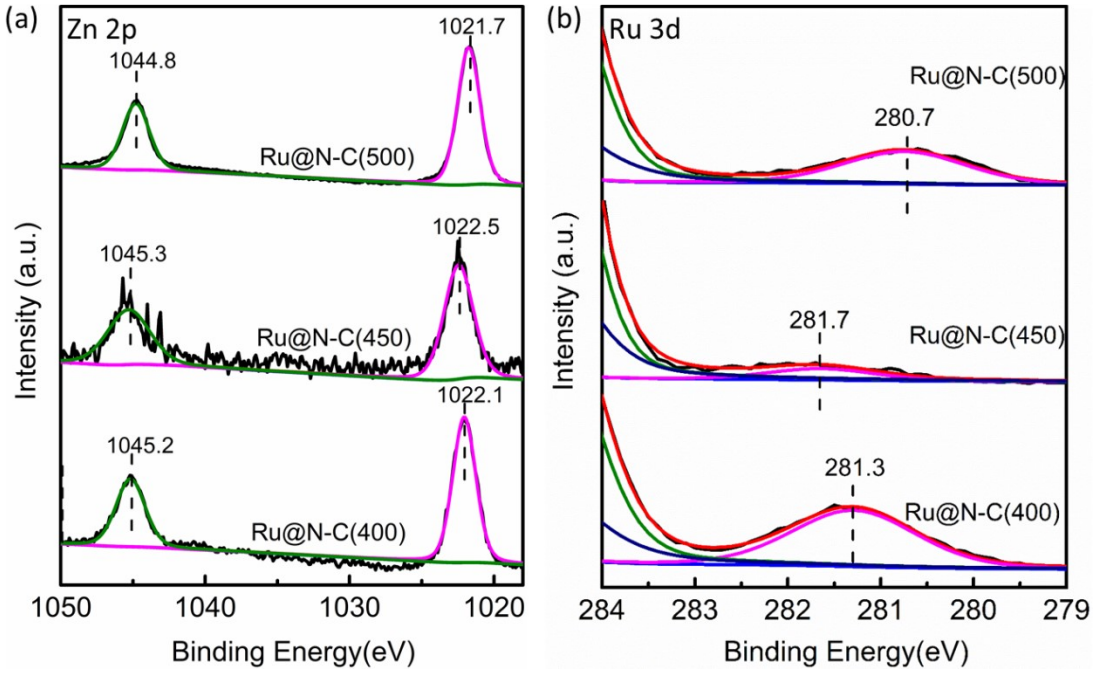

Figure S7. The XPS spectra of (a) Zn 2p and (b) Ru 3d in Ru@N-C(500), Ru@N-C(450) and Ru@N-C(400) catalysts.

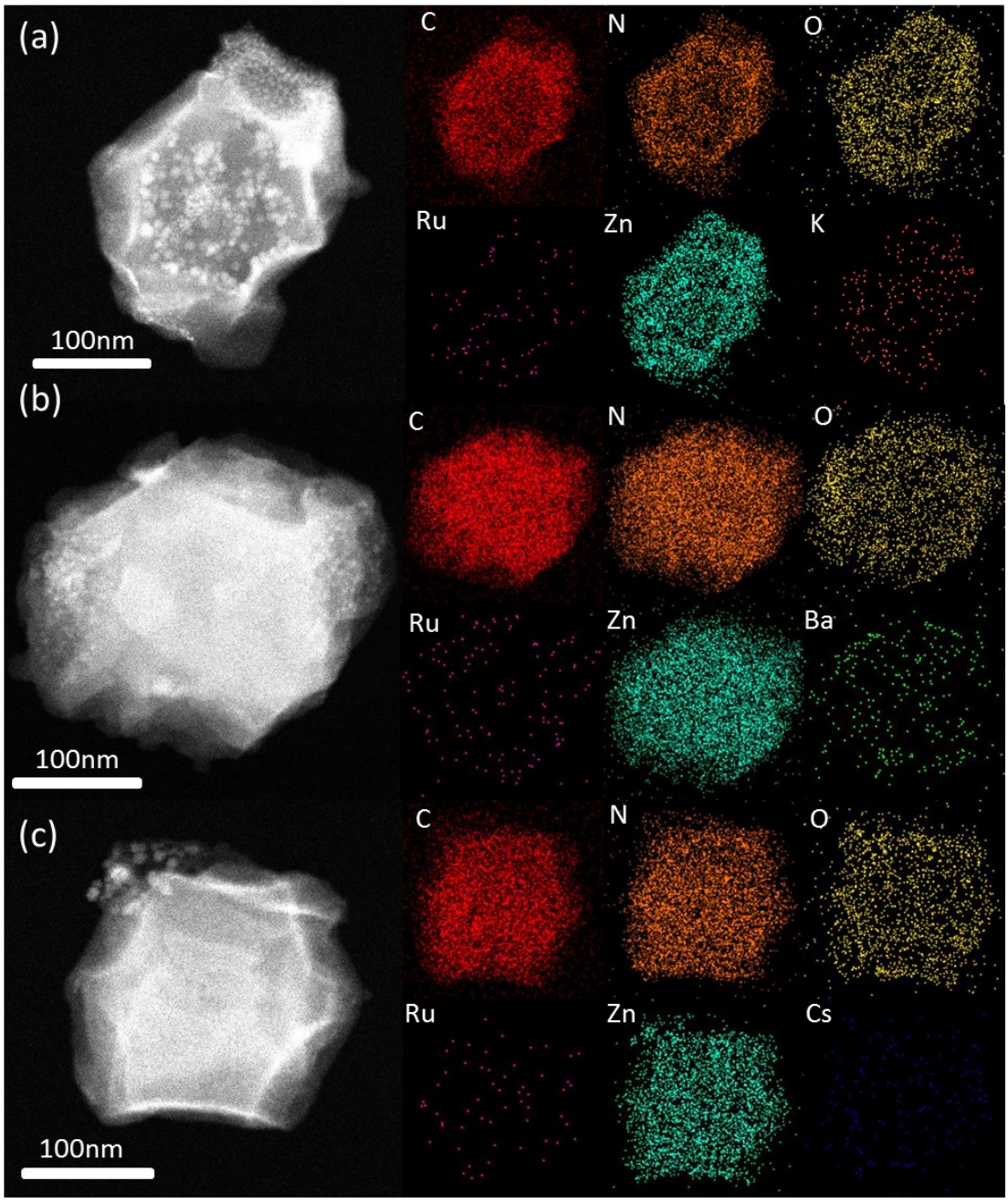

Figure S8 The elemental mapping of (a) 2K-Ru@N-C(450), (b) 2Ba-Ru@N-C(450), (c) 2Cs-Ru@N-C(450)

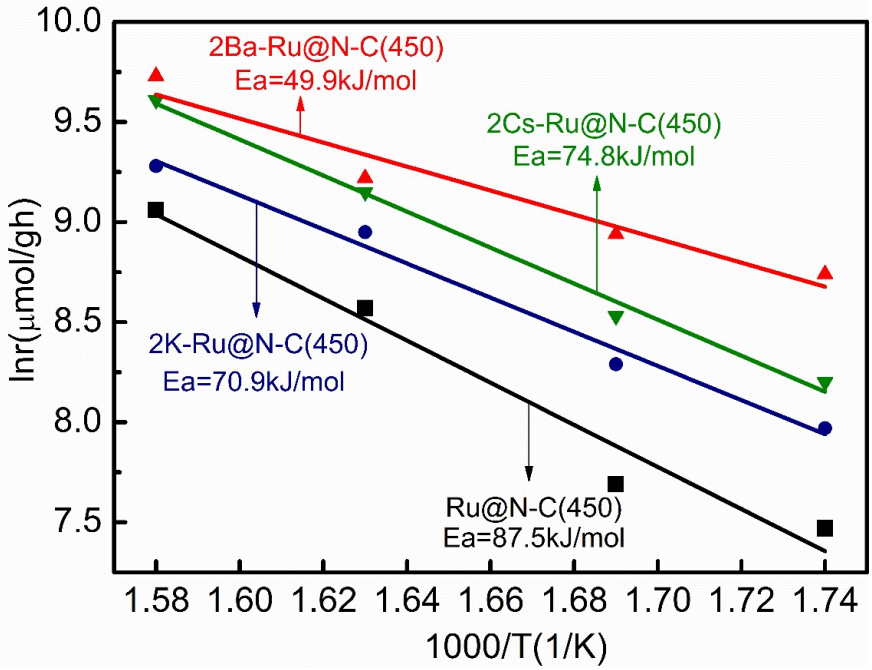

Figure S9. Arrhenius plots of Ru@N-C catalysts in the temperature range of 573–633 K.

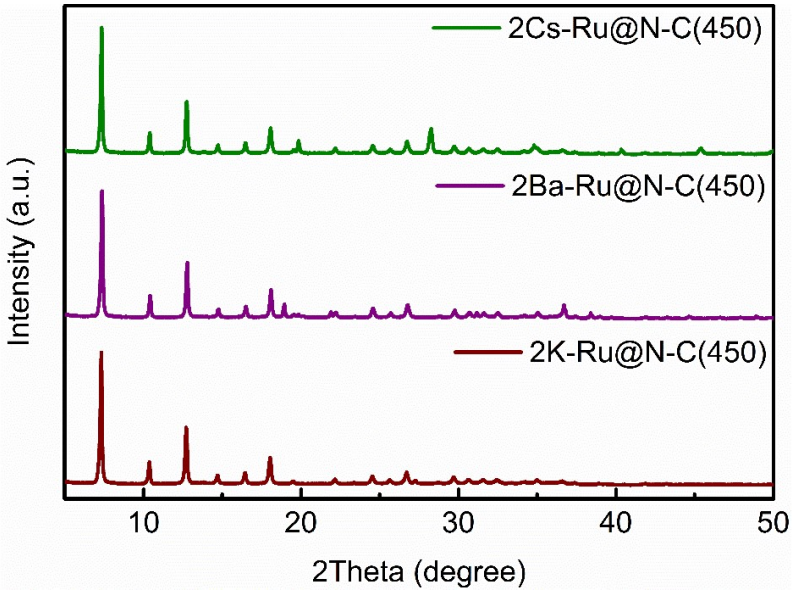

Figure S10. XRD patterns of 2Cs-Ru@N-C(450), 2Ba-Ru@N-C(450), and 2K-Ru@N-C(450).

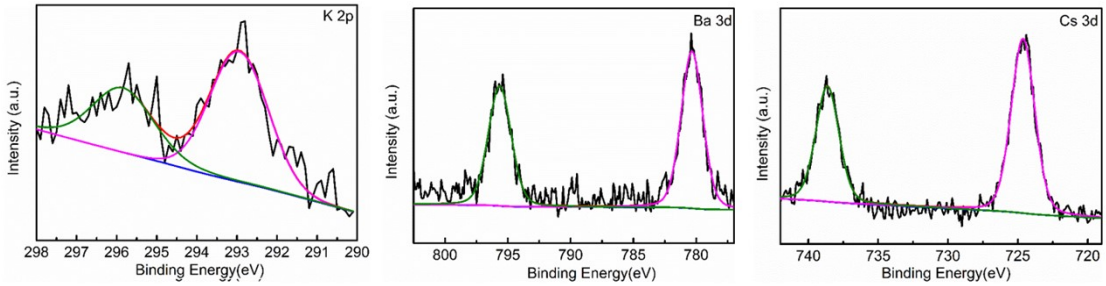

Figure S11. XPS spectra of K 2p, Ba 3d, and Cs 3d of 2K-Ru@N-C(450), 2Ba-Ru@N-C(450), and 2Cs-Ru@N-C(450) catalysts.

It can be noted that the Cs $3d^{5/2}$ binding energy at 724.3eV is much lower than that of Cs_2O (725.2 eV) in Fig. S4. According to the previous reports [1,2], Ru nanoparticle can facilitate the decomposition of $CsNO_3$, KNO_3, and $Ba(NO_3)_2$ at around 120 °C and partial Cs reduction has been observed by XAS. Thus, the Cs $3d^{5/2}$ binding energy at 724.3 eV can be attributed to the partially reduced cesium (CsO_x). The Ba $3d^{5/2}$ binding energy at 780.4 eV is ascribed to the formation of BaO, which is in accordance with the previous report [3].

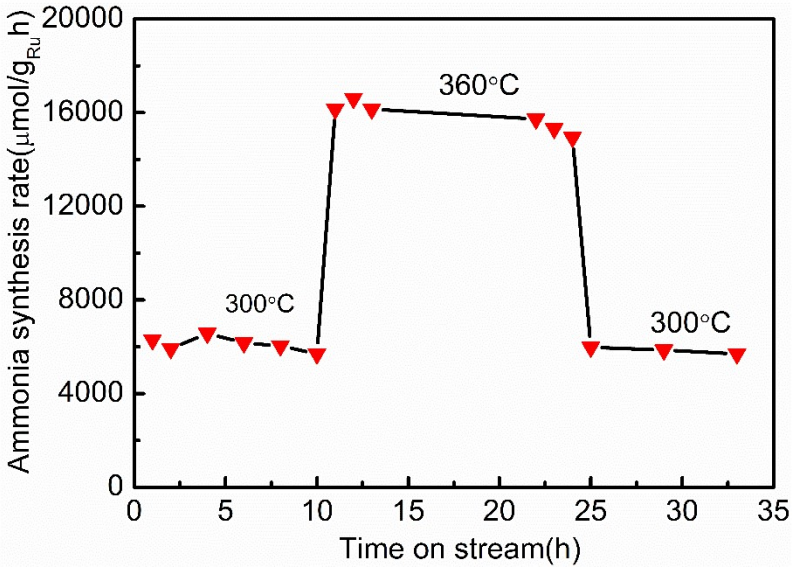

Figure S12. Time dependence of the catalytic activities of the 2Ba-Ru@N-C(450) catalysts. Reaction conditions: 0.5 g, N_2 : H_2 = 1 : 3, 60 mL min^{-1}, and 1 MPa.

Table S2. Rate of ammonia synthesis over Ru catalysts supported on various supports.

Catalysts	Ru (wt %)	Pressure (MPa)	Temperature (℃)	Rate ($\mu mol \bullet h^{-1} \bullet g^{-1}_{Ru}$)	Rate ($\mu mol \bullet h^{-1} \bullet g^{-1}_{cat}$)	Ref.
Ru@N-C(450)	3.0	1	360	8604.2	258.1	***This work***
2Ba-Ru@N-C(450)	3.0	1	360	16817.3	504.5	***This work***
Co(0.3 %)/$BaTiO_3$	-	5	400	-	14	4
Fe(0.4 %)/$BaTiO_3$	-	5	400	-	200	4
Co(0.3 %)/$BaTiO_{2.35}H_{0.65}$	-	5	400	-	550	4
Ru/Eu_2O_3-m	3	1	400	15366	461	5
Ba–Ru/MgO	8	1	315	6037.5	483	6
Ru/spherical CeO_2	4	1	400	13225	529	7
Ru Cs/MgO	5	1	300	11060	553	8
Mn_4N-NaH	-	1	300	-	~50	9
Mn_4N-CaH_2	-	1	300	-	~400	9
Mn_4N-KH	-	1	300	-	~500	9
Cs-MgO-Ru/MS	8.7	0.4	500	1095.4	92.2	10
MgO-Ru/MS	8.4	0.4	500	184.5	15.6	10
Cs-Ru/MS	5.0	0.4	500	304	15.2	10
Ru/r-Al_2O_3	1.9	0.1	400	421.06	8	11
Ru/CaO	1.5	0.1	350	800	12	12
Ba Ru/AC	1.0	0.1	350	1400	14	12
Ni+ Ni_2Mo_3N	-	0.1	400	-	15	13
Cs-Ru/r-Al_2O_3	2.0	0.1	315	1450	29	14
Ru/CaNH	1.8	0.1	300	2944.4	53	15

$Ru/C_{12}A_7{:}O_2$	1.2	0.1	350	4916.7	59	12
CaRuSi	-	0.1	400	-	60	16
Ba-Ru/AC	1.0	0.1	400	14800	148	12
Ru/CaO	1.5	0.1	400	10533.3	158	12
$CoNiMo_3N$	-	0.1	400	-	160	13
Ru/BaH_2	10	0.1	340	2000	200	17
$Ni_{1.7}Cu_{0.2}Mo_3N$	-	0.1	500	-	231	18
$Ru/CaTiO_3$	2	0.1	400	13400	268	19
Ni_2Mo_3N	-	0.1	500	-	272	18
Ba–Ru/MgO	8	0.1	315	3662.5	293	6
Ru/CaNH	1.8	0.1	340	17111.1	308	15
$Fe\text{-}K_2O\text{-}Al_2O_3$	-	0.1	400	-	330	16
$Ni_{1.1}Fe_{0.9}Mo_3N$	-	0.1	500	-	354	19
Ni_2Mo_3N	-	0.1	400	-	383	13
Co_3Mo_3C	-	0.1	500	-	461	21
Co_3Mo_3N	-	0.1	500	-	489	21
$Ru/C_{12}A_7{:}O_2$	1.2	0.1	400	45500	546	12
$Ru/r\text{-}Al_2O_3$	6.3	0.1	450	14650.8	923	5

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