

## Supporting information

### Effect of nitrogen co-doping with ruthenium on the catalytic performance of Ba/Ru-N-MC catalysts for ammonia synthesis

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Table S1 Textural properties and Ru dispersion of the Ru-MC and Ba/Ru-MC samples.

Samples	Ru <sup>a</sup> (wt%)	S. A. <sup>b</sup> (m <sup>2</sup> ·g <sup>-1</sup> )	P. V. <sup>c</sup> (cm <sup>3</sup> ·g <sup>-1</sup> )	P. D. <sup>d</sup> (nm)	CO uptake (μmol/g)	Dispersion (%)	Particle size (nm)
Ru-MC	4.59	928	1.44	9.2	154.2	34.2	3.9
Ba/Ru-MC	4.21	920	1.41	9.2	140.8	34.0	3.9

<sup>a</sup> Ru wt% was measured by the spectrophotometric method. <sup>b</sup> The specific surface area. <sup>c</sup> The total pore volume. <sup>d</sup> Pore diameter calculated by the desorption branches of the isotherms using the BJH method.

Table S2 Comparison of ammonia synthesis reaction activity reported in other literatures.

Samples	Ru (%)	Reaction rate (mmol·g <sup>-1</sup> ·h <sup>-1</sup> )	TOF (s <sup>-1</sup> )	Temp. (°C)	Pressure (MPa)	GHSV (h <sup>-1</sup> )	Ref.
Ba/Ru-N-MC	3.75	175	0.387	450	10	10000	This work
Ba/Ru-N-MC	3.75	79	0.160	400	10	10000	This work
Ba-Ru/N-MC	4.07	27	0.034	400	10	10000	This work
Ba-Ru/CNTs	4.0	69	-	450	10	10000	[1]
Ba-Ru/AC	9.1	-	0.098	400	6.3	6500	[2]
Ru-Ba/AC	4.0	-	0.048	400	3	3000	[3]
Ru-Ba/ACF	4.0	-	0.030	400	3	3000	[4]
Ru-Ba/CMS	4.0	-	0.089	400	3	3000	[4]

Table S3 The peak position of various catalysts measured by H<sub>2</sub>-TPR.

Catalysts	Peak Temperature (°C) of various possible species					
	18/H <sub>2</sub> O RuO <sub>x</sub> <sup>+</sup> H <sub>2</sub>	18/H <sub>2</sub> O Ba(OH) <sub>2</sub>	15/CH <sub>4</sub> C+H <sub>2</sub>	18/H <sub>2</sub> O SFGs+H <sub>2</sub>	28/CO SFGs decomposition	44/CO <sub>2</sub> SFGs decomposition
Ru/N-MC	237	-	282-505	589	652	603
Ba-Ru/N-MC	183	203	277	523	640	none
Ru-N-MC	155	-	230	550	608	155, 210, 559
Ba/Ru-N-MC	190	200	220	none	672	182

Table S4 Textural properties of Ba-Ru/N-MC-used and Ba/Ru-N-MC-used catalysts.

Catalysts	S. A. <sup>a</sup> (m <sup>2</sup> ·g <sup>-1</sup> )	P. V. <sup>b</sup> (cm <sup>3</sup> ·g <sup>-1</sup> )	P. D. <sup>c</sup> (nm)	S. A. decreased (%)
Ba-Ru/N-MC-used	678	0.98	9.2	6.4
Ba/Ru-N-MC-used	630	0.88	9.2	2.6

<sup>a</sup> The specific surface area. <sup>b</sup> The total pore volume. <sup>c</sup> Pore diameter calculated by the desorption branches of the isotherms using the BJH method.

Table S5 The elemental composition of the carbon materials is measured by elementary analysis.

Catalysts	Elemental content (wt.%)			
	N	C	H	S
Ru-N-MC	1.44	72.37	1.85	0.48
Ba/Ru-N-MC	1.41	68.79	1.78	0.24
Ba/Ru-N-MC-used	1.64	66.96	1.92	0.19

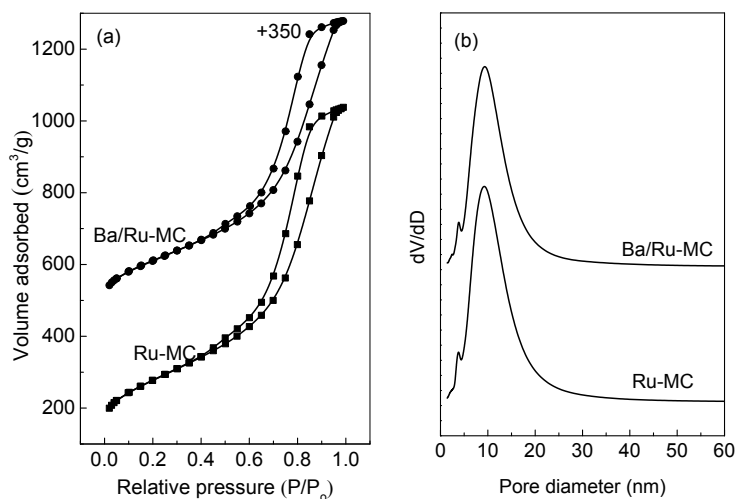


Fig. S1 (a) N<sub>2</sub> adsorption-desorption isotherms and (b) pore size distribution curves of the Ru-MC and Ba/Ru-MC samples.

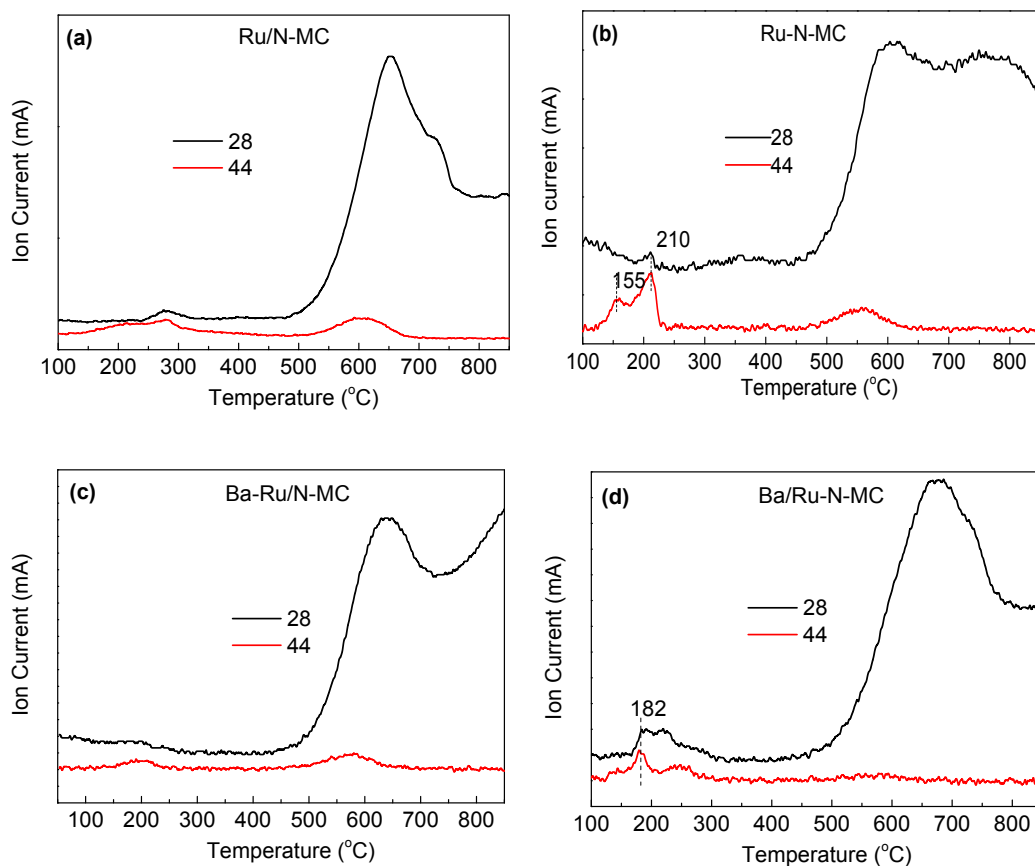


Fig. S2 The signal of CO and CO<sub>2</sub> in Temperature-programmed reduction profiles of the (a) Ru/N-MC, (b) Ru-N-MC, (c) Ba-Ru/N-MC and (d) Ba/Ru-N-MC catalysts under 5% H<sub>2</sub>/Ar atmosphere detected with a mass spectrometer.

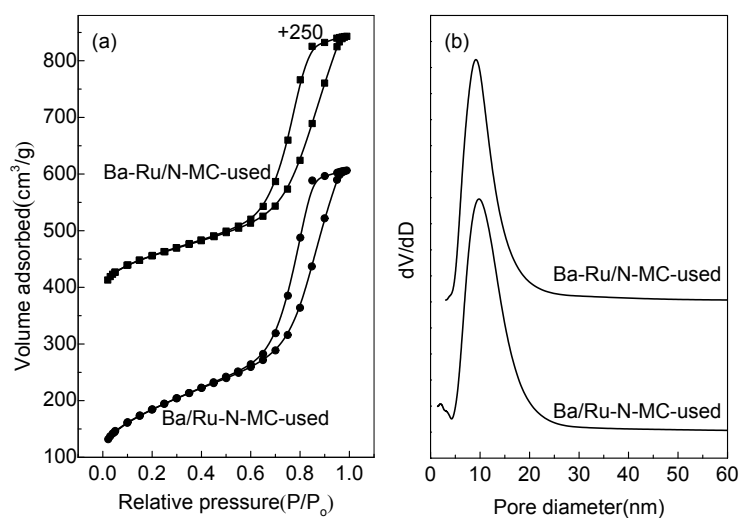


Fig. S3 (a) N<sub>2</sub> adsorption-desorption isotherms and (b) pore size distribution curves of Ba-Ru/N-MC-used and Ba/Ru-N-MC-used catalysts.

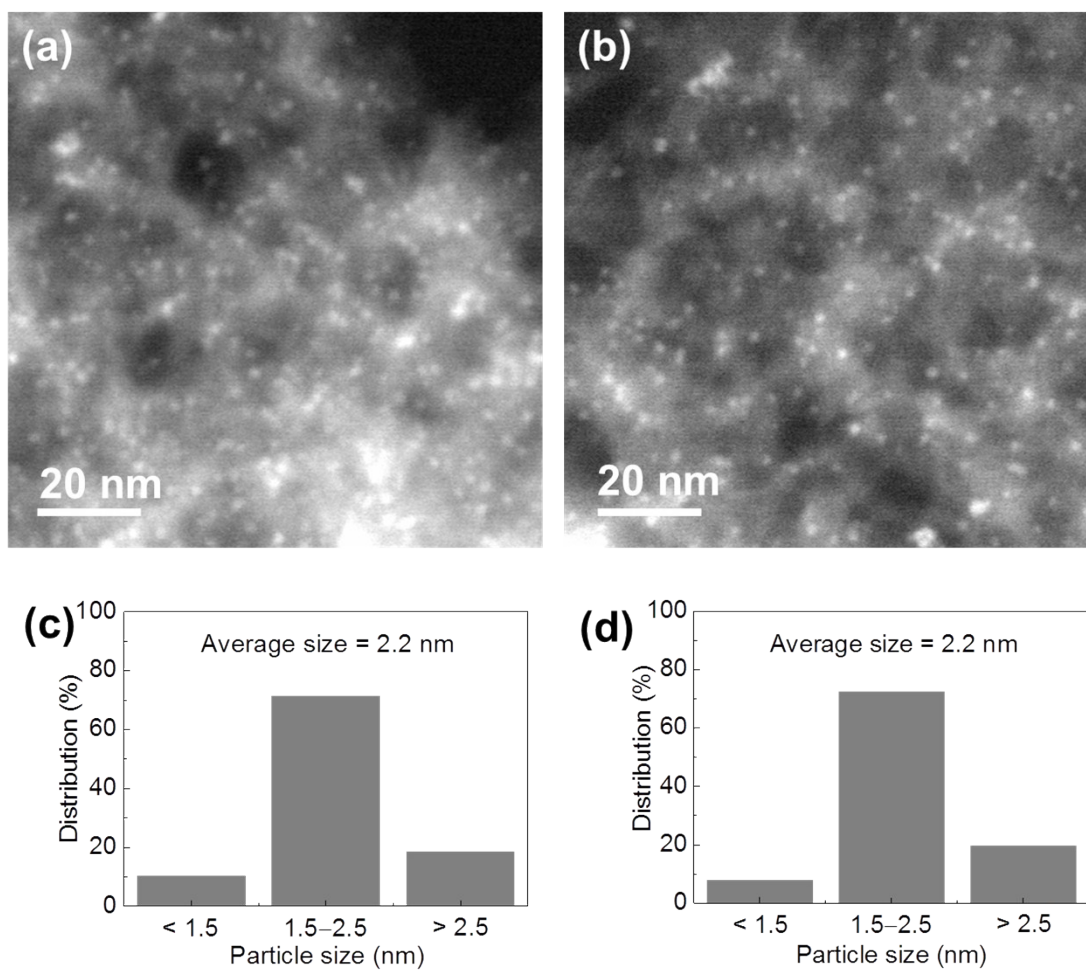


Fig. S4 HRTEM images and particle size distributions of (a, c) Ba-Ru/N-MC-used, (b, d) Ba/Ru-N-MC-used.

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