

Mullite-supported Rh catalyst:

a promising catalyst for the decomposition of N₂O propellant[†]

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Supplemental Materials

Experimental details

The supports were prepared in our laboratory by the co-precipitation method, with inexpensive $\text{Al}(\text{NO}_3)_3$ and tetraethylorthosilicate (TEOS) as precursors and $(\text{NH}_4)_2\text{CO}_3$ as a precipitant. Mullite precursors was firstly prepared by mixing 18.75 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 2.49 g ml TEOS homogenized in the 10 ml ethanol at pH 1 and 36.7 g $(\text{NH}_4)_2\text{CO}_3$, followed by stirring for 5 h in the water bath at 60 °C. The resultant precipitate was then dried at 120 °C in an air oven for 64 h and followed by calcination in air for 4 h at 500 °C and 1200 °C. By the impregnation method, the precursor of the active phase ($\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$) is introduced from aqueous solutions onto the surface of the support. After the impregnation step the catalyst precursors were dried at 120 °C in air oven for overnight. One portion of the catalysts was calcined at 500 °C for 4 h, the other was calcined at 1200 °C for 4 h. Finally, all the catalysts were pelletized into grain of 20-40 meshes for the catalytic tests.

The catalytic reactor is a fix-bed flow quartz reactor with inner diameter of 6 mm. 100 mg catalyst diluted with 400 mg quartz sand was fixed in the middle part of the reactor. The reacting gas contained 30 v/v% N_2O in Ar, and was introduced at a flow rate of 50 mL min^{-1} , corresponding to a gas hourly space velocity of 30,000 $\text{mL g}^{-1} \text{h}^{-1}$. The remaining N_2O at the exit of the reactor was determined by a gas chromatography (Agilent GC-6890N, TCD detector) with a Porapak Q column (2 m in length). Amounts of N_2 and O_2 which produced from N_2O decomposition were examined with a 13 X column (2.5 m in length). Prior to each test, the catalysts were

in situ reduced with pure H₂ at 500 °C for 2 h, and then cooled to 40 °C in Ar. Each data point in *X*-versus-temperature curves was measured after staying at a set temperature for 0.5 h to ensure both the reaction and thermal environment reached steady state.

Oxygen adsorption was carried out with a BT2.15 heat-flux calorimeter. Prior to the measurement, a catalyst sample was preheated in a special treatment quartz cell in H₂ from room temperature to 500 °C and held at that temperature for 2 h. Then, the samples were outgassed in situ in high vacuo (3×10^{-4} Pa) at 500 °C for 0.5 h. After being cooled to room temperature, the sample was transferred to a side-armed Pyrex vessel and sealed in a Pyrex capsule. The capsule can minimize the possible contamination in the high vacuum system in the course of thermal equilibrium (6–8 h) with the calorimeter. After thermal equilibrium was reached, the capsule was broken by a vacuum feedthrough and fresh catalyst was exposed. The microcalorimetric data were then collected by sequentially introducing small doses (1–10 μmol) of O₂ onto the sample until it became saturated (665– 798 Pa).

Table S1 Physico-chemical properties of the Rh impregnated catalysts

| Sample | Rh content (wt %) | S _{BET} /m ² g ⁻¹ | V _{pore} (cm ³ g ⁻¹) | d (nm) | Dispersion(%) |
|----------|-------------------|--|--|--------|---------------|
| Rh/M | 4.24 | 46 | 0.134 | 8.34 | 46 |
| Rh/AS | 4.08 | 276 | 0.418 | 6.048 | 87 |
| Rh/Al | 4.01 | 265 | 0.868 | 6.09 | 83 |
| Rh/M-HT | 1.01 | 23 | 0.116 | 20 | |
| Rh/AS-HT | 0.96 | 37 | 0.121 | 15.63 | |
| Rh/Al-HT | 0.96 | 7 | 0.013 | 9.16 | |

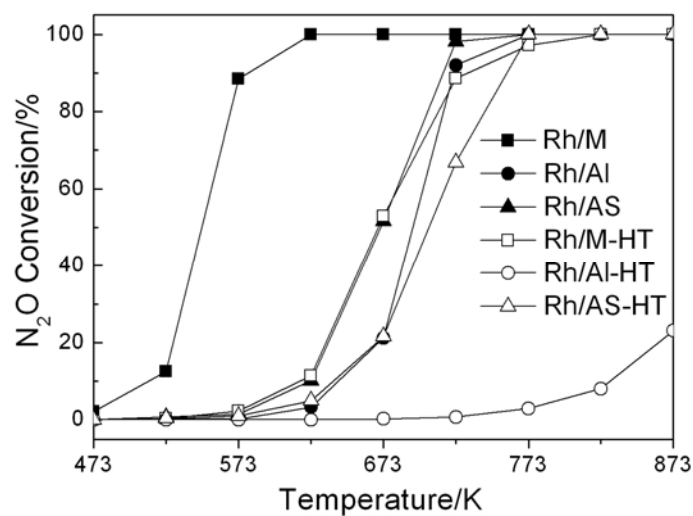


Fig. S1 N₂O conversion as a function of temperature over the Rh impregnated catalysts.

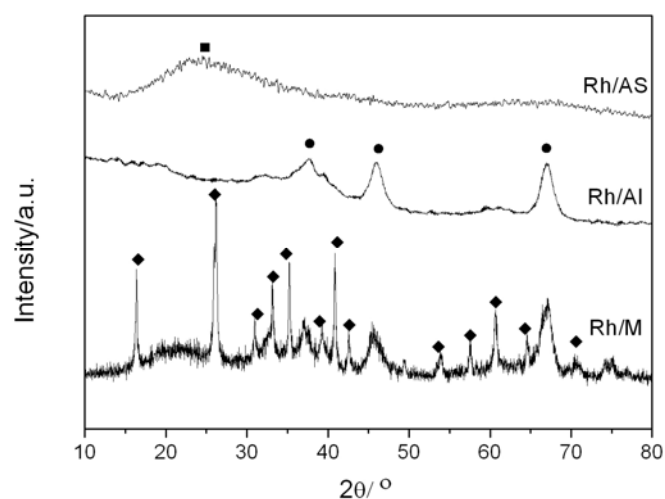


Fig. S2 X-Ray diffraction patterns of Rh impregnated catalysts calcined at 773 K: (●) γ -Al₂O₃ (JCPDS 1-1303), (◆) mullite (JCPDS 79-1275), (■) SiO₂ (JCPDS 29-0085).

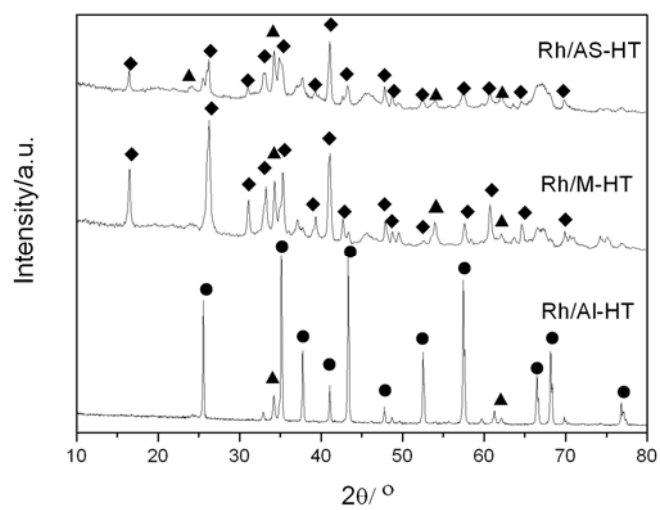


Fig. S3 X-Ray diffraction patterns of Rh impregnated catalysts calcined at 1473 K :
(●) α -Al₂O₃ (JCPDS 81-2267) , (◆) mullite , (▲) Rh₂O₃ (JCPDS 76-0148) .