Supported Pd nanoclusters with enhanced hydrogen spillover for NO$_x$ removal via H$_2$-SCR: The elimination of "volcano-type" behaviour

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Supporting information

1. Experimental Section

1.1 Catalysts preparation

The CeZrO$_4$ and Al-CeZrO$_4$ support oxides with a ratio of Ce:Zr = 0.5:0.5 or Al:Ce:Zr = 0.1:0.45:0.45 were prepared using a co-precipitation method. Briefly, appropriate amount of Ce(NO$_3$)$_3$·6H$_2$O, ZrOCl$_2$·8H$_2$O, Al(NO$_3$)$_3$·9H$_2$O as precursors and PEG as surfactant were dissolved in an ethanol solution at 50 ºC in a water bath. Ammonium hydroxide was added dropwise until the pH ≥ 10. After washing, the samples were dried in a vacuum oven at 80 ºC for 12 h and calcined in a muffle oven at 500 ºC for 4 h, yielding the CeZrO$_4$ and Al-CeZrO$_4$ support oxides. The 1wt.%Pd/CeZrO$_4$ and 1wt.%Pd/Al-CeZrO$_4$ catalysts were provided by wet incipient impregnation method. The as-prepared support oxide was impregnated with a suitable volume of Pd(NO$_3$)$_2$·2H$_2$O solution containing desired amount of Pd and kept overnight at room temperature. After thermal treating at the same conditions for the preparation of support oxides, the Pd catalysts were molded and crushed to 20-40 meshes for use. XRF analysis of the as-prepared samples showed that the errors of mass loading amounts of Pd, Al, Ce, Zr are less than 5%.

1.2 Catalysts characterization

The specific surface area (SSA) of the as-prepared materials was determined by nitrogen adsorption at 77 K using the Brunauer–Emmett–Teller (BET) method (Micrometrics ASAP2020). All samples were outgassed at 150 °C for 1 h prior to analysis. The pore-size distribution was determined from the desorption branch of a fully recorded isotherm of the as-prepared powders by the Barrett, Joyner and Halenda (BJH) method.

The phase composition and the crystal structure of the as-prepared powders were determined from powder X-ray diffraction patterns by using a Rigaku D/Max-IV X-ray diffractometer employing Cu Kα radiation operated at 40 kV and 40 mA. Data were collected over the 2θ range from 20 ° to 80 ° at a scan rate of 1 ° min^{-1}. Rietveld refinement was conducted using the PDXL program (Rigaku Corporation, PDXL 2.1).

Raman analysis (IDSpec ARCTIC Raman Spectrometer) was carried with the excitation wavelength is 532 nm and the power is 1.5 mW.

Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM)

images were recorded on a JEM-2010 and a JEM-2100F, respectively, at 200 kV, and the sample to be measured was first dispersed in ethanol and then collected on copper grids covered with carbon film.

H_2 and CO adsorption isotherm measurements (Micrometrics ASAP2020) were measured at 0 ºC and 0 ~ 1 atm after degassed in vacuo at 350 ºC for 4 h and cooled to 0 ºC while degassing. CO and H_2 Pulse Chemisorption (Micromeritics AutoChem II 2920) used a certain amount of 10% H_2/Ar gas to test the volume of H_2 adsorbed after the samples were retreated in Ar atmosphere at 300 ºC for 1 h and cooled down to 0 ºC. The palladium dispersions and hydrogen spillover are evaluated by the following equation:

$$D = \frac{2V_0 \times M_{Pd}}{22414W \times P}$$

where W is mass of the sample (g), P is mass fraction of Pd (%) and M_{Pd} represents molar weight of Pd (106.4 g mol^{-1}). For the calculation of palladium metal dispersion, V_0 depicts the volume of CO chemisorption (mL), and V_0 depicts the difference between the volume of chemisorbed H_2 and CO (mL) when counting the value of hydrogen spillover.

H_2-TPD (Micromeritics AutoChem II 2920) was proceeded after the catalysts being saturated with H_2 and purged in pure Ar at 0 ºC at a heating rate of 10 ºC min^{-1} to 500 ºC while recording the concentration profile of desorbed hydrogen.

XPS (AXIS-HSi, Kratos Analytical) analysis was conducted using a monochromatized Al Kα exciting radiation (hv = 1286.71 eV) with a constant analyzer-pass-energy of 40.0 eV. All binding energies (BEs) were referenced to C 1s peak (BE set at 284.5 eV) arising from C−C bonds.

1.3 Catalytic performance studies

The evaluation of the selective catalytic reduction of NO by hydrogen of the catalysts were carried out in a tubular reactor with an inner diameter of 0.8 cm at a GHSV of ~60,000 h^{-1}. A 0.5 g sample of the catalyst was placed in the reactor, connected to a gas chromatograph (Shimadzu GC 2010 plus, equipped with TCD, Japan) and a NO/NO$_2$ analyzer (Testo 340, Germany) to measure the gas-phase composition in the reactor outlet. The reaction feed gas mixture consisted of 1000 ppm NO$_x$ (NO: NO$_2$ ratio ~ 9: 1), 1 vol.% H_2, 5 vol.% O_2 and Ar as balance gas. The reaction temperature was increased from 80 to 300 ºC and the activity data were collected when the reaction reached steady-state condition at each temperature. The performances of catalysts were evaluated by means of NO$_x$ conversion as described by the following equation:

$$NO_x \text{ conv.}\% = \frac{c(NO_x)in - c(NO_x)out}{c(NO_x)in} \times 100\%$$

2. Supporting Figures and Tables
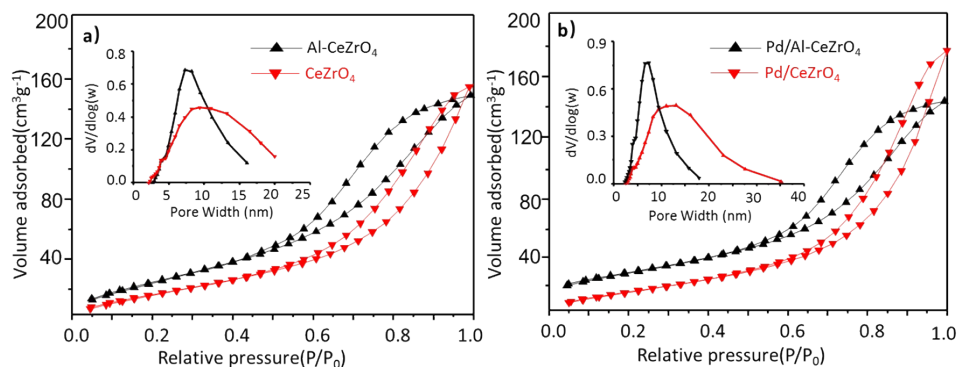
2.1 N$_2$ sorption isotherms and pore size distribution

Figure S1 N$_2$ sorption isotherms and pore size distributions of CeZrO$_4$, Al-CeZrO$_4$, Pd/CeZrO$_4$ and Pd/Al-CeZrO$_4$.

2.2 Raman analysis

Raman spectra of supported Pd catalysts were shown in Figure S2. Note that six Raman active modes of $A_{1g} + 3E_g + 2B_{1g}$ symmetry are observed for tetragonal ZrO_2 (space group P42/nmc), while for the cubic fluorite structure (space group Fm3m) only one F_{2g} mode centered at around 490 cm^{-1} is Raman-active. In pure CeO_2, which also has the fluorite structure, the F_{2g} mode is observed at 465 cm^{-1}.
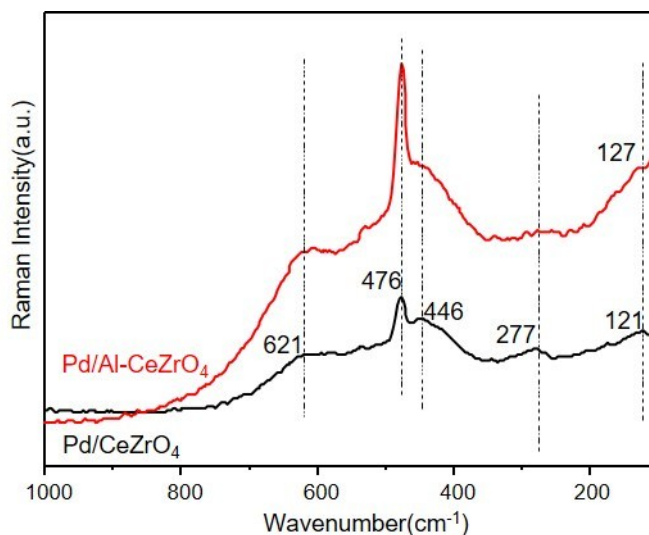

Figure S2 Raman spectra of as-prepared $CeZrO_4$ and $Al-CeZrO_4$ supported Pd catalysts.

2.3 HRTEM and EDX analysis

HRTEM images of as prepared Pd catalysts were put on Figure S3 a~d) in case the picture in the paper is not clear enough. Measurement of lattice fringe spacing based on the HRTEM images were also shown in Figure S3 e~f).

Element mappings and Energy Dispersive X-Ray (EDX) analysis were carried out, as shown in Figure S4 a~g). All elements examined including Pd could be obviously identified, which are homogeneously distributed over the selected area of the Pd/Al-CeZrO$_4$ catalyst. Note that the element mapping was done within a relatively large area (that is, under relatively low magnification). This is because that the Pd loading was very low (1 wt%) and the as-deposited Pd nanoclusters are very small in size, which consequently gives very weak signals and lead to severe drifts when conducted under relatively high magnifications.

Pd/CeZrO$_4$

Pd/Al-CeZrO$_4$

a)

Microscope JEM-2100F | Accelerating Voltage 200 kV | Magnification 300000 x | ——20 nm——

b)

Microscope JEM-2100F | Accelerating Voltage 200 kV | Magnification 300000 x | ——20 nm——

c)

Microscope JEM-2100F | Accelerating Voltage 200 kV | Magnification 400000 x | ——10 nm——

d)

Microscope JEM-2100F | Accelerating Voltage 200 kV | Magnification 400000 x | ——10 nm——

e)

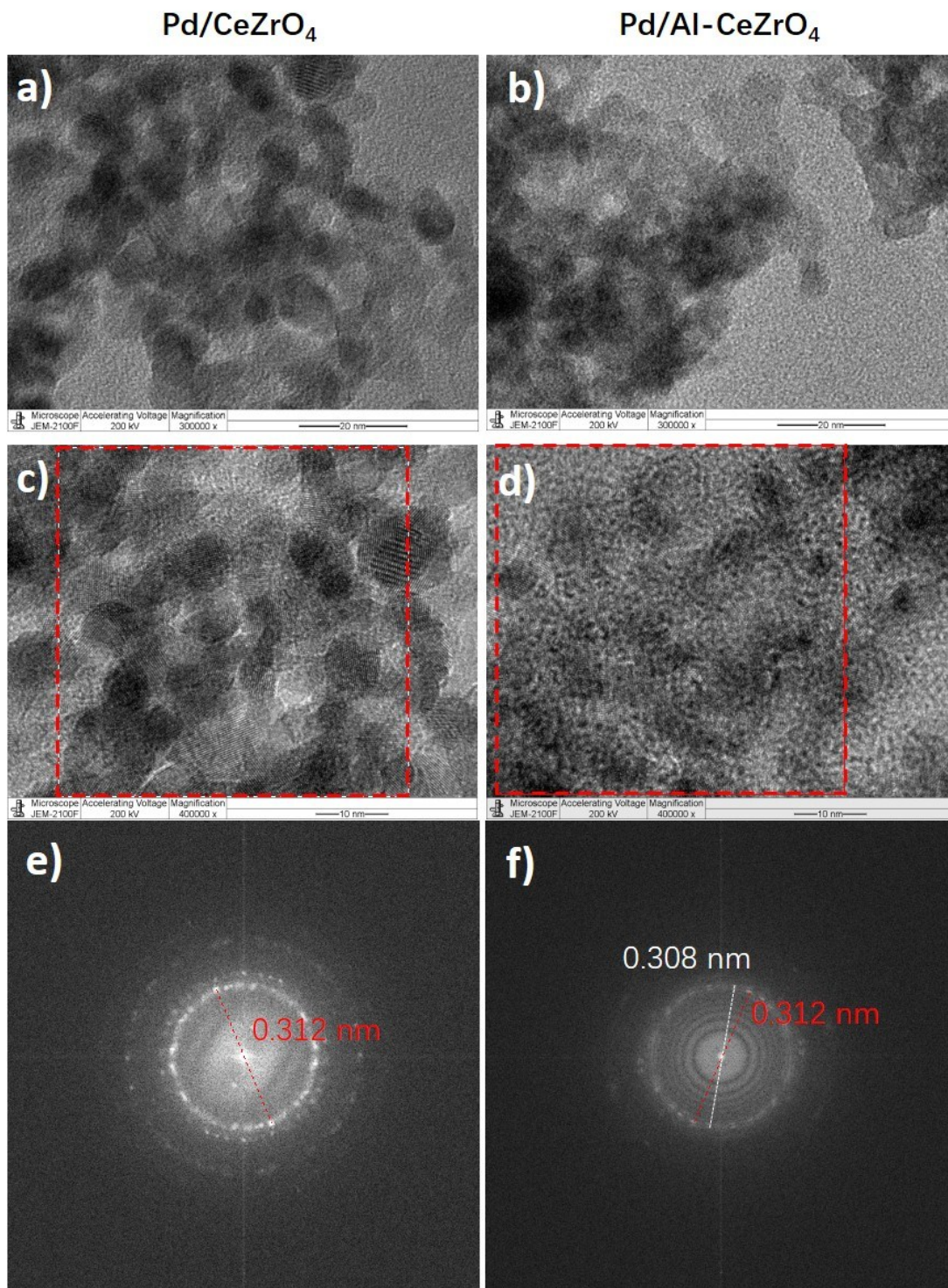0.312 nm

f)

0.308 nm

0.312 nm

Figure S3 a~d) HRTEM images and e~f) Measurement of lattice fringe spacing based on the HRTEM images of the as prepared Pd catalysts.
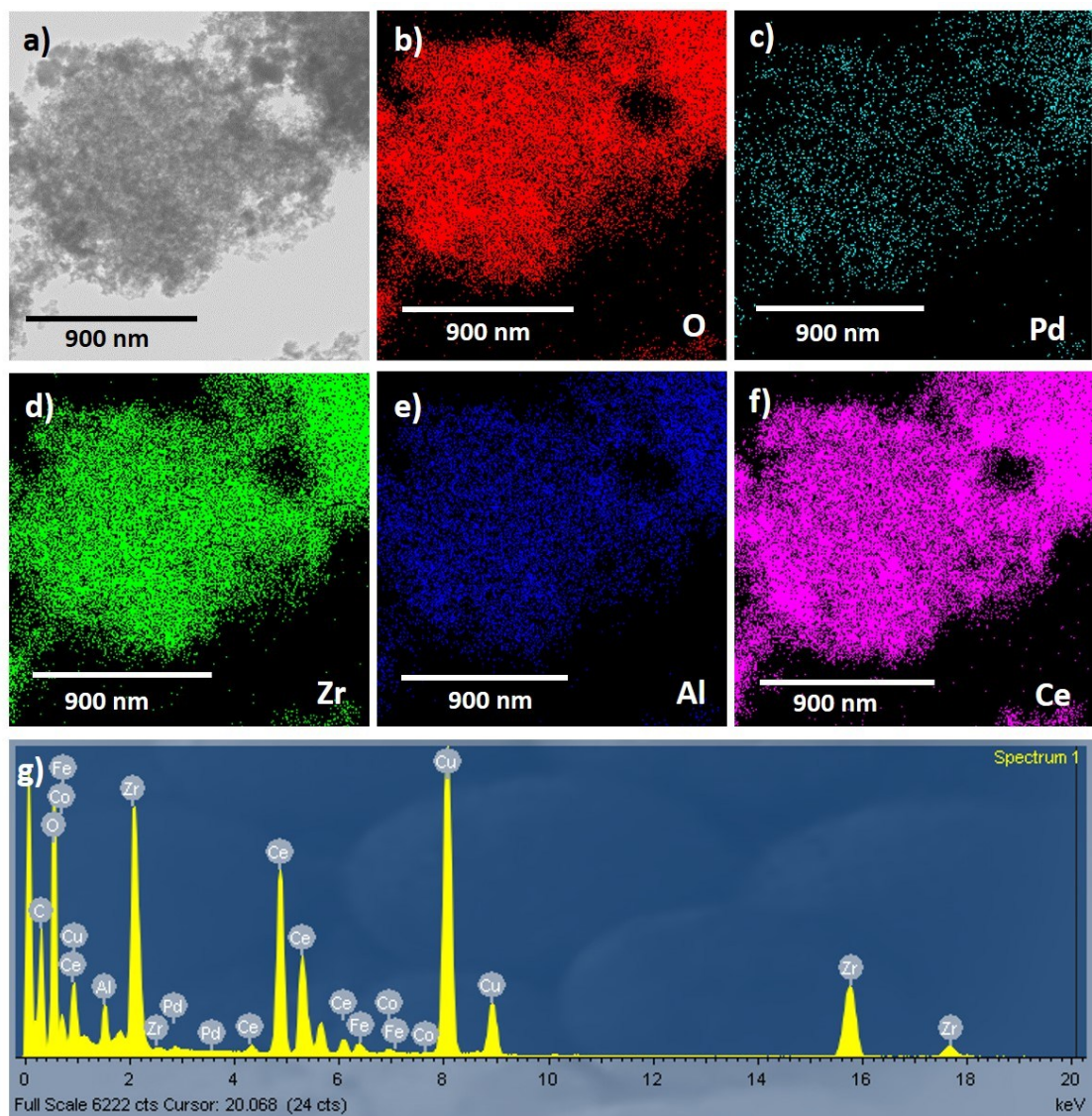
Figure S4 a~g) Element maps and EDX spectroscopy from a randomly region of Pd/Al-CeZrO$_4$ catalyst.

2.4 XPS analysis

Table S1 listed the binding energy (B.E.) and integral area (IA) of each peak in the Ce 3d XPS spectra of as-prepared Pd/CeZrO$_4$ and Pd/Al-CeZrO$_4$ catalysts.

Table S1 Peak information of Ce 3d XPS spectra of as-prepared Pd catalysts

Sample		v	v′	v″	v‴	u	u′	u″	u‴
Pd/CeZrO$_4$	B.E., eV	882.3	884.3	888.8	898.2	900.8	902.3	907.6	916.6
	I.A, a.u.	20144	12728	8962	21254	13437	3466	7604	17753
Pd/Al-CeZrO$_4$	B.E., eV	882.1	884.2	888.5	898.1	900.5	902.6	907.4	916.5
	I.A, a.u.	15443	19522	8809	17107	15024	6943	6648	16451