

Electronic Supplementary Information

Enhanced performance of a Pt-based three-way catalyst using a double-solvent method

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1.1 Support preparations

The composite oxide $\text{CeO}_2\text{-ZrO}_2\text{-La}_2\text{O}_3\text{-Al}_2\text{O}_3$ (CZLA) sample used as a support was prepared by co-precipitation method.¹ The precursors of $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, $\text{Zr}(\text{NO}_3)_4$, $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ and $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ were dissolved together in deionized water and then mixed with a buffer solution consisting of $\text{NH}_3\cdot\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{CO}_3$. During titration process, pH was kept at 10. The precipitates were dried at 110 °C for 12 h, heated at 600 °C for 3 h, and then calcined at 900 °C for 3 h. The resulting CZLA composite oxide had a C / Z / A molar ratio of 1:1:2 and CZA / L mass ratios of 95:5.

1.2 Catalyst activity testing

The activity test was carried out in a multiple fixed bed continuous flow reactor by passing a gas mixture simulating the exhaust from natural gas vehicles (NGV) under stoichiometric conditions. The simulated exhausts contained 700 ppm CH_4 , 3500 ppm CO, 700 ppm NO, 10 vol% H_2O , 12 vol% CO_2 and N_2 (as balance gas). The content of O_2 was adjusted carefully to obtain a stoichiometric mixed gas. The simulated gases were regulated by mass-flow controllers before entering reactor. The catalysts were pretreated at 550 °C for 1 h in the simulated exhausts prior to the test. The inlet gas temperature was obtained by using a K-thermocouple, in order to avoid the effect of catalytic oxidation reactions (exothermic reactions) on the inlet gas temperature, and the thermocouple was fixed 20 mm in front of the monolith.² The temperatures given in this study were the temperatures of inlet gas. Trials were performed from 100 °C to 500 °C with a gas hourly space velocity (GHSV) of 34000 h^{-1} and the products

were monitored continuously using a Thermo Scientific AntarisIGS Gas Analyzer on line.

The conversions of CH₄, CO and NO and the selectivity of N₂ were calculated using the following formulas:

$$\text{CH}_4 \text{ Conversion (\%)} = \frac{[\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}}{[\text{CH}_4]_{\text{in}}} \times 100\%$$

$$\text{CO Conversion (\%)} = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100\%$$

$$\text{NO Conversion (\%)} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100\%$$

$$\text{N}_2 \text{ Selectivity (\%)} = \frac{([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} - [\text{NO}_2]_{\text{out}} - 2 * [\text{N}_2\text{O}]_{\text{out}} - [\text{NH}_3]_{\text{out}})}{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}} \times 100\%$$

1.3 Characterization

The textural properties of the samples were obtained by nitrogen adsorption-desorption method at -196 °C with a Quantachrome SI instrument. Prior to each measurement, samples were outgassed at 300 °C for 3 h under vacuum to desorb moisture from the surface. The pore size distribution (PSD) and the pore diameter (D_p) were calculated from the desorption branch using the Barret–Joyner–Halenda (BJH) method, while the special surface area (SSA) values were calculated on the basis of the Brunauer–Emmett–Teller (BET) model.

The crystal structures of the samples were performed on a D/max-RA diffractometer (Japan Science, Rigaku, Tokyo, Japan) using CuKα radiation (λ = 0.15406 nm) and operating at 40 kV and 25 mA. The XRD patterns of the samples were recorded for 2θ values between 10° and 80°, with a scanning step size of 0.06°.

The crystalline phases were identified by comparison with the reference data from the International Center for Diffraction Data (ICDD).

Temperature programmed reduction (TPR) experiments were performed on a quartz tubular microreactor, equipped with a thermal conductivity detector (TCD). The samples (100 mg, 40–60 mesh) were pretreated with pure N₂ at 450 °C for 1 h and then cooled to room temperature under the flow of N₂. Then, reduction was performed under a flow of 5 %H₂ / N₂ (30 mL / min) between room temperature and 900 °C at a heating rate of 8 °C / min. The consumption of H₂ was monitored by a TCD.

The average particle diameter of Pt was determined by CO-chemisorption method³ over the reduced catalysts and that was calculated assuming that CO was adsorbed on the surface of spherical Pt particles at CO/(surface Pt atom) = 1/1 stoichiometry.⁴ Each sample (200 mg, 40–60 mesh) was pretreated at 550 °C for 1 h in H₂ and then purged with pure He. After cooling to room temperature, same doses of CO was injected per time until CO content in the outlet gas reached a constant value.^{4, 5} The Pt dispersion (D) and active metal surface area (MSA) were calculated using the formulas and constants reported in literature, while the average Pt particle size (d_{Pt}) was obtained by $d_{Pt}(\text{nm}) = 1.1 / D$.⁴⁻⁶

The oxygen storage capacity (OSC) measurements were carried out on a self-assembled experimental device according to our previous work.⁷ Each sample (200 mg, 40–60 mesh) was pretreated at a testing temperature for 30 min in pure H₂ and then purged with pure He. Next, the pulse of oxygen was injected into the sample

until no further oxygen consumption could be monitored by a TCD. The test temperature range was from 200 °C to 600 °C with intervals of 100 °C.

X-ray photoelectron spectroscopy (XPS) experiments were carried out on a Kratos XSAM 800 spectrometer with Mg K α radiation at 13 kV and 20 mA and calibrated internally using the C1s binding energy (BE) of 284.6 eV. The morphology and microstructure of the samples were analysed on a Tecnai G² F20 S-TWIN Transmission electron microscopy (FEI Company, USA, 200 kV accelerating voltage).

1.4 Figure

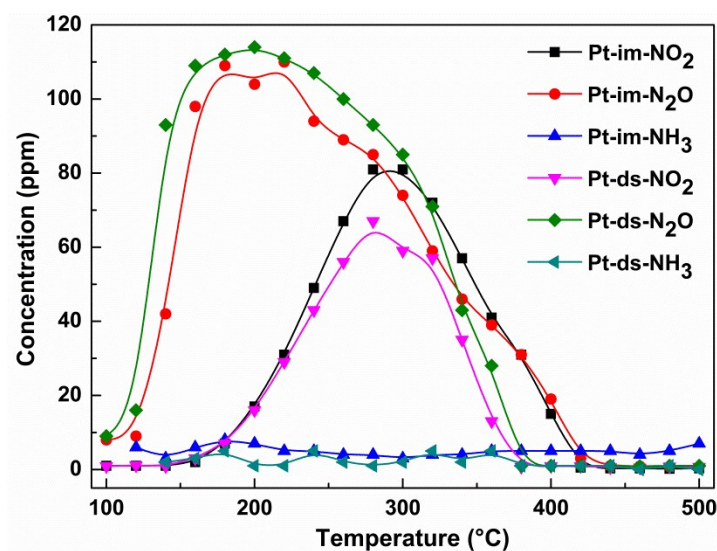


Fig. S1 The concentration curves of NO₂, N₂O and NH₃ as function of temperature over Pt-im and Pt-ds.

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