# Support information

## Decoration of Ru nanoparticles on γ-alumina with sub-nanometer ceria species for efficient catalytic ammonia synthesis

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## 1. Supporting results

Table S1. The comparation of catalytic performances of typical Ru-based catalysts for ammonia synthesis.

| Catalysts | Loading (wt%) | T (°C) | Pressure (MPa) | GHSV (mL $g_{cat}^{-1}$ $h^{-1}$) | $NH_3$ synthesis rate (μmol $g_{cat}^{-1}$ $h^{-1}$) | Specific $NH_3$ synthesis rate (mmol $g_{Ru}^{-1}$ $h^{-1}$) | Ref. |
|---|---|---|---|---|---|---|---|
| Ru/rod-$CeO_2$ | 4 | 400 | 1.0 | 18000 | 3830 | 95.8 | 1 |
| Ru/cubic-$CeO_2$ | 4 | 400 | 1.0 | 18000 | 1289 | 32.2 | 1 |
| Ru/spherical-$CeO_2$ | 4 | 400 | 1.0 | 18000 | 529 | 13.2 | 1 |
| Cs–Ru/rod-$CeO_2$ | 4 | 400 | 1.0 | 18000 | 14266 | 356.7 | 1 |
| Ru/$La_{0.5}Ce_{0.5}O_{1.75}$ | 5 | 350 | 1.0 | 72000 | 31300 | 626.0 | 2 |
| Ru/$La_2O_3$ | 5 | 350 | 1.0 | 72000 | 10800 | 216.0 | 2 |
| Ru/$Ce_{0.6}Zr_{0.4}O_2$ | 4.0 | 390 | 1.0 | 18000 | 1700 | 42.5 | 3 |
| Ru/$Ti_xCe_{1-x}O_2$ | 3.0 | 400 | 1.0 | 36000 | 14580 | 486.0 | 4 |
| Ru/$BaCeO_3$ | 1.3 | 450 | 3.0 | 36000 | 24000 | 1846.2 | 5 |
| Ru/CaO | 1.5 | 400 | 0.1 | 18000 | 160 | 10.7 | 6 |
| Cs–Ru/MgO | 6.0 | 400 | 0.1 | 18000 | 3350 | 55.8 | 6 |
| Ba–Ru/AC | 9.1 | 400 | 0.1 | 18000 | 2230 | 24.5 | 6 |
| Ru/C12A7:$e^-$ | 1.2 | 400 | 0.1 | 18000 | 2760 | 230.0 | 6 |
| Sm–Ru/$Al_2O_3$ | 12.0 | 400 | 10.0 | 240000 | 145000 | 1208.3 | 7 |
| Ru/$Al_2O_3$ | 10.0 | 315 | 0.08 | | 25.0 | 0.3 | 8 |
| Cs–Ru/$Al_2O_3$ | 10.0 | 315 | 0.08 | | 141.5 | 1.4 | 8 |
| Sm–Ru/$Al_2O_3$ | 10.0 | 315 | 0.08 | | 114.6 | 1.1 | 8 |
| Ru/γ-$Al_2O_3$ | 6.3 | 400 | 0.1 | 9000 | 789.2 | 12.5 | 9 |
| K–Ru/$Al_2O_3$ | 8.0 | 350 | 0.1 | 9000 | 2470 | 30.9 | 10 |
| Ce–Ru(1:1)/$Al_2O_3$ | 3.0 | 400 | 1.0 | 24000 | 14352 | 478.4 | This work |
| Ru/$Al_2O_3$ | 3.0 | 400 | 1.0 | 24000 | 1432 | 47.7 | This work |

Table S2 Physical and chemical properties of γ-$Al_2O_3$, Ru/$Al_2O_3$ and Ce–Ru(x:1)/$Al_2O_3$ samples.

| Samples | Ru loading (wt%) | Ce loading (wt%) | Surface area ($m^2$ $g^{-1}$) | Ru particle size by TEM (nm) | Metal dispersion by CO chemisorption (%) | Ru particle size by CO chemisorption (nm) |
|---|---|---|---|---|---|---|
| $Al_2O_3$ | – | – | 159 | – | – | – |
| Ru/$Al_2O_3$ | 3.0 | – | 169 | 1.3 ± 0.5 | 51.1 | 2.6 |
| Ce–Ru(0.125:1)/$Al_2O_3$ | 3.0 | 0.45 | 161 | 1.9 ± 0.5 | 51.5 | 2.6 |
| Ce–Ru(0.25:1)/$Al_2O_3$ | 3.0 | 0.92 | 168 | 1.8 ± 0.5 | 47.2 | 2.9 |
| Ce–Ru(0.5:1)/$Al_2O_3$ | 3.0 | 2.0 | 168 | 1.8 ± 0.5 | 61.2 | 2.2 |
| Ce–Ru(1:1)/$Al_2O_3$ | 3.0 | 4.1 | 169 | 1.9 ± 0.5 | 46.2 | 2.9 |

Table S3. Kinetic parameters for ammonia synthesis over various Ru-based catalysts.

| Catalysts | α($NH_3$) | β($N_2$) | γ($H_2$) | Ea (kJ $mol^{-1}$) | Ref. |
|---|---|---|---|---|---|
| Ce–Ru(1:1)/$Al_2O_3$ | –0.2 | 1.0 | 0.8 | 75 | This work |
| Ru/$Al_2O_3$ | –1.1 | 1.0 | –0.1 | 82 | This work |
| Ru/MgO | –0.3 | 0.8 | –0.3 | 69 | [11] |
| Cs–Ru/MgO | 0 | 0.8 | –0.9 | 109 | [11] |
| Ba–Ru/MgO | –0.6 | 0.8 | –0.6 | 77 | [12] |
| La–Ru/MgO | –0.17 | 0.85 | –0.15 | 86 | [13] |
| Ru/$Al_2O_3$ | –0.4 | 0.9 | –0.1 | 70 | [11] |
| Ru/K–$Al_2O_3$ | 0 | 1.0 | –0.5 | 125 | [11] |
| Ru/$MgAl_2O_4$ | –0.4 | 1.0 | –0.5 | – | [14] |
| Ru/C12A7:$e^-$ | –1.0 | 0.46 | 0.97 | 49 | [15] |
| Ru/$La_{0.5}Ce_{0.5}O_{1.75}$ | –0.36 | 0.76 | 0.15 | 64 | [2] |
| Ru powder | –0.15 | 0.96 | –0.72 | 117 | [16] |
| Ru/$BaTiO_{2.5}H_{0.5}$ | –0.64 | 0.7 | 0.2 | 83 | [17] |
| Ru/$CaH_2$ | –1.11 | 0.55 | 0.87 | 51 | [3] |
| Ru/$Ca_2N$:$e^-$ | –1.03 | 0.53 | 0.79 | 60 | [3] |

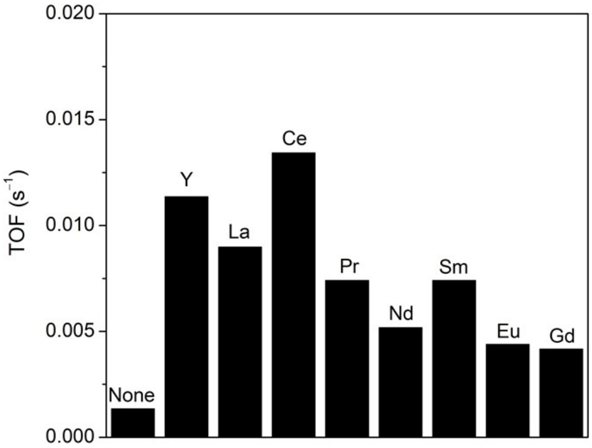


**Fig. S1** $TOF_{NH3}$ values of different RE–Ru(1:1)/$Al_2O_3$ catalysts under 1.0 MPa and 400 °C.

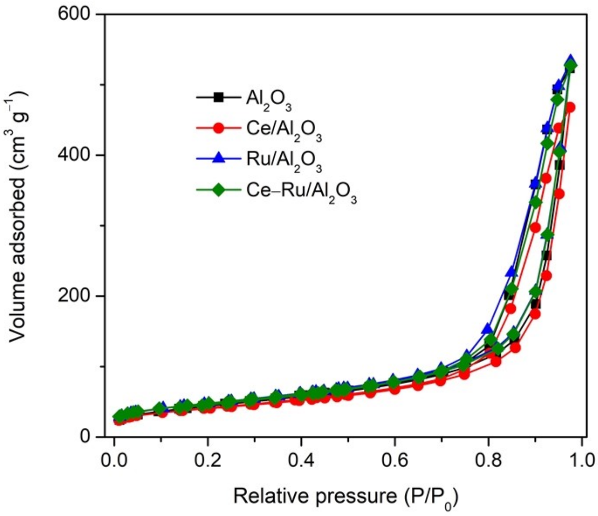


**Fig. S2** $N_2$ sorption isotherms of the $Al_2O_3$, Ru/$Al_2O_3$ and Ce–Ru(x:1)/$Al_2O_3$ samples.

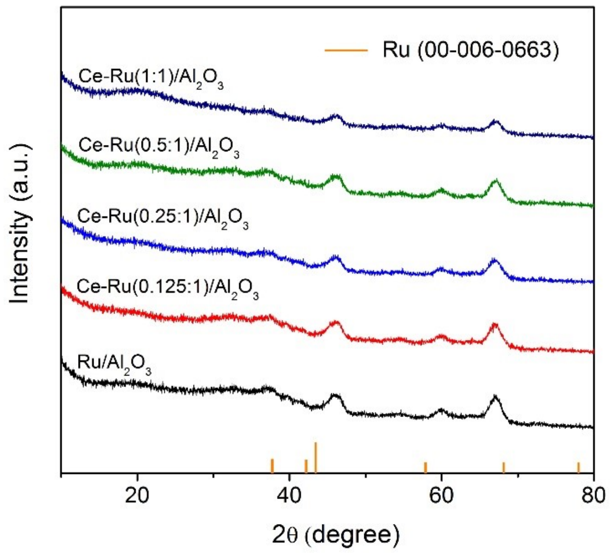


**Fig. S3** XRD patterns of $Ru/Al_2O_3$ and Ce–Ru(x:1)/$Al_2O_3$ samples with different Ce/Ru ratios.

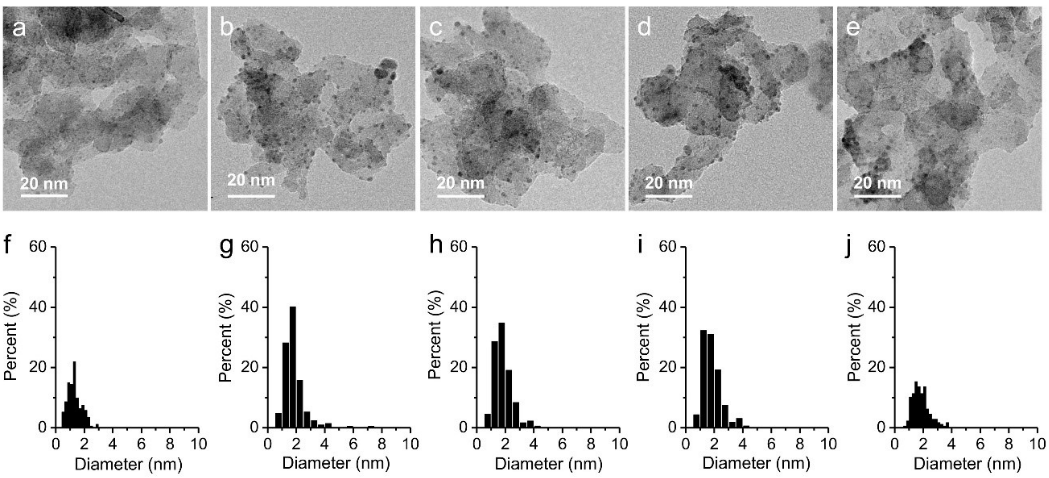


**Fig. S4** TEM images and Particle size distribution of $Ru/Al_2O_3$ (a and f), Ce–Ru(0.125:1)/$Al_2O_3$ (b and g), (c) Ce–Ru(0.25:1)/$Al_2O_3$ (c and h), Ce–Ru(0.5:1)/$Al_2O_3$ (d and i) and Ce–Ru(1:1)/$Al_2O_3$ (e and j) samples.

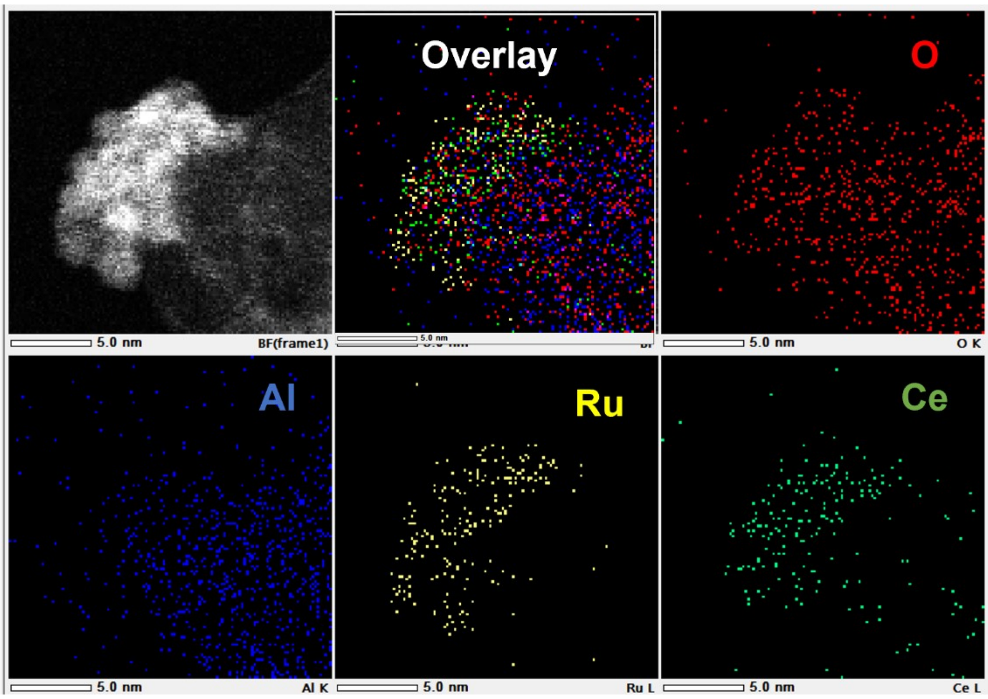


**Fig. S5** STEM and EDX-Mapping of Ce-Ru(1:1)/$Al_2O_3$ catalysts after stability test.

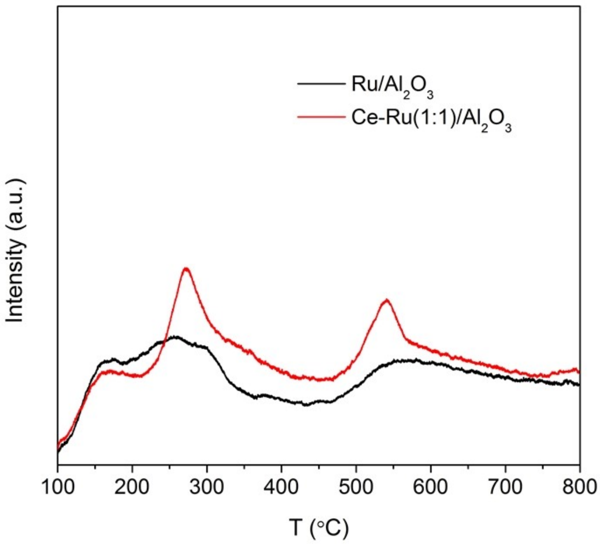


**Fig. S6** $NH_3$-TPD profiles of Ru/$Al_2O_3$ and Ce–Ru(1:1)/$Al_2O_3$ samples.

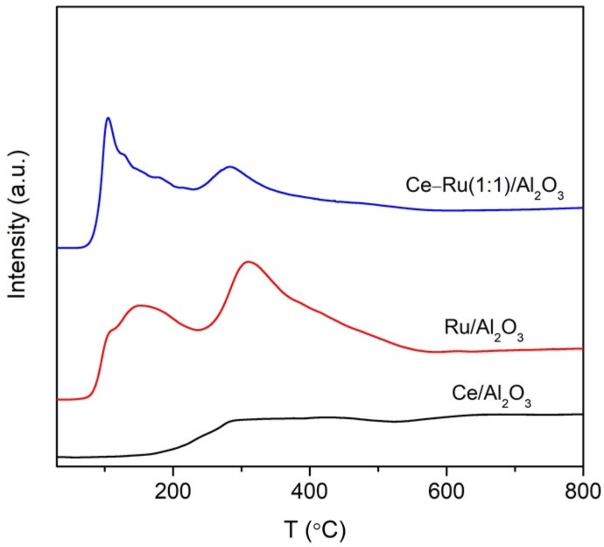


**Fig. S7** $H_2$-TPR profiles of Ce/$Al_2O_3$, Ru/$Al_2O_3$ and Ce–Ru(1:1)/$Al_2O_3$ samples.

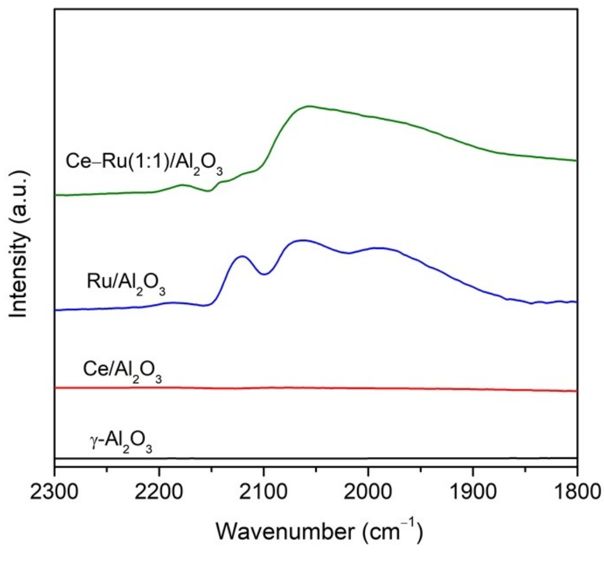


**Fig. S8** DRIFTS spectra of CO adsorption on $Al_2O_3$, Ce/$Al_2O_3$, Ru/$Al_2O_3$ and Ce–Ru(1:1)/$Al_2O_3$ catalysts.

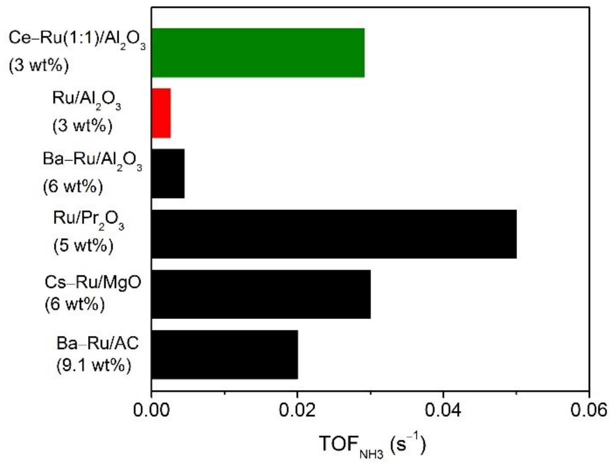


**Fig. S9** $TOF_{NH3}$ values of $Ru/Al_2O_3$, Ce–Ru(1:1)/$Al_2O_3$ and typical supported Ru catalysts for ammonia synthesis at 400 °C under 1.0 MPa.

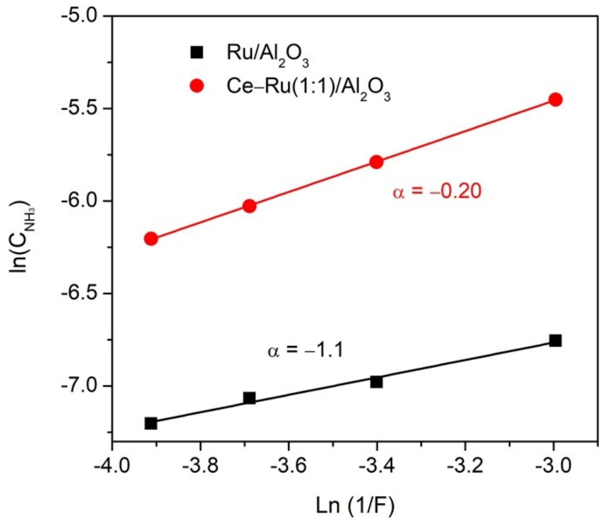


**Fig. S10** $NH_3$ reaction order of $Ru/Al_2O_3$ and Ce–Ru(1:1)/$Al_2O_3$ catalysts at 350 °C under 1.0 MPa.

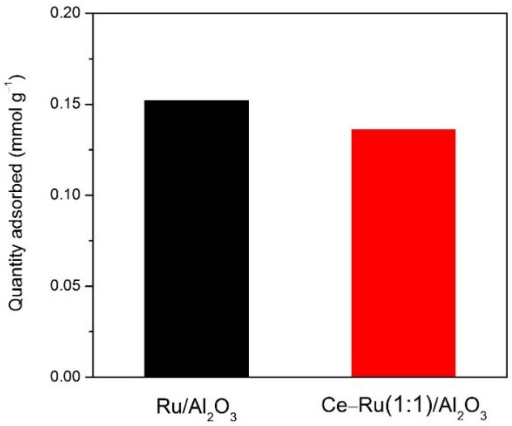


**Fig. S11** Chemisorption measurements of CO on the Ru in Ru/$Al_2O_3$ and Ce–Ru(1:1)/$Al_2O_3$ catalysts.

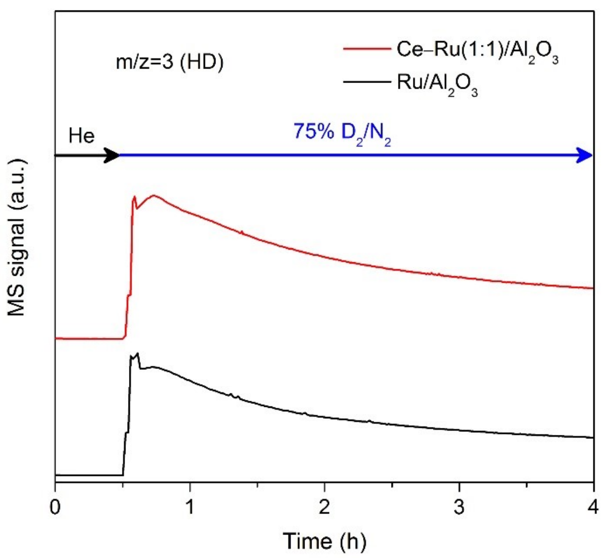


**Fig. S12** Formation of products over $H_2$ pretreated Ru/$Al_2O_3$ and Ce–Ru(1:1)/$Al_2O_3$ upon switching from He to 75% $D_2$/$N_2$ at 450 °C under 1.0 MPa.

## 2. References


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