Supplementary Material

Doped barium cerate perovskite catalysts for simultaneous NO_x storage and soot oxidation

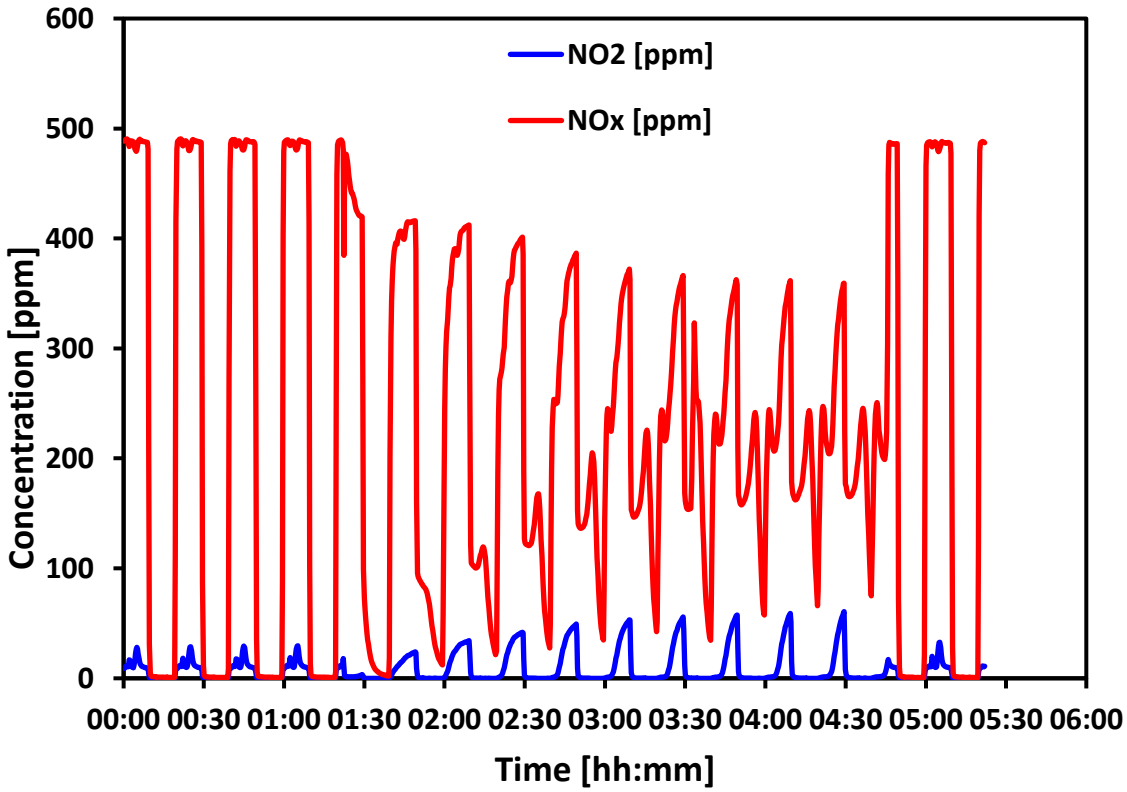

Fig. S1 NO_x concentration versus time for $BaCe_{0.8}Zr_{0.1}Co_{0.1}O_3$ at 380°C for consecutive NO_x storage/reduction cycles. The samples were pretreated at 400°C for 0.5 h under a nitrogen flow of 500 mL min^{-1}. During the storage cycle (10 min) the gas composition was 500 ppm NO, 10 vol. % O_2, 5 vol. % H_2O balance nitrogen. For the reduction cycle (10 min) the gas composition was 10 vol. % H_2, 5 vol. % H_2O balance nitrogen. The gas flow for both cycles was 500 mL min^{-1}. The effluent gas was analyzed using an MKS Multi Gas 2030 FTIR analyzer.

The first 4 storage/reduction cycles in Fig. S1 show the NO_2 and NO_x concentration as a function of time. These data were generated by allowing the gas feed to be directed to the MKS FTIR analyzer via a by-pass valve. The gases in these cycles did not interact with the catalyst. The data show that the NO_x concentration was ~500 ppm. The presence of a small amount of NO_2 was due to the oxidation of NO in the feed gas by oxygen, also present in the feed gas. The gas feed was then introduced to the catalyst and the resulting NO_2 and NO_x concentrations for storage/reduction cycles are shown in the subsequent 10 cycles. The data show a significant drop in NO_x concentration during the storage cycle and is ascribed to storage on the catalyst. The data also reveal an NO_2 concentration of ~50 ppm during the storage

cycles. This suggests that the catalyst is producing NO_2 as well as storing NO_x. The storage capacity of the catalyst was calculated on the 10th storage cycle by integrating the area under the curve. For the last three storage/reduction cycles the feed gas was again fed directly to the MKS FTIR analyzer via the by-pass valve. The data show that the concentration of NO_x was the same as at the beginning of the experiment.

Table S1 through S3 show the chemical breakdown of the XPS spectra for each key atom present.

Table S1: The chemical breakdown of the barium spectra, by sample.

Peak Designation	$BaCeO_{3-*}$ [SSS]	$BaCeO_{3-*}$ [SSS+HEBM]	$BaCe_{0.8}Zr_{0.2}O_{3-*}$ [SSS]	$BaCe_{0.8}Zr_{0.2}O_{3-*}$ [SSS+HEBM]	$BaCe_{0.8}Zr_{0.1}Co_{0.1}O_{3-*}$ [SSS]	$BaCe_{0.8}Zr_{0.1}Co_{0.1}O_{3-*}$ [SSS+HEBM]
a	10.15%	4.29%	6.12%	9.71%	7.53%	13.05%
a’	6.81%	2.88%	4.11%	6.15%	5.05%	8.75%
b	9.38%	17.63%	13.91%	14.47%	13.23%	10.67%
b’	6.29%	11.82%	9.33%	9.70%	6.87%	7.15%
c	10.03%	16.61%	9.67%	14.16%	10.50%	16.06%
c’	6.72%	11.14%	6.48%	9.49%	7.04%	10.77%
d	4.41%	3.86%	7.81%	6.96%	5.74%	6.65%
e	27.21%	17.88%	26.42%	16.28%	25.71%	7.80%
f	18.97%	13.88%	16.15%	12.49%	16.22%	18.74%
g	0.03%	0.02%	0.00%	0.23%	0.10%	0.37%

Table S2: The chemical breakdown of the cerium spectra, by sample.

Peak Designation	$BaCeO_{3-*}$ [SSS]	$BaCeO_{3-*}$ [SSS+HEBM]	$BaCe_{0.8}Zr_{0.2}O_{3-*}$ [SSS]	$BaCe_{0.8}Zr_{0.2}O_{3-*}$ [SSS+HEBM]	$BaCe_{0.8}Zr_{0.1}Co_{0.1}O_{3-*}$ [SSS]	$BaCe_{0.8}Zr_{0.1}Co_{0.1}O_{3-*}$ [SSS+HEBM]
s	4.66%	0.12%	1.79%	0.00%	0.00%	0.41%
t	28.64%	20.87%	30.97%	18.16%	32.09%	15.52%
u	7.53%	16.70%	4.80%	16.47%	4.33%	20.05%
v	37.63%	47.58%	34.29%	47.20%	35.49%	48.60%
w	0.40%	0.18%	0.09%	0.15%	0.07%	0.08%
x	5.86%	3.22%	7.19%	4.17%	7.56%	2.84%
y	3.74%	2.82%	7.30%	4.21%	7.85%	4.26%
z	11.55%	8.52%	13.57%	9.63%	12.61%	8.24%

Table S3: The chemical breakdown of the oxygen spectra, by sample.

Peak Designation	$BaCeO_{3-*}$ [SSS]	$BaCeO_{3-*}$ [SSS+HEBM]	$BaCe_{0.8}Zr_{0.2}O_{3-*}$ [SSS]	$BaCe_{0.8}Zr_{0.2}O_{3-*}$ [SSS+HEBM]	$BaCe_{0.8}Zr_{0.1}Co_{0.1}O_{3-*}$ [SSS]	$BaCe_{0.8}Zr_{0.1}Co_{0.1}O_{3-*}$ [SSS+HEBM]
Lattice oxide	5.20%	13.80%	10.43%	9.39%	18.69%	12.73%
Hydroxide, Defect oxide	20.06%	31.53%	22.84%	38.23%	26.62%	33.22%
Organics	16.02%	1.19%	6.76%	0.00%	0.00%	0.00%
Ba Shake-up 1	2.60%	6.90%	5.21%	4.69%	9.34%	6.37%
Ba Shake-up 2	10.03%	15.76%	11.42%	19.11%	13.31%	16.61%
Ce Shake-down 1	1.20%	3.18%	2.40%	2.16%	4.30%	2.93%
Ce Shake-down 2	6.02%	9.46%	6.86%	11.47%	7.99%	9.97%
O to f-orbital interact. 1	1.56%	4.14%	3.13%	2.82%	5.61%	3.82%
O to f-orbital interact. 2	6.05%	9.47%	6.86%	11.48%	7.99%	9.97%
Other f-orbital interact.	13.96%	4.58%	7.33%	0.66%	6.14%	4.37%
Distinct O to f-orbital 1	2.35%	0.00%	2.03%	0.00%	0.00%	0.00%
Distinct O to f-orbital 2	2.47%	0.00%	1.06%	0.00%	0.00%	0.00%
Secondary lattice oxide	12.52%	0.00%	13.66%	0.00%	0.00%	0.00%