Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

New Insights into Support Morphology-Dependent Ammonia Synthesis Activity of Ru/CeO_2 catalyst

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Table S1 the microstrain, S_{BET} and Pore volume of different morphology of CeO_2 and the supported Ru catalysts.

Sample	Ru (wt %)[a]	S_{BET} (m^2/g)	Pore volume (cm^3/g)	D (%)[b]	Microstrain (%)	
					(1 0 0)	(1 1 0)
r-CeO_2		61.2	0.47		2.64	1.53
c-CeO_2		31.4	0.26		0.17	0.13
p-CeO_2		65.8	0.54		0.42	0.32
Ru/p-CeO_2	3.94	63.7	0.49	36.3 (0.07)[c]	0.37	0.30
Ru/r-CeO_2	3.91	58.4	0.41	40.4 (0.09)[c]	1.60	0.91
Ru/c-CeO_2	3.97	31.2	0.24	23.1 (0.04)[c]	0.40	0.37

a. Values determined by XRF

b. Values calculated based on the CO chemisorption results.

c. Values determined by XPS (the values was obtained from the intensity ratio I_{Ru}/I_{ce})

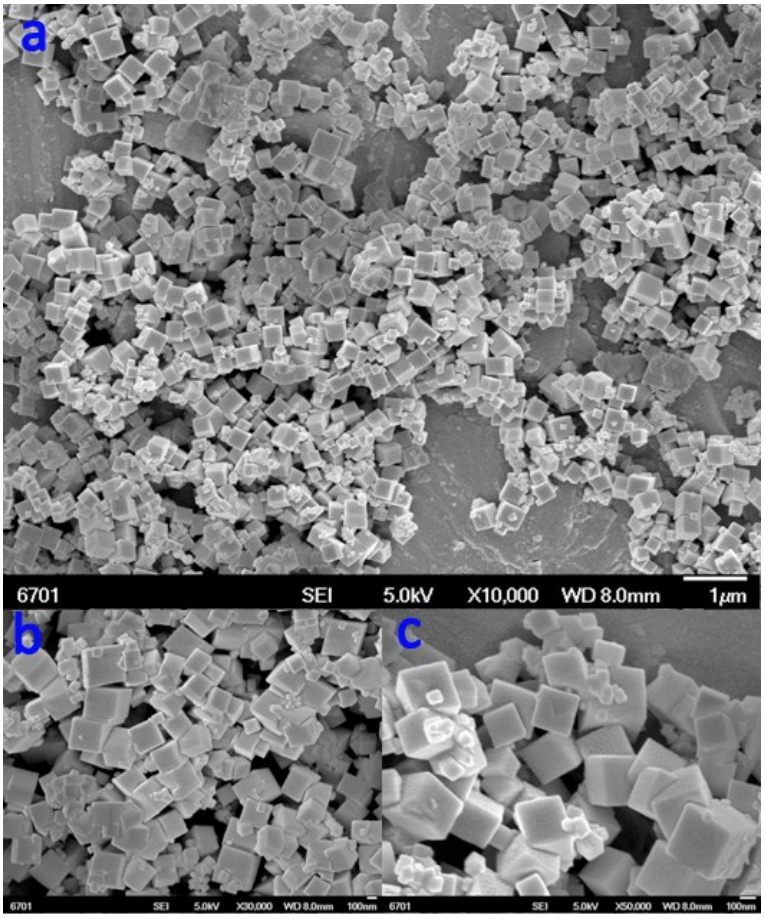

Figure S1 the SEM images of c-CeO_2

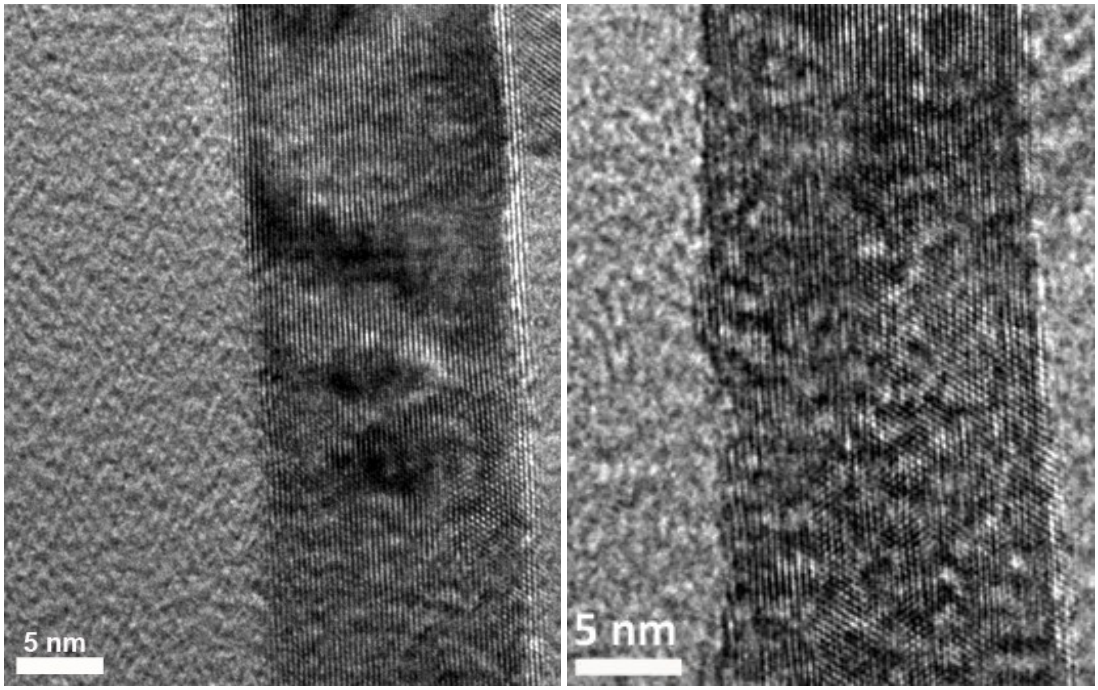

Figure S2 the TEM images of r-CeO_2

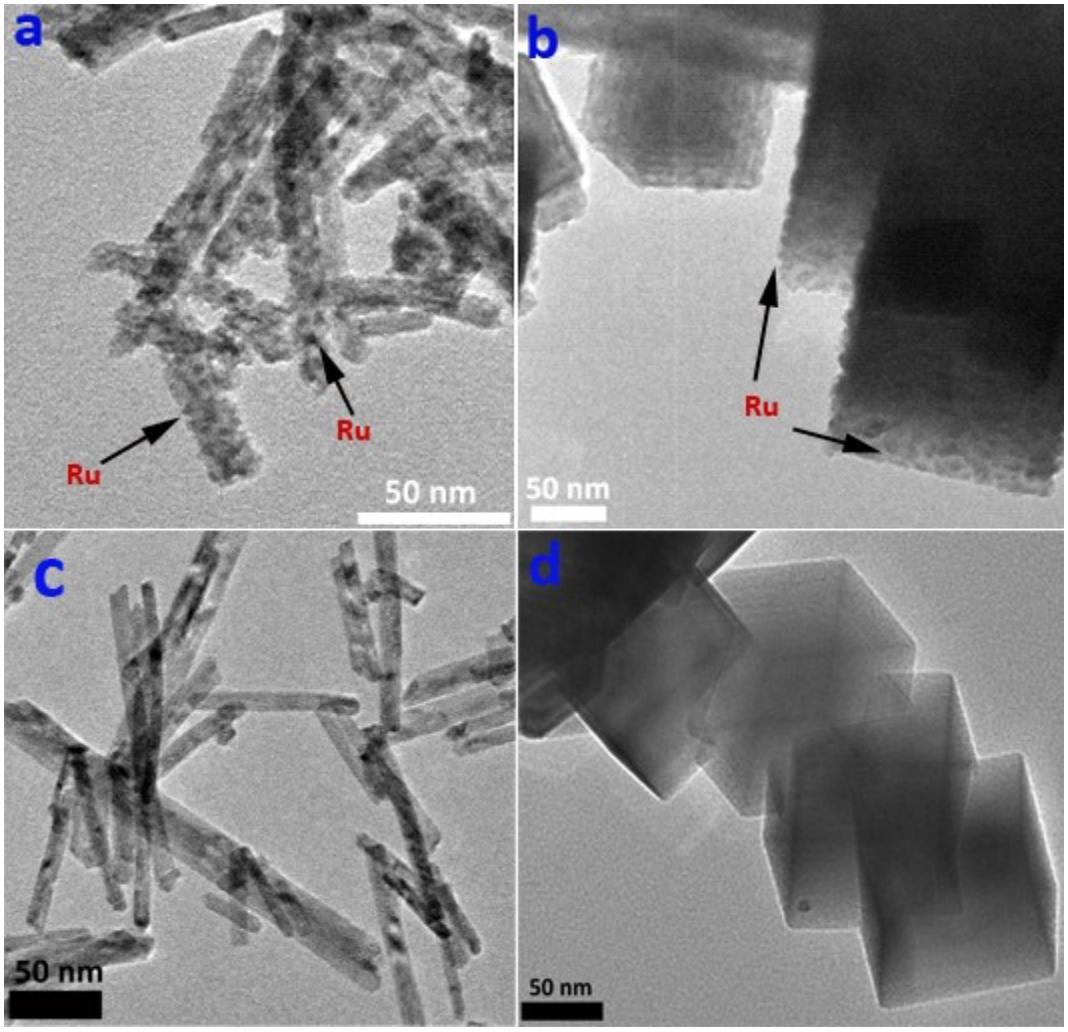

Figure S3 TEM images of Ru/r-CeO_2 (a), Ru/c-CeO_2 (b), r-CeO_2 (c), and c-CeO_2 (d).

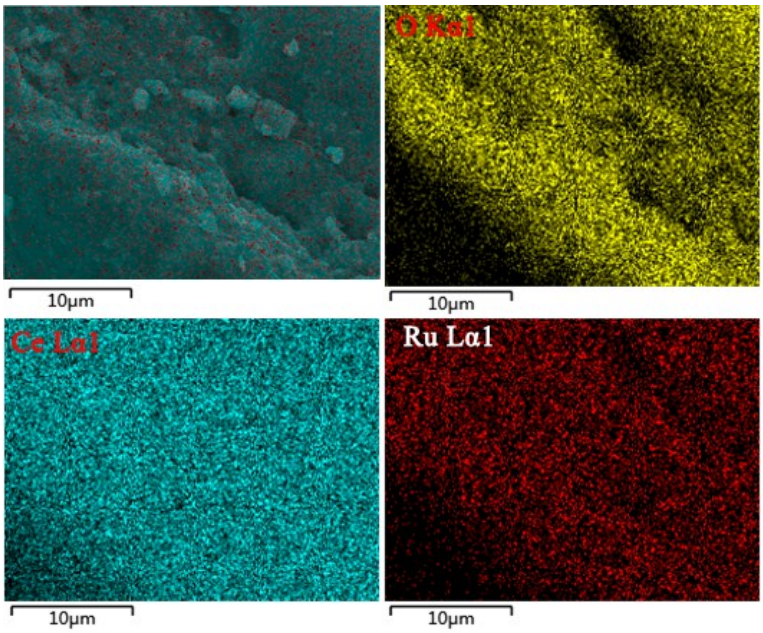

Figure S4 the elemental mapping of O, Ce and Ru in Ru /c-CeO_2.

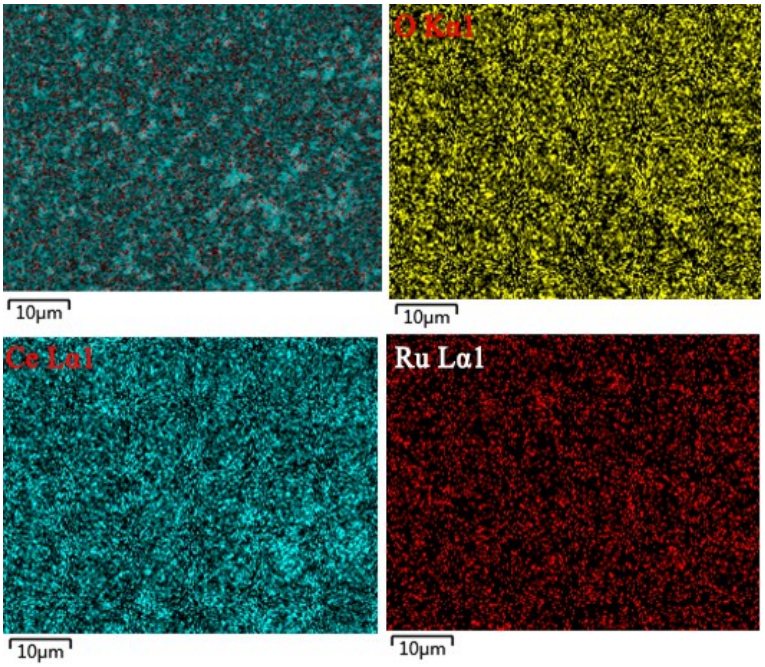

Figure S5 the elemental mapping of O, Ce and Ru in Ru /r-CeO_2.

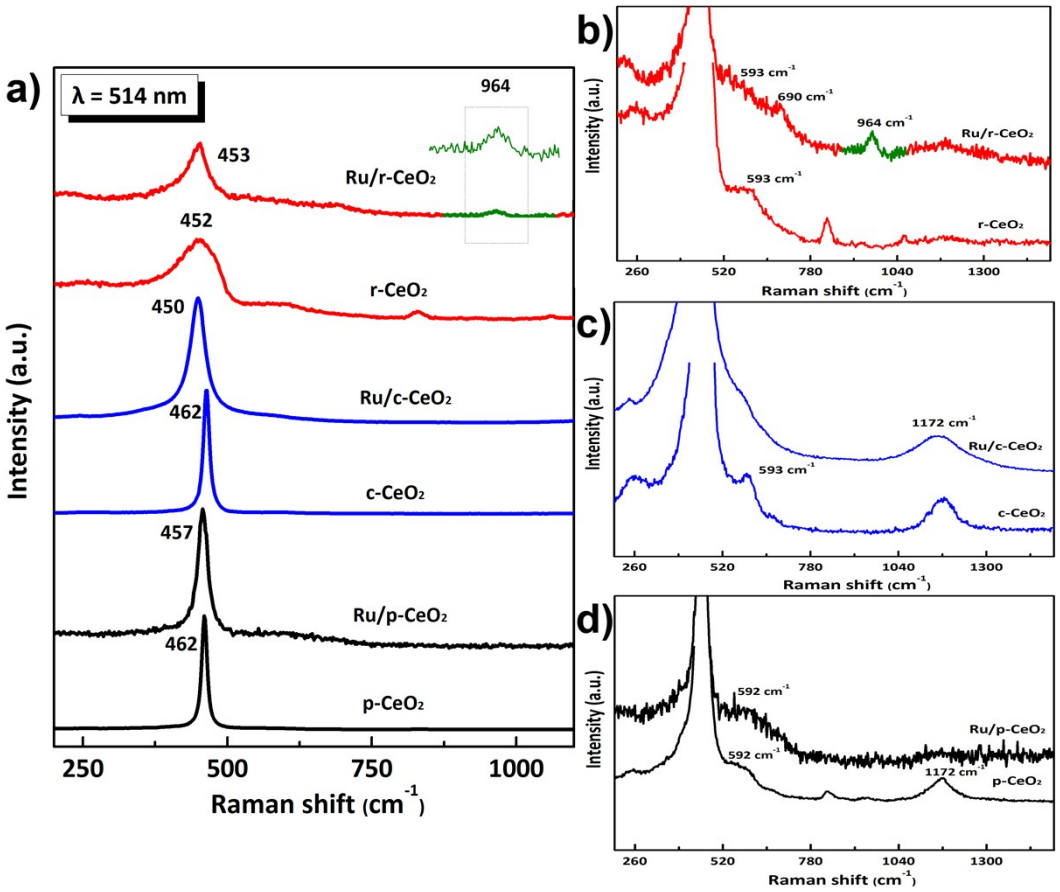

Figure S6 Visible Raman spectra of the different morphology of CeO_2 and the corresponding catalysts, λ = 514 nm.

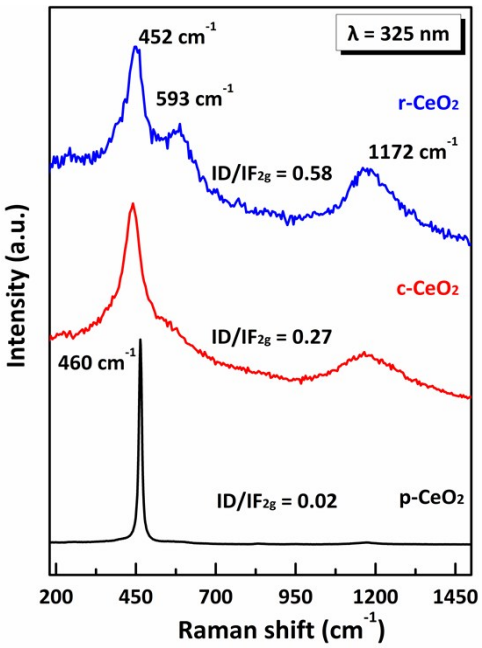

Figure S7 UV Raman spectra of different morphology of CeO_2, λ = 325 nm.

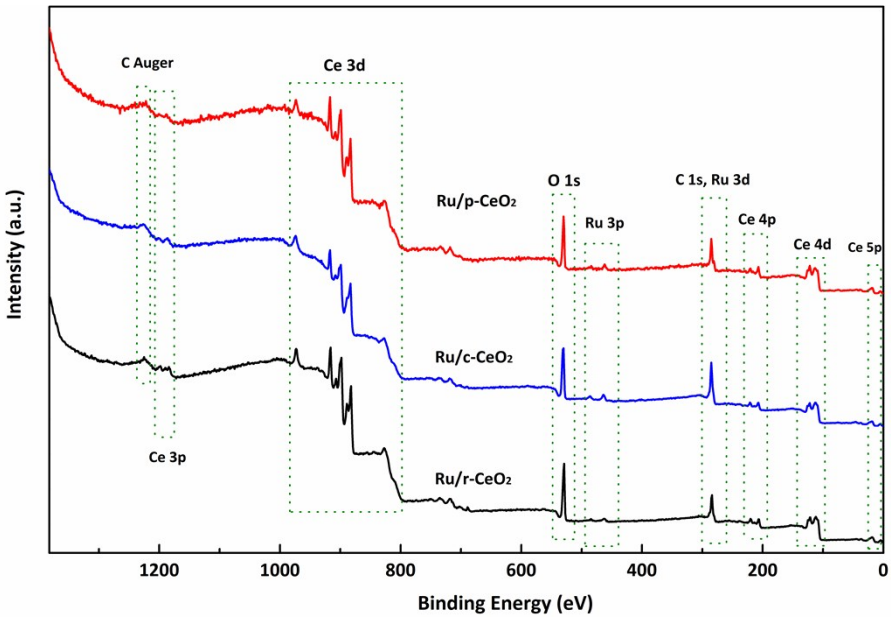

Figure S8 XPS survey spectra of three Ru/CeO_2 catalysts.

Table S2. The relative amount of different components.

Sample	Ce^{4+}	Ce^{3+}	Ce^{3+}/Ce^{4+}	O_C	O_V	O_L	O_V/O_L	Ru^0	Ru_n^+
c-CeO_2	76.0 %	24.0%	0.32	7.6%	15.4%	77.0%	0.2	-	-
r-CeO_2	70.2 %	29.8%	0.42	12.5%	20.4%	67.1%	0.3	-	-
Ru/p-CeO_2	74.4 %	25.6%	0.34	12.4%	13.6%	74%	0.18	56.3%	43.7%
Ru/c-CeO2	67.3 %	30.7%	0.46	14.9%	20.9%	64.2%	0.33	20.2%	79.8%
Ru/r-CeO2	62.9 %	37.1%	0.59	18.5%	26.2%	55.3%	0.47	15.8%	84.2%

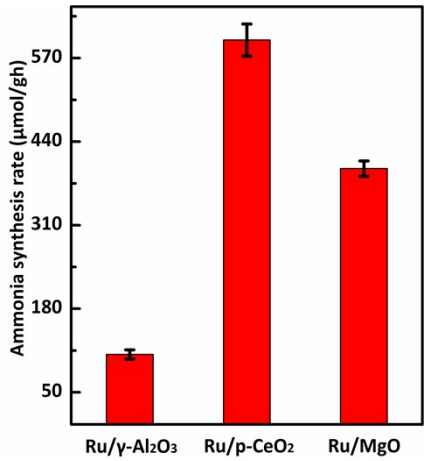

Figure S9 Activity comparison of Ru/γ-Al_2O_3, Ru/p-CeO_2 and Ru/MgO catalysts. Reaction conditions: N_2:H_2 = 1:3, 60 mL/min, 1 MPa, 400 °C.

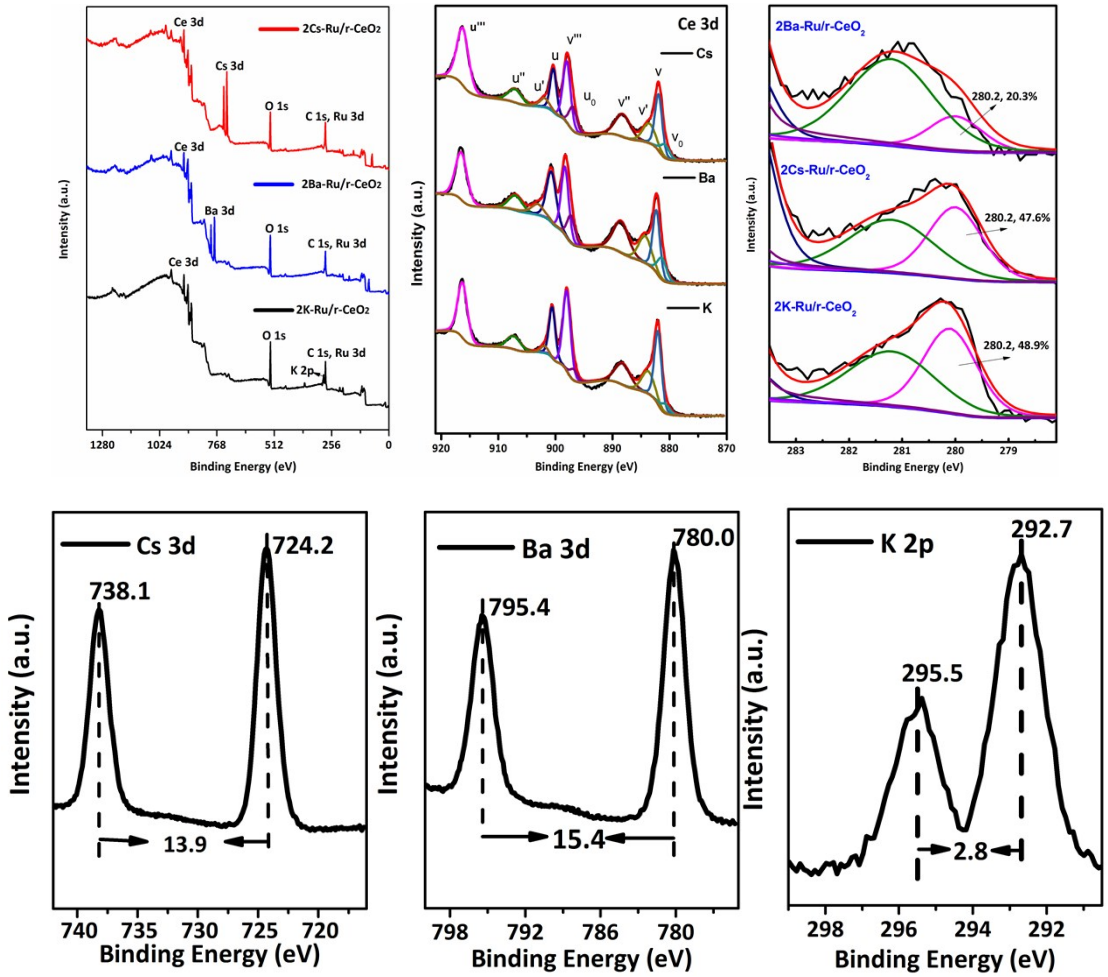

Figure S10 XPS survey spectra of 2M-Ru/R-CeO_2 catalysts and the high resolution XPS spectra: Ce 3d, Ru 3d, Cs 3d, Ba 3d and K 2p. Before the XPS test, the catalysts were pretreated with H_2 at 400 °C for 2h.

Table S3 The relative amount of different components.

Sample	Ce^{4+}	Ce^{3+}	Ce^{3+}/Ce^{4+}	Ru^0	Ru_n^+
Ru/r-CeO2	62.9%	37.1%	0.59	15.8%	84.2%
2Cs-Ru/r-CeO_2	77.8%	22.2%	0.29	47.6%	52.4%
2Ba-Ru/r-CeO_2	83.2%	25.5%	0.31	20.3%	79.7%
2K-Ru/r-CeO_2	74.5%	16.8%	0.23	48.9%	51.1%

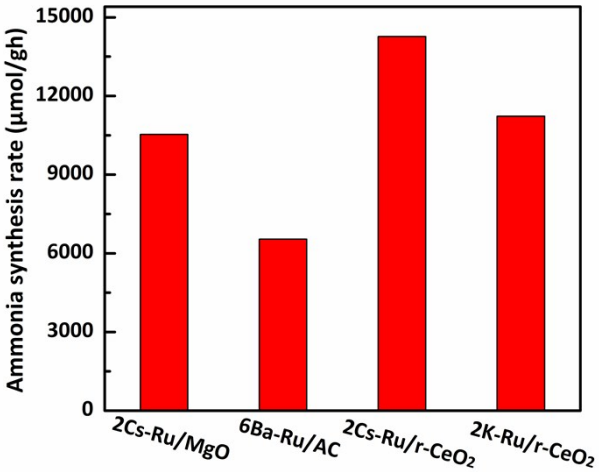

Figure S11 Activity comparison of 2Cs-Ru/MgO, 6Ba-Ru/AC, 2Cs-Ru/r-CeO_2 and 2K-Ru/r-CeO_2 catalysts. Reaction conditions: N_2:H_2 = 1:3, 1 MPa, 400 °C, 60 mL/min.

Table S4 Rate of ammonia synthesis over Ru catalysts supported on various supports and precursors.

catalysts	Ru (wt %)	Pressure (MPa)	Precursor	Rate (mmol/(g • h)) 653 K	673 K	698 K	Ref.
2K-Ru/r-CeO_2	4	1 3	$Ru_3(CO)_{12}$	8.8 12.5	11.2 19.6		this work this work
2Ba-Ru/r-CeO_2	4	1 3	$Ru_3(CO)_{12}$	4.9 7.4	6.6 12.3		this work this work
2Cs-Ru/r-CeO_2	4	1 3	$Ru_3(CO)_{12}$	13.3 29.4	14.2 33.5		this work this work
2Cs-Ru/MgO	4	1	$Ru_3(CO)_{12}$		10.53		this work
6Ba-Ru/AC	4	1	$RuCl_3$		6.54		this work
Ba-Ru/GNF	-	3	$RuCl_3$	-	19.2		**[1]**
K-Ru/GNF	4	3	$RuCl_3$	-	4.85		**[2]**
Ba-K-Ru/AC	4	10	$RuCl_3$	-	-	88	**[3]**
Ru/ZrO_2-KOH	3.8	3	K_2RuO_4	-	11.1	16.9	**[4]**
K-Ru/MgO	3.92	3	K_2RuO_4	-	8.91	13.87	**[4]**
K-Ru/Al_2O_3	3.79	3	K_2RuO_4	-	2.08	2.86	**[4]**

Reference

[1]. C. Liang, Z. Li, J. Qiu and C. Li, Journal of Catalysis, 2002, **211**, 278-282.

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[3]. Y. Zhou, G. Lan, B. Zhou, W. Jiang, W. Han, H. Liu and Y. Li, Chinese Journal of Catalysis, 2013, **34**, 1395-1401.

[4]. Z. Q. Wang, Y. C. Ma and J. X. Lin, Journal of Molecular Catalysis A: Chemical, 2013, **378**, 307-313.