Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Supporting Information

# The role of platinum on the $NO_x$ storage and desorption behavior of ceria: An online FT-IR study combined with *in situ* Raman and UV-Vis spectroscopy

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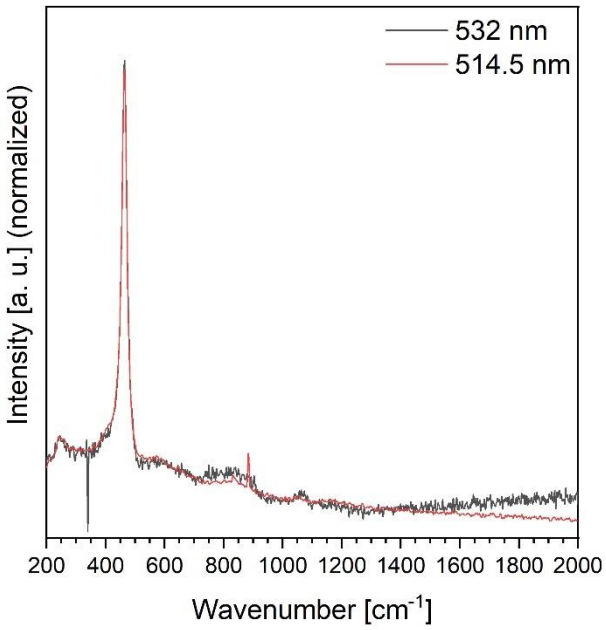


**Fig. S1** Raman spectra of reductively pretreated $Pt/CeO_2$ at 514.5 and 532 nm laser excitation.

**Table S1** Surface composition of $Pt/CeO_2$ samples after respective treatment determined by XPS analysis.

| sample | Pt [at%] | C [at%] | O [at%] | Ce [at%] | O/Ce |
|---|---|---|---|---|---|
| $Pt/CeO_2$ as synthesized | 0.24 | 14.3 | 56.6 | 28.9 | 1.96 |
| $Pt/CeO_2$ ox. | 0.17 | 7.2 | 61.3 | 31.3 | 1.96 |
| $Pt/CeO_2$ red. | 0.17 | 13.0 | 55.7 | 31.1 | 1.79 |

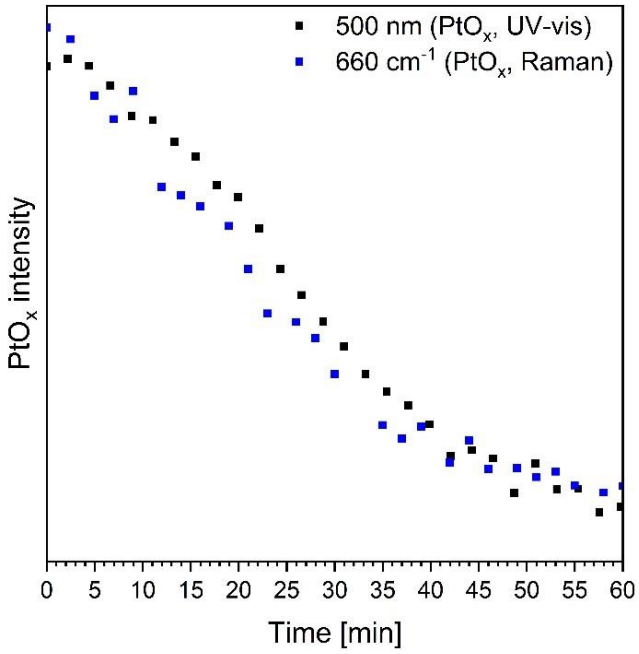


**Fig. S2** Temporal behavior of $PtO_x$ signals in UV-Vis (500 nm) and Raman spectra (660 $cm^{-1}$) during $NO_x$ storage in oxidatively pretreated $Pt/CeO_2$ at 30°C.

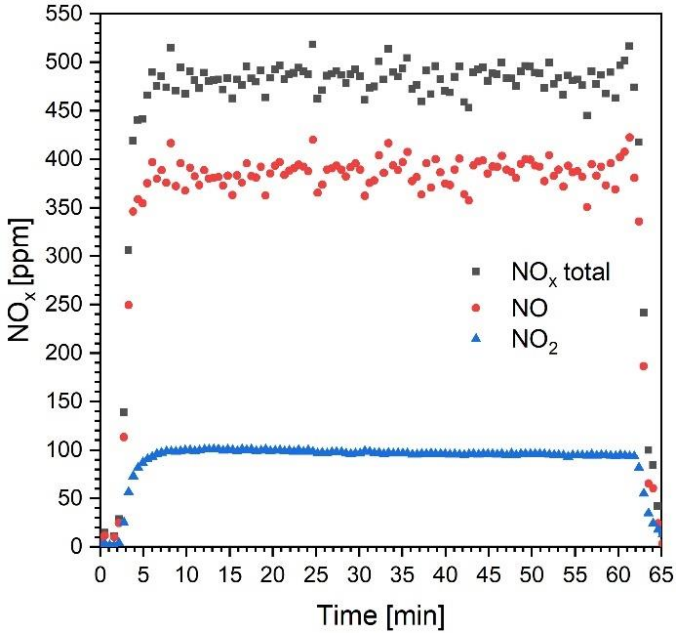


**Fig. S3** $NO_x$ breakthrough of the empty cell measured at 30°C by gas phase FT-IR spectroscopy.

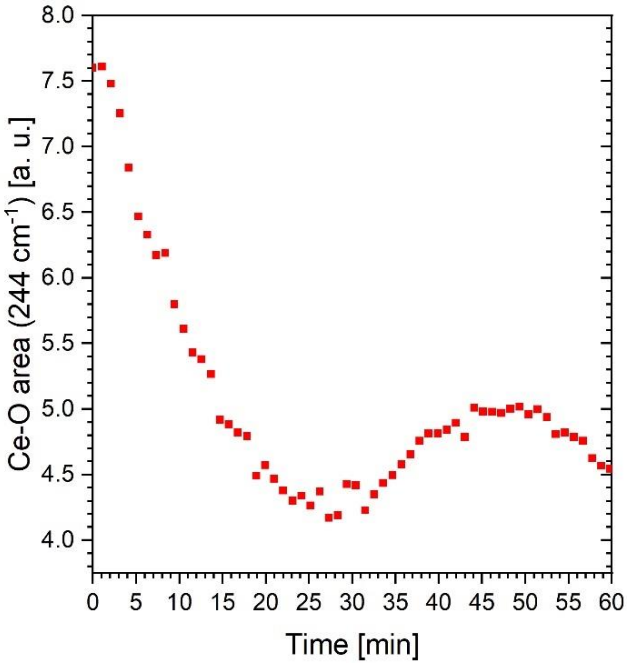


**Fig. S4** Temporal behavior of Ce-O area during $NO_x$ storage with oxygen at 30°C in oxidatively pretreated ceria.

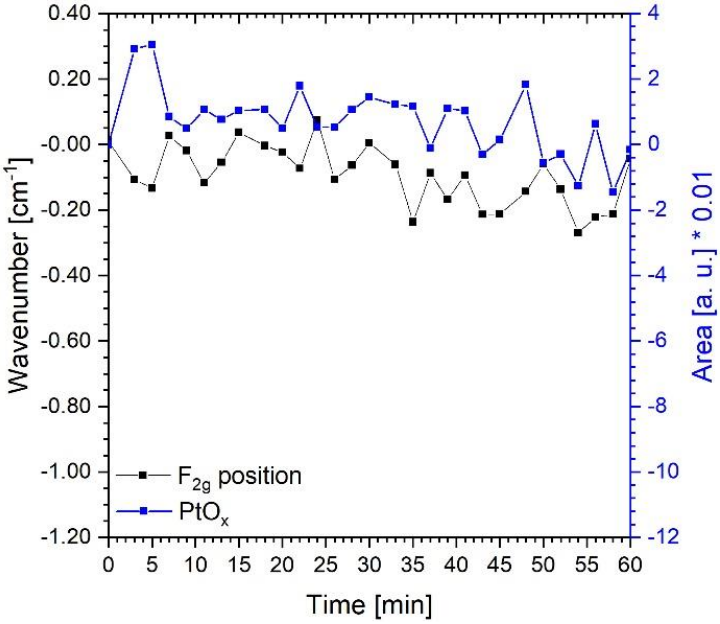


**Fig. S5** Temporal behavior of Pt-O and $F_{2g}$ position during $NO_x$ storage without oxygen at 30°C in oxidatively pretreated $Pt/CeO_2$.

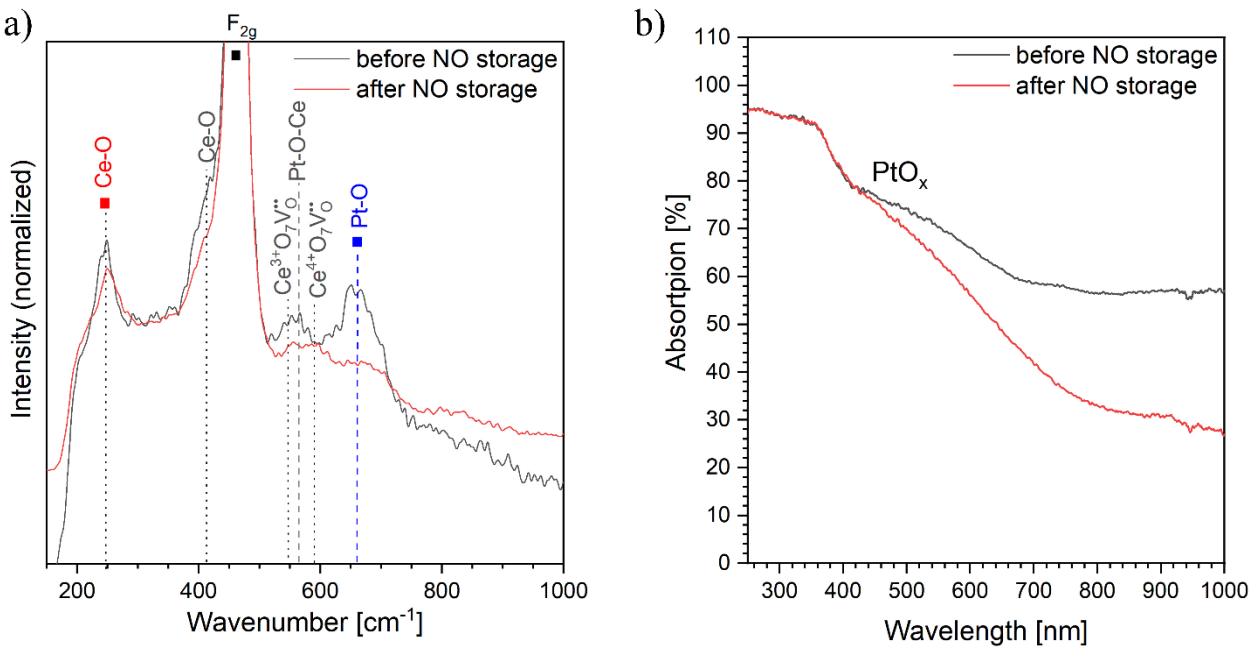


**Fig. S6** a) Raman spectra within the range 150-1000 $cm^{-1}$ and b) UV-vis spectra before (black) and after (red) $NO_x$ storage at 30°C with oxygen in oxidatively pretreated $Pt/CeO_2$.

**Table S2** Percentage of stored $NO_x$ released and $NO/NO_2$ ratio of desorbed $NO_x$ at the respective temperature ranges as determined by FT-IR gas-phase analysis.

| sample | 30-100°C | | 100-200°C | | 200-300°C | | 300-400°C | | 400-500°C | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $NO_x$ [%] | $NO/NO_2$ | $NO_x$ [%] | $NO/NO_2$ | $NO_x$ [%] | $NO/NO_2$ | $NO_x$ [%] | $NO/NO_2$ | $NO_x$ [%] | $NO/NO_2$ | $NO_x$ total [%] |
| $CeO_2$ ox. | 2.4 | 3.3 | 1.3 | 0.4 | 17.1 | 0.1 | 48.9 | 0.2 | 20.9 | 1.3 | 90.6 |
| $Pt/CeO_2$ ox. | 9.3 | 3.4 | 18.5 | 0.2 | 28.3 | 0 | 21.6 | 0.3 | 11.5 | 1.2 | 89.2 |
| $CeO_2$ red. | 31.5 | 3.0 | 26.6 | 2.1 | 3.0 | 0.6 | 10.5 | 0.4 | 14.3 | 1.4 | 85.9 |
| $Pt/CeO_2$ red. | 39.8 | 2.9 | 15.7 | 2.5 | 1.8 | 0 | 13.1 | 0.4 | 10.8 | 1.5 | 81.2 |