Supporting Information for

Real-time Observation of the Effect of Oxygen Storage Material on Pd-based Three-Way Catalysts under Ideal Automobile Exhaust Condition: An *Operando* Study

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Figure S1 | XRD patterns of 1 wt% $\rm Pd/Al_2O_3$ and 1 wt% $\rm Pd/CeO_2$

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Figure S2 | Pd K-edge XANES spectra of 1 wt% Pd/Al₂O₃ during *operando* XAS measurement. (a) pretreatment, (b) 0:00 - 0:25, (c) 0:25 - 1:00, (d) 1:00 - 1:25, (e) 1:25 - 2:10, (f) 2:10 - 3:00, (g) 3:00 - 3:20, (h) 3:20 - 3:35, (i) 3:35 - 4:00, (j) 4:00 - 4:10, and (k) 4:10 - 4:20.



Figure S3 | Pd oxidation state estimated by linear combination of a series of XANES spectra with Pd metal and PdO standard samples during operando XAS measurement of Pd/Al_2O_3 .



Figure S4 | Q-Mass spectra during three-way catalysis over 1 wt% Pd/Al₂O₃ and the O₂ concentration indicator (λ). The mass number are assigned as H₂ (m/z=2), N₂ or CO (m/z=28), NO (m/z=30), O₂ (m/z=32), CO₂ or N₂O (m/z=44).



Figure S5 | Pd K-edge Fourier transform of EXAFS spectra of 1 wt% Pd/Al₂O₃ during operando XAS measurement. (i) Before/after pretreatment, (ii) After pretreatment and at 0:25, (iii) At 0:25 and 1:00, (iv) At 1:00 and 2:10, (v) At 2:10 and 3:00, (vi) At 3:00 and 3:45, (vii) At 3:45 and 4:10, (viii) After pretreatment, at 2:10 and 3:40, and (ix) At 0:25, 3:00, and 4:10.



Figure S6 | Pd oxidation state estimated by linear combination of a series of XANES spectra with Pd metal and PdO standard samples during operando XAS measurement of Pd/CeO₂.



Figure S7 | Q-Mass spectra during three-way catalysis over 1 wt% Pd/CeO₂ and the O₂ concentration indicator (λ). The mass number are assigned as H₂ (m/z=2), N₂ or CO (m/z=28), NO (m/z=30), O₂ (m/z=32), CO₂ or N₂O (m/z=44).



Figure S8 | Pd K-edge XANES spectra of 1 wt% Pd/CeO₂ during *operando* XAS measurement. (a) pretreatment, (b) 0:00 - 1:00, (c) 1:00 - 2:00, (d) 2:00 - 2:30, (e) 2:30 - 3:10, (f) 3:10 - 3:20, (g) 3:20 - 3:40, (h) 3:40 - 4:00, and (i) 4:00 - 4:25.



Figure S9 | Pd K-edge Fourier transform of EXAFS spectra of 1 wt% Pd/CeO₂ during operando XAS measurement. (a) Before/after pretreatment, (b) At 0:00 and 1:00, (c) At 1:00 and 2:00, (d) At 2:00 and 2:30, (e) At 2:30 and 3:05, (f) At 3:05 and 3:20, (g) At 3:20 and 3:45, (h) At 3:45 and 4:10, and (i) At 4:10 and 4:20.



Figure S10 | Difference of total carbon balance to expected value (1750 ppm). Note: The cause of excess amount of carbon species in the first lean condition is assumed to be small amount of carbon species such as carbonate on the surface of the catalyst.