

**Strong Ru^{δ+}-Ce³⁺ electronic interaction induced by CeO_y overlayer
for enhanced low temperature N₂-to-NH₃ conversion**

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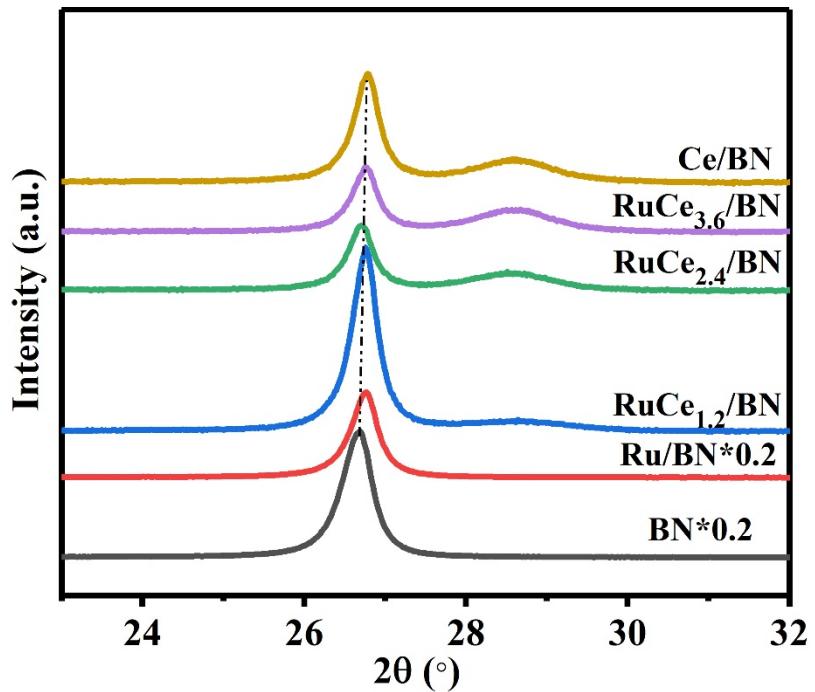


Figure S1. Enlarged XRD patterns at 2θ in the range of $23\text{--}32^\circ$ over as-prepared catalysts.

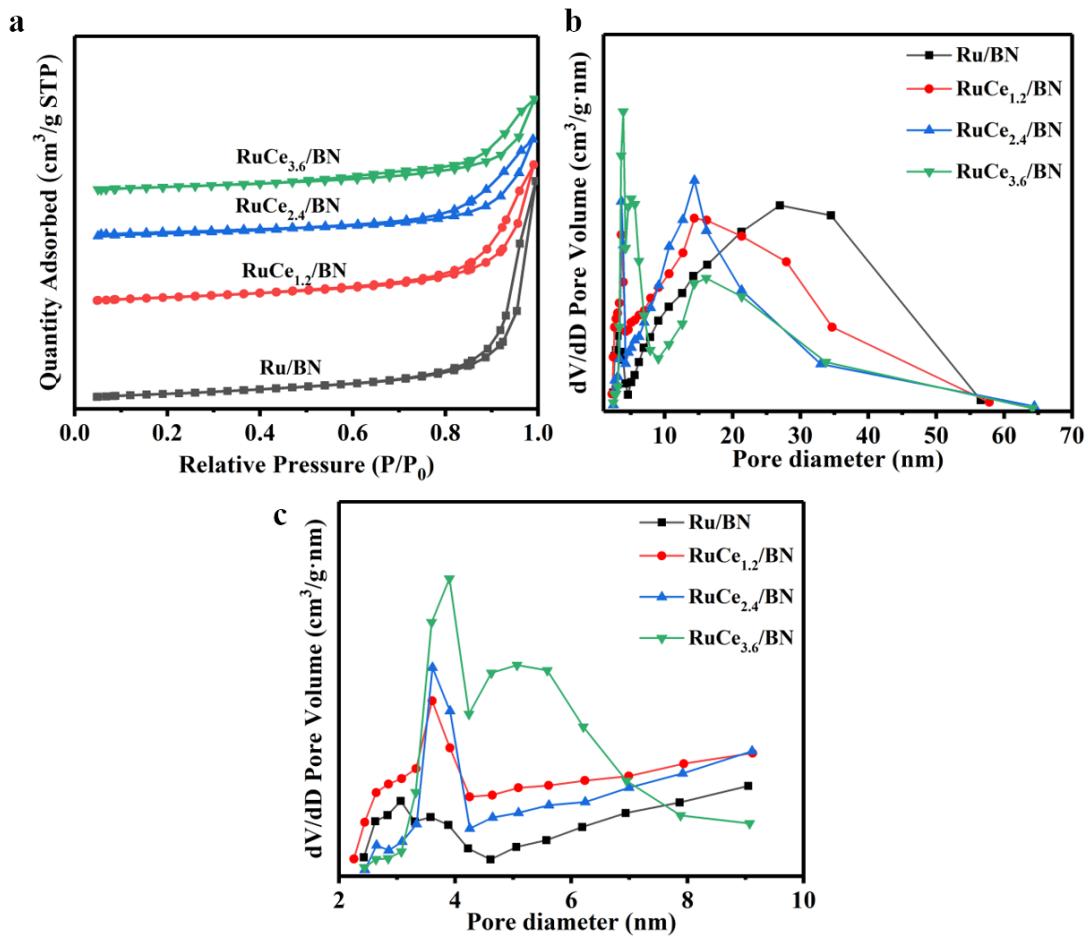


Figure S2. **a.** Nitrogen adsorption–desorption isotherms, **b.** pore-size distribution profiles and **c.** partially enlarged pore-size distribution of Ru/BN, RuCe_{1.2}/BN, RuCe_{2.4}/BN and RuCe_{3.6}/BN.

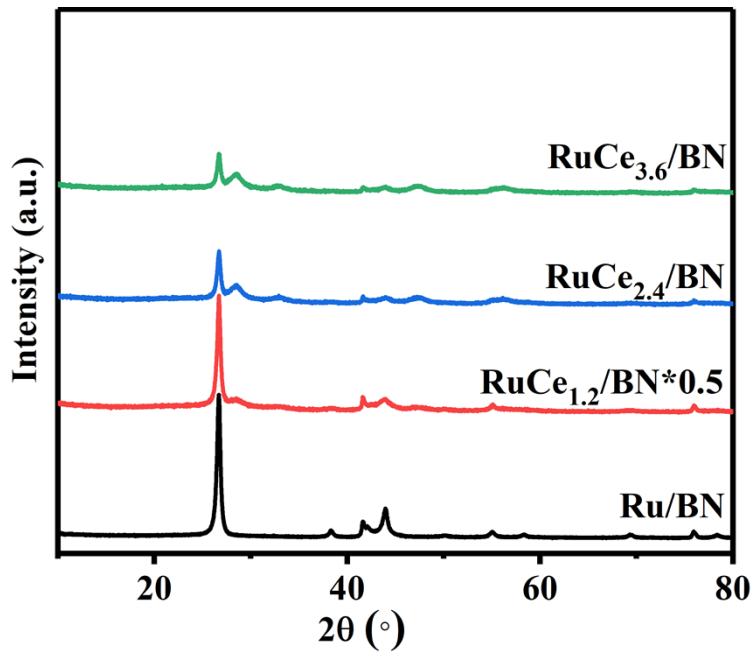


Figure S3. XRD patterns over the used catalysts.

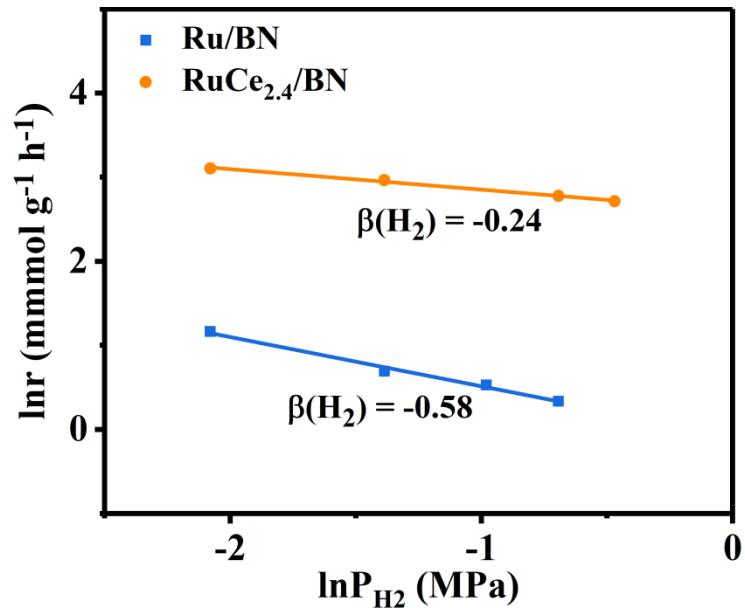


Figure S4. H₂ reaction order over Ru/BN and RuCe_{2.4}/BN catalysts.

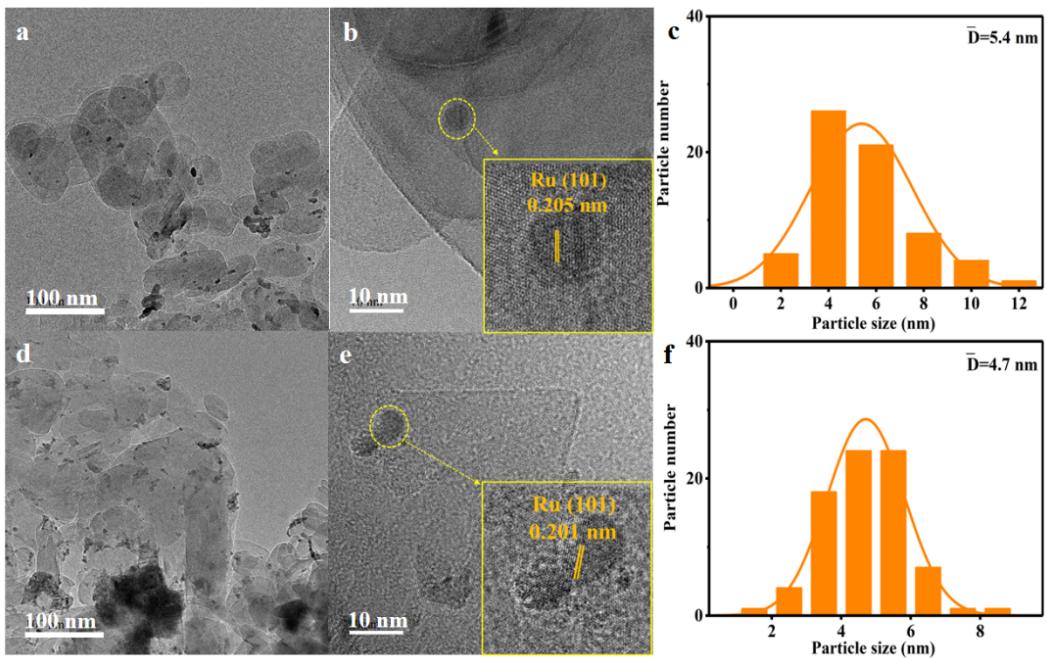


Figure S5. TEM and HR-TEM images as well as particle distribution profiles of **a-c** Ru/BN and **d-f** RuCe_{2.4}/BN.

Table S1. Physicochemical properties over RuCe_x/BN catalysts.

Sample	Ce/Ru molar ratio	Ru content ^a (wt.%)	Ce content ^a (wt.%)	BET surface area ^b (m ² g ⁻¹)	Average pore diameter ^b (nm)	H ₂ consumption (mmol g _{Ru} ⁻¹) ^c
Ru/BN	0	4.5	0	45	26	20
RuCe _{1.2} /BN	1.0	3.6	5.9	42	18	57
RuCe _{2.4} /BN	2.4	3.0	10.2	45	16	62
RuCe _{3.6} /BN	3.6	3.0	14.9	52	14	52

^aICP results.^bObtained from N₂ physisorption measurement.^cObtained from H₂-TPR result.

Table S2. Crystallite sizes and lattice parameters over the as-prepared samples^a.

sample	crystallite size (nm)	a (Å)	b (Å)	c (Å)
BN	15	2.507	2.507	6.888
Ru/BN	17	2.507	2.507	6.888
RuCe _{1.2} /BN	17	2.507	2.507	6.885
RuCe _{2.4} /BN	17	2.508	2.508	6.893
RuCe _{3.6} /BN	17	2.507	2.507	6.891
Ce/BN	17	2.505	2.505	6.877

^aXRD results for the BN phase in the samples.

Table S3. Surface Ru contents and $\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$ ratios over RuCe_x/BN catalysts obtained from XPS results.

Sample	Ru (%)	$\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$ (%)
Ru/BN	0.6	-
$\text{RuCe}_{1.2}/\text{BN}$	0.4	27
$\text{RuCe}_{2.4}/\text{BN}$	0.3	34
$\text{RuCe}_{3.6}/\text{BN}$	0.3	29

Table S4. NH₃ synthesis performance over various Ru-based catalysts reported in this work and previous literatures under the given conditions.

Sample	Ru content (wt.%)	T (°C)	P (MPa)	WHSV (mL·g ⁻¹ ·h ⁻¹)	NH ₃ synthesis rate (mmol _{NH3} g _{cat} ⁻¹ h ⁻¹)	TOF _{Ru sur} (10 ⁻³ s ⁻¹)	E _a (kJ mol ⁻¹)	Ref.
RuCe _{2.4} /BN	3.0	400	0.2	60 000	9.6	-	-	This work
RuCe _{2.4} /BN	3.0	400	1.0	60 000	14.6	230	68	This work
RuCe _{2.4} /BN	3.0	350	1.0	60 000	5.8	91	68	This work
Ru/CeO ₂	3.0	400	1.0	60 000	0.5	-	-	This work
Ba/Ru/BN	4.5	400	5.0	-	2.0	-	95	1
Ru–Cs/MgO	6.0	400	0.1	18 000	3.3	8	73	2
Ru/C12A7:e ⁻	4.0	400	0.1	18 000	2.1	76	56	2
Ru/LaCoSi	4.3	400	0.1	18 000	3.4	30	50	3
Ru/Y ₅ Si ₃	7.8	400	0.1	18 000	1.9	70	52	4
Ru/Ca ₂ N:e ⁻	1.8	300	0.1	36 000	1.7	91	60	5
Ru/r-CeO ₂	4.0	400	1.	18 000	3.8	-	108	6
Ru/BaZr _{0.9} Y _{0.1} O _{3-δ}	2.0	400	0.1	36 000	4.0	-	-	7
YRu ₂	69.5	400	0.1	18 000	0.5	19	73	8
LaRuSi	37.7	340	0.1	36 000	0.8	28	40	9

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