

Electronic supplementary information (ESI) for

# DRIFTS study of the role of alkaline earths in promoting the catalytic activity of HC and NO<sub>x</sub> conversion over Pd-only three-way catalyst

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## SI text

### Experimental details

**NO<sub>x</sub> storage ability.** Temperature programmed desorption of NO<sub>x</sub> (NO<sub>x</sub>-TPD-MS) was conducted in a quartz fixed-bed micro-reactor equipped with mass spectrometer apparatus (Hiden QIC-20). Individual m/z profiles were determined from their known relative contribution to the fragments m/z = 30 (NO<sup>+</sup>) amu. Prior to the NO<sub>x</sub> desorption experiments, the catalysts were pretreated at 450 °C for 0.5 h under 20 % O<sub>2</sub>/Ar flow gas and were subsequently exposed to the reaction gas (0.1 % NO-0.03 % NO<sub>2</sub>-0.745 % O<sub>2</sub>, Ar balance) at 100 °C for 0.5 h. Afterward, the samples were heated from 100 up to 550 °C at a heating rate of 10 °C/min using purified Ar as the carrier gas.

**UV Raman.** Raman spectra were recorded on a UV-HR Raman spectrograph with a He-Gd laser of 325 nm excitation wavelength. It consisted of two accumulations of 30 s with a resolution of 4 cm<sup>-1</sup>. The samples were in powder form to eliminate diffusion problems.

**XPS.** Samples were measured using a Thermo K-Alpha equipped with Al K $\alpha$  radiation (1486.6 eV), operating at 84 W and with energy pass of 40 eV. Binding energies were calibrated using C 1s hydrocarbon peak at 284.6 eV.

## SI Figs and Table

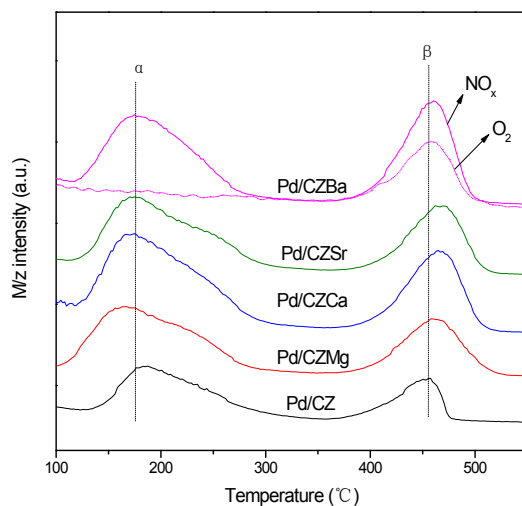


Fig. S1. The  $\text{NO}_x$ -TPD-MS profiles of the indicated catalysts.

Notes: Desorption profiles of  $\text{NO}_x$  over the indicated catalysts are displayed in Fig. S1. There are two peaks ( $\alpha$  and  $\beta$ ) assigned to  $\text{NO}_x$  desorption can be observed. The desorption peak  $\alpha$  in the temperature range of 100-300 °C is correlated to the decomposition of the less stable adsorbed species proceeds via the evolution of  $\text{NO}$ ,  $\text{NO}_2$ , and to a lesser extent  $\text{N}_2\text{O}$  and  $\text{N}_2$ <sup>1</sup>. However, the desorption peak of  $\text{O}_2$  could be observed in the temperature range of 350-500 °C, indicating that the desorption peak  $\beta$  at about 460 °C can be attributed to the decomposition of stable nitrates as  $\text{NO} + \text{O}_2$ <sup>2</sup>. Compared with Pd/CZ catalyst, the intensity of these desorption peaks over the alkaline earth doped catalysts obviously increases. Moreover, the peak  $\beta$  also shifts to higher temperature, meaning that the stability of the adsorbed species is promoted. These results indicate that the presence of alkaline earth obviously improves the  $\text{NO}_x$  storage ability of Pd/CZ catalyst, especially for Pd/CZBa catalyst.

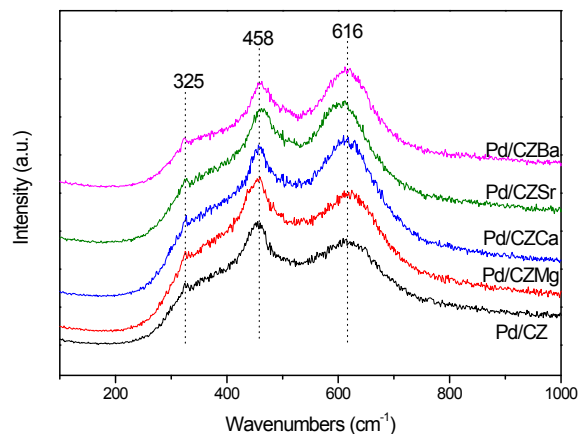


Fig. S2. The UV-Raman spectra of the indicated catalysts.

Notes: From Fig. S2, it can be seen that all the catalysts show three Raman peaks in the range of 200 to 800  $\text{cm}^{-1}$ . The appearance of weak band at about 325  $\text{cm}^{-1}$  is attributed to the presence of  $t''$  phase, where cation sublattice remains cubic structure while oxygen atoms undergo a tetragonal distortion. The band at 454  $\text{cm}^{-1}$  can be associated with the  $F_{2g}$  symmetry vibration of the fluorite-type lattice, and the band at 616  $\text{cm}^{-1}$  can be linked to oxygen vacancies in the  $\text{CeO}_2$  lattice and attributed to the presence of lattice defects<sup>3, 4</sup>. Moreover, the intensity ratio ( $I_{616}/I_{454}$ ) between the peaks at 616 and 454  $\text{cm}^{-1}$  can reflect the oxygen vacancy concentration<sup>5</sup>. The intensity of the bands at 616  $\text{cm}^{-1}$  increases with the doping of alkaline earth, and the intensity ratio (as shown in Table S1) follows the sequence of  $\text{Pd/CZBa} > \text{Pd/CZSr} \approx \text{Pd/CZCa} > \text{Pd/CZMg} > \text{Pd/CZ}$ . This result indicates that the introduction of alkaline earth is favorable to the formation of oxygen vacancy, which is the main factor that influences the oxygen mobility and results in the high dynamic oxygen storage capacity<sup>6</sup>.

Table S1. Surface elemental composition, surface atom ratios in catalysts and the intensity ratio ( $I_{616}/I_{454}$ ) derived from XPS and UV-Raman results.

Sample	Surface composition (at. %)					Ce/Zr	Ce <sup>3+</sup> 3d <sub>5/2</sub> in Ce (%)	I <sub>616</sub> /I <sub>454</sub>
	Ce 3d	Zr 3d	M	Pd 3d	O 1s			
Pd/CZ	21.4	7.82	0	0.52	70.3	2.74	16.9	0.78
Pd/CZMg	18.3	6.45	7.64	0.31	67.3	2.84	17.0	0.85
Pd/CZCa	19.8	6.68	2.18	0.10	71.2	2.96	18.6	0.99
Pd/CZSr	21.1	7.24	1.14	0.28	70.3	2.91	19.4	1.01
Pd/CZBa	21.4	7.38	0.67	0.21	70.4	2.90	19.6	1.09

Notes: The surface elemental contents as well as the relative concentrations of Ce<sup>3+</sup> over the catalysts are presented in Table S1. From Table S1, it can be seen that the surface atom ratios of Ce/Zr in the modified catalysts are obviously higher than that of Pd/CZ, indicating that the doped alkaline earth enters into CeO<sub>2</sub> lattice and part of Zr atoms of the surface layer is replaced by alkaline earth metal atoms. Moreover, the surface content of Mg for Pd/CZMg catalyst is apparently higher than the theoretical value (3.70 at. %), which means that surface enrichment phenomena of Mg exists in Pd/CZMg, which may be the possible reason that leads to lower dispersity of Pd species for Pd/CZMg. Whereas the surface content of Ca, Sr and Ba is lower than the theoretical value (Ca 2.70 at. %, Sr 1.51 at. % and Ba 1.03 at. %), suggesting that more doped Ca, Sr and Ba atoms could enter into the CeO<sub>2</sub> lattice. These results are in accordance with the previous XRD results<sup>7</sup> that the doped alkaline earth with proper quantity could enter into CeO<sub>2</sub> lattice and form homogenous Ce-Zr-M solid solution with higher thermal stability. However, we have not obtained an accuracy formation about the surface elemental content of Pd due to

two influencing factor. One is the low loading of Pd metal (1.0 wt. %) which approaches the detection limit of the XPS technique, and the other is the overlapping of Pd 3d peak with the strong Zr 3p peak<sup>8</sup>. In addition, the relative concentration of Ce<sup>3+</sup> 3d<sub>5/2</sub> in total Ce increases with the introduction of alkaline earth, especially for the Pd/CZSr and Pd/CZBa catalysts, indicating that the modification of alkaline earth is favorable to the transfer from Ce<sup>4+</sup> to Ce<sup>3+</sup> possibly due to the formation of homogenous Ce-Zr-M solid solution. It is generally recognized that the presence of Ce<sup>3+</sup> is associated with the formation of oxygen vacancies due to the equilibrium of electric charge<sup>9</sup>, which is consisted with the Raman results.

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