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Electronic Supporting Information (ESI)

Electrical promotion-assisted automotive exhaust catalyst: highly active and selective NO reduction to N₂ at low-temperatures

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1. Experimental procedure

Catalyst preparation

Preparation of ceria-zirconia ($Ce_{0.7}Zr_{0.3}O_2$) was conducted using a citric acid complex method with aqueous solutions of $Ce(NO_3)_3 \cdot 6H_2O$ and $ZrO(NO_3)_2 \cdot 2H_2O$ (Kanto Chemical Co. Inc.), with excess amounts of citric acid and ethylene glycol (Kanto Chemical Co. Inc.). The molar ratio of metal: citric acid: ethylene glycol was 1: 3: 3. After the obtained solution was evaporated in a water bath at 353 K for 16 h, the solution was dried on a hot plate with stirring. The obtained powder was pre-calcined at 673 K for 2 h and was calcined at 1123 K for 10 h.

Next, we impregnated Pd nanoparticles on the $Ce_{0.7}Zr_{0.3}O_2$ using an impregnation method with an acetone solution of Pd(OCOCH₃)₂ (Kanto Chemical Co. Inc.). We dried it at 393 K for 20 h and calcined it in air at 823 K for 3 h. Then, the catalyst of 0.5 wt% Pd/Ce_{0.7}Zr_{0.3}O₂ was obtained.

Activity tests

Catalytic activity tests were conducted in a fixed-flow-type quartz reactor at atmospheric pressure. In this study, the powder of Pd/Ce_{0.7}Zr_{0.3}O₂ catalyst was pressed, ground and sieved to a particle size of 250–500 μ m. The image of the sieved catalyst and histogram for the particle size are

shown in Fig. S4. The catalytic activity tests were conducted using the catalyst particles with this distribution of size. An electric field was applied with a power supply *via* stainless steel electrodes, contacting the catalyst bed (amount of fixed catalyst was 80 or 200 mg; denoted in each caption) on the upper side and bottom side. The activity tests were performed under a simulated stoichiometric exhaust gas (2500 ppm NO, 3000 ppm CO, 500 ppm C_3H_6 , 2500 ppm O_2 , 7 vol% H₂O and Ar as a balance gas) with a total flow rate of 200 mL min⁻¹. A pre-treatment for the catalyst was conducted for oxidation (5% O_2 , Ar-balanced at 773 K for 15 min) and reduction (5% H_2 , Ar-balanced at 773 K for 15 min) sequentially before the reaction. In the activity tests, the furnace temperature was increased stepwise from 338 to 623 K. Steady-state activity was evaluated at each temperature. To evaluate catalytic activity in an electric field, direct current of 1–12 mA was applied between the electrodes, monitoring the response voltage using an oscilloscope (TDS 2001C with a voltage probe P6015A; Tektronix Inc.). A thermocouple was set in the bottom of the catalyst bed to measure the real temperature of catalyst bed. The outlet gas was analyzed using an online GC-TCD (GC-8A; Shimadzu Corp.) and a chemiluminescent method NO_x analyzer (NOA-7000; Shimadzu Corp.). The NO conversion and N₂ selectivity are defined as shown in equations (1) and (2).

$$X_{\rm NO} (\rm NO \ conversion \ rate \ / \ \%) = ([\rm NO]_{in}-[\rm NO]_{out})/[\rm NO]_{in} \times 100 \quad (1)$$
$$N_2 \ selectivity (\%) = 2r_{\rm N2}/r_{\rm NO} \times 100 \quad (2)$$

In these equations, $[NO]_{in}$, $[NO]_{out}$, r_{N2} , and $r_{NO \text{ conv.}}$ respectively represent the inlet NO concentration, outlet NO concentration, N₂ formation rate and NO conversion rate. The NO-CO-O₂-H₂O reaction (2500 ppm NO, 3000 ppm CO, 250 ppm O₂, 7 vol% H₂O and Ar as a balance gas) and NO-C₃H₆-O₂-H₂O reaction (2500 ppm NO, 500 ppm C₃H₆, 1000 ppm O₂, 7 vol% H₂O and Ar as a balance gas) tests were conducted similarly. Partial-pressure-dependent testing of oxygen was conducted under a NO-CO-O₂-H₂O condition (2500 ppm NO, 3000 ppm CO, 0–1500 ppm O₂, 7 vol% H₂O and Ar as a balance gas) and NO-C₃H₆-O₂-H₂O condition (2500 ppm NO, 3000 ppm CO, 0–1500 ppm O₂, 7 vol% H₂O and Ar as a balance gas) and NO-C₃H₆-O₂-H₂O condition (2500 ppm NO, 500 ppm NO, 500 ppm CO, 0–1500 ppm O₂, 7 vol% H₂O and Ar as a balance gas) and NO-C₃H₆-O₂-H₂O condition (2500 ppm NO, 500 ppm NO, 500 ppm CO, 0–1500 ppm O₂, 7 vol% H₂O and Ar as a balance gas) and NO-C₃H₆-O₂-H₂O condition (2500 ppm NO, 500 ppm NO, 500 ppm CO, 0–1500 ppm O₂, 7 vol% H₂O and Ar as a balance gas) and NO-C₃H₆-O₂-H₂O condition (2500 ppm NO, 500 ppm NO, 500 ppm CO, 0–1500 ppm O₂, 7 vol% H₂O and Ar as a balance gas) and NO-C₃H₆-O₂-H₂O condition (2500 ppm NO, 500 ppm NO, 500 ppm CO, 0–1500 ppm O₂, 7 vol% H₂O and Ar as a balance gas) and NO-C₃H₆-O₂-H₂O condition (2500 ppm NO, 500 ppm CO, 0–1500 ppm O₂, 7 vol% H₂O and Ar as a balance gas) similarly.

Elucidation of intermediates on the catalyst

In-situ DRIFTS measurements were taken using a Fourier transform infrared spectrometer (FT/IR 6200; Jasco Corp.) with an MCT detector and a ZnSe window. Catalyst sample powder (ca. 40 mg) was filled into a hand-made Teflon cell with platinum electrodes. Background spectra (donated as BKG) were measured under inert Ar gas (100 mL min⁻¹ at 373 K, 448 K, and 473 K)

after the same pre-treatment as the activity tests. After the measurement of BKG, the following measurements were taken. 3000 ppm C_3H_6 (Ar balanced) was supplied to the IR cell followed by obtaining the spectra of adsorbed species on the catalyst. To evaluate the adsorbed species on the catalyst with an electric field, DC current of 3 mA was applied between the electrodes whereas 3000 ppm C_3H_6 gas was supplied, and the spectra for the catalyst in an electric field. The spectral range was 1000–4000 cm⁻¹, with resolution of 4.0 cm⁻¹ and an accumulation of five scans.

Structural characterization of the catalyst

X-ray diffraction patterns were measured to confirm the crystalline structures of Pd/Ce_{0.7}Zr_{0.3}O₂ catalysts (SmartLab 3; Rigaku Corp.). The Cu $K\alpha$ radiation condition was at 40 kV and 40 mA. The BET-specific surface area of the catalyst was measured using N₂ adsorption at 77 K (Gemini VII; Micromeritics Instrument Corp.).

XRD patterns for $Ce_{0.7}Zr_{0.3}O_2$ and Pd/Ce_{0.7}Zr_{0.3}O₂ and BET surface area are presented in Fig. S3 and Table S2 respectively. BET surface changed slightly, but both of $Ce_{0.7}Zr_{0.3}O_2$ and Pd/Ce_{0.7}Zr_{0.3}O₂ have a fluorite structure. Furthermore, it is expected that Pd was dispersed finely on $Ce_{0.7}Zr_{0.3}O_2$ because peaks assigned Pd metal was not observed.

2. Supplementary Tables and Figures

Table S1 The response voltage and input electric power to $Pd/Ce_{0.7}Zr_{0.3}O_2$ (catalyst weight was 200 mg) during activity test at each temperature.

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	Temperature / K	response voltage / kV	Power / W	
	428.4	0.813	1.22	
	471.9	0.833	1.25	
	480.2	0.687	1.03	
	496.8	0.547	0.82	
	517.2	0.600	0.90	
	541.6	0.420	0.63	
	588.4	0.373	0.56	
Table S2 Surface area of $Ce_{0.7}Zr_{0.3}O_2$ and 0.5 wt% Pd/ $Ce_{0.7}Zr_{0.3}O_2$.				
	Catalyst	Surfa	Surface area / m ² g ⁻¹	
	Ce _{0.7} Zr _{0.3} O ₂		16.3	
0.5wt% Pd/Ce _{0.7} Zr _{0.3} O ₂		0.3O2	14.6	



Fig. S1 Schematic image of the reactor.



Fig. S2 NO, CO and O₂ reaction rate, O₂ conversion and N₂ selectivity over 0.5wt% Pd/Ce_{0.7}Zr_{0.3}O₂ under NO-CO-O₂-H₂O reaction (NO: 2500 ppm, CO: 3000 ppm O₂: 0, 250, 500, 750, 1000 and 1500 ppm, H₂O: 70000 ppm Ar balance, total flow: 200 cc min⁻¹) with/without the electric field at 413 K.



Fig. S3 XRD patterns of the prepared $Ce_{0.7}Zr_{0.3}O_2$ and Pd/ $Ce_{0.7}Zr_{0.3}O_2.$



Fig. S4 (A) The image of particles of $Pd/Ce_{0.7}Zr_{0.3}O_2$ filled in the reactor and (B) histogram for the particle size of the catalyst.