

Electronic Supplementary Information for Chemical Communication

Active three-way catalysis of rhodium particles with low oxidation state maintained under oxidative atmosphere on La-containing ZrO₂ support

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Experimental details

ZrO₂-La₂O₃ mixed oxide was prepared by an ammonium co-precipitation method. ZrO(NO₃)₂·6H₂O (60.8 g) and La(NO₃)₃·6H₂O (5.2 g) or Pr(NO₃)₃·6H₂O (5.2 g) were dissolved in 200 g of water, followed by addition of an aqueous NH₄OH solution (1.0%) to raise the pH to 12 or more. The precipitate was dried at 423 K for 2 h in air, and calcined at 773 K for 2 h in air. The additive content of the lanthanoid was 5.0 wt% as oxide (La₂O₃ or Pr₆O₁₁). Pure ZrO₂ support (BET surface area: 52.3 m² g⁻¹) was purchased from Kishida Chemical Co., Ltd (Osaka, Japan). Rhodium (0.33 wt% as rhodium metal) was loaded on these oxide supports by impregnation using an aqueous solution of Rh(NO₃)₃·H₂O, followed by calcination in air at 773 K.

The catalytic activity was evaluated using a fixed-bed continuous flow reactor. The Rh/ZrO₂, Rh/Zr-La-O, or Rh/Zr-Pr-O catalysts were dispersed on a Cordierite honeycomb (loading amount: 100 g L⁻¹). The reaction gas was a mixture of 500 ppm C₃H₆, 1000 ppm NO, 0.7% CO, 0.2% H₂, 0.6% O₂, 10% H₂O and the balance of nitrogen. Oxygen, carbon monoxide and hydrogen were added periodically under fluctuating conditions. One cycle of 1.0 Hz frequency consisted of four periods. The first period involved oxygen insertion into the static gas for 0.25 s; the second, no insertion of added gas; the third, insertion of carbon monoxide and hydrogen for 0.25 s; and the last, no insertion resulting in oxygen, carbon monoxide and hydrogen concentrations changing periodically between 0.43 and 1.86%, 0.7 and 2.9% and 0.20 and 0.74% for the three gases, respectively. The flow rate of the reaction gas was 26 dm³ min⁻¹ corresponding to a GSHV of 60,000 h⁻¹. Before measurement of the catalytic performance, the catalysts were pre-treated under a flow of gas mixture at 773 K for 10 min and then cooled to 373 K under flowing nitrogen. Products were analysed continuously using a flame ionisation detector for hydrocarbon, infrared for carbon monoxide, and chemical luminescence for NO contents with a Horiba MEXA-9100 evaluation system (Kyoto, Japan).

XPS spectra were obtained with a PerkinElmer ESCA5600 by using Mg K α radiation (400 W). Binding energies were referred to as C1s (284.5 eV). Before measurement of the XPS spectra, two types of pre-treatment were carried out. The first pre-treatment method was used to obtain information on rhodium during the reaction, using TEM measurements where samples were treated under the reaction gas at 773 K for 10 min and then cooled to room temperature under nitrogen flow. The other was to obtain information on rhodium under oxidative gas conditions, where samples were pre-treated under a flow of 5.0% O₂ at 773 K for 10 min, and then cooled to room temperature under nitrogen flow. CO-TPR was carried out using CO (0.6%)/He as reducing gas (100 cm³ min⁻¹) at a heating rate of 30 K min⁻¹. Prior to TPR measurements, samples were pre-treated under a flow of 5.0% O₂ at 773 K for 10 min, and then cooled to 323 K under a flow of helium.

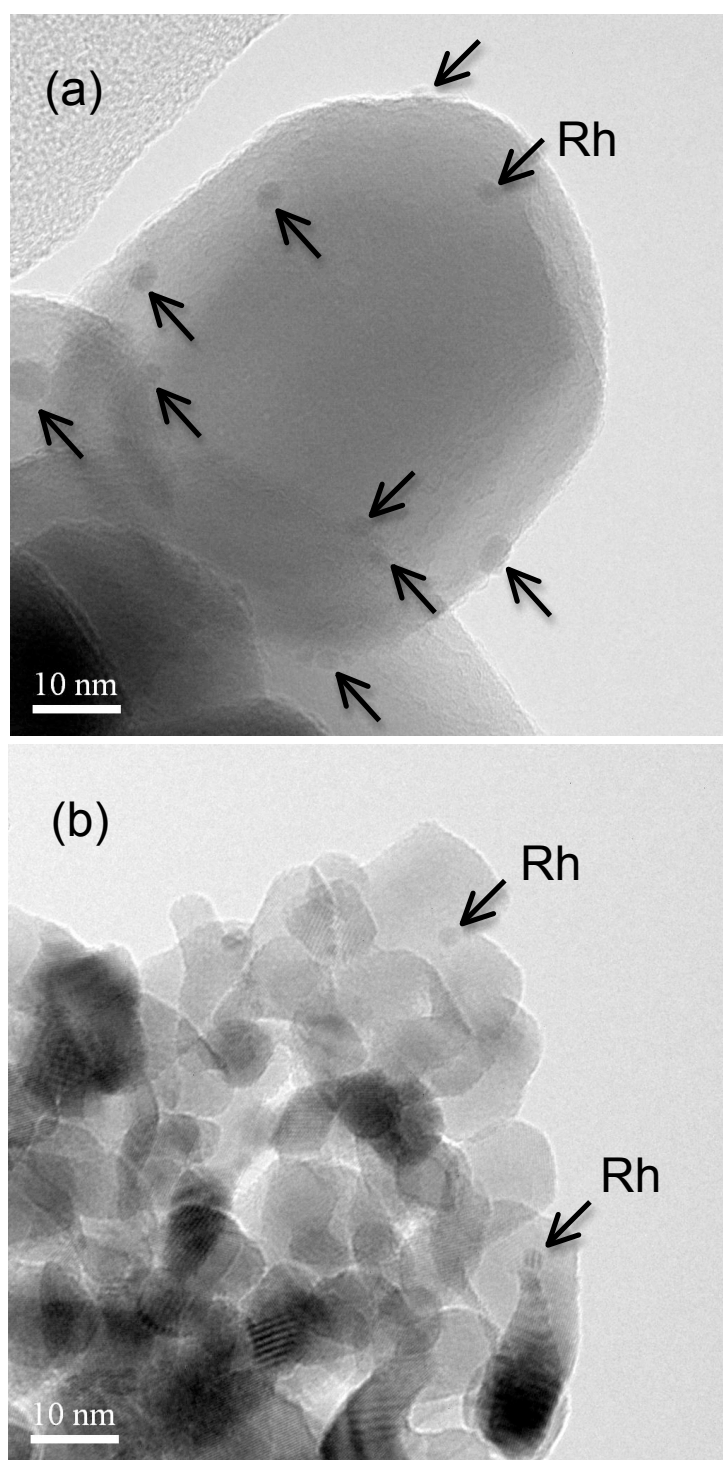


Fig.S1 TEM micrographs of (a) Rh/ZrO₂, (b) Rh/Zr-La-O after three-way catalytic reaction at 773 K for 10 min.

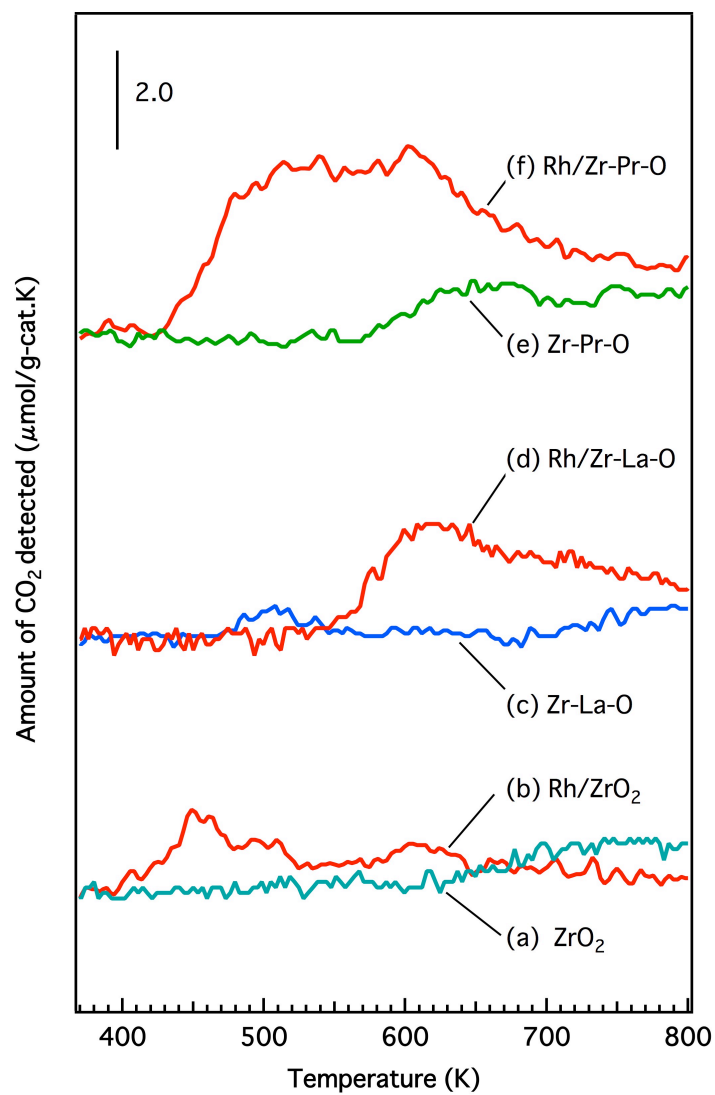


Fig. S2 CO-TPR of (a)ZrO₂, (b)Rh/ZrO₂, (c) Zr-La-O, (d) Rh/Zr-La-O, (e) Zr-Pr-O and (f) Rh/Zr-Pr-O after 5% O₂/He treatment for 10 min at 773 K.