catalysts

Supporting Information: Modifying the Surface Structure of Perovskite-Based Catalysts by Nanoparticle Exsolution

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1. Calculation and use of pO_2 partial pressure

The oxygen partial pressure was calculated from the chemical equilibrium of the hydrogen oxidation reaction

$$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O, \quad (1)$$

with the equilibrium constant

$$K = \frac{p(H_2O)}{\sqrt{p(O_2)}\,pH_2} = \exp\left(-\frac{\Delta_R G}{RT}\right). \quad (2)$$

There $\Delta_R G^0$ is the Gibbs free energy of reaction 1, when all species have standard pressure of 1 atm, R and T are gas constant and temperature, respectively. The oxygen partial pressure is therefore calculated by the relation

$$p(O_2) = \frac{p(H_2O)^2}{p(H_2)^2}\exp\left(\frac{\Delta_R G}{RT}\right). \quad (3)$$

The (temperature dependent) value of $\Delta_R G^0$ is available at the NIST Chemistry WebBook.

For the reduction conditions used in this study (H_2:H_2O = 32:1, 923 K), the corresponding partial pressure is $5.3 \cdot 10^{-26}$ bar.

2. Signal shift in XRD patterns when changing from oxidative to reductive conditions

After switching from oxidative to reductive atmosphere, there is a 2θ-shift to smaller angles with increasing temperature. This is due to an increase of the lattice parameters, which is again the result of two combined effects. On one hand, thermal expansion increases the lattice parameters. On the other hand, there is a property that has been called chemical expansivity. Due to the introduction of Ca^{2+} there is an inherent charge imbalance in the perovskite structure, giving rise to a complex defect chemistry. To re-establish charge balance, either oxygen vacancies are formed or Fe partly changes its valance by a conversion from Fe^{3+} to Fe^{4+}. After oxidation, the latter is the more prominent mechanism. Upon exposure to the reductive atmosphere, with increasing temperature more and more oxygen vacancies are formed and at the same time Fe^{4+} is reduced to Fe^{3+} or even Fe^{2+}. As the ionic radius of the Fe species increases with decreasing valence, this also results in larger lattice parameters.

3. XPS analysis of nanoparticle exsolution from $Nd_{0.6}Ca_{0.4}FeO_3$

Figure S1 displays the results from XPS measurements prior (pristine sample) and after reductive treatment. For the latter, the sample used for the *in situ* XRD measurements, was

transferred to the UHV system (with a short exposure to air). The XPS spectra were collected with Al Kα radiation, the energy calibration was done using adventitious carbon, fixed at 284.8 eV.

XPS analysis of pristine $Nd_{0.6}Ca_{0.4}FeO_3$ revealed main signals at 709.7 eV and 711.0 eV for Fe $2p_{3/2}$, figure S1. They could be assigned to Fe^{2+} and Fe^{3+} respectively. The most interesting change after reduction was a signal appearing at 707.0 eV that can be attributed to metallic Fe from nanoparticle exsolution. This agrees with the results from *in situ* XRD and SEM analysis.

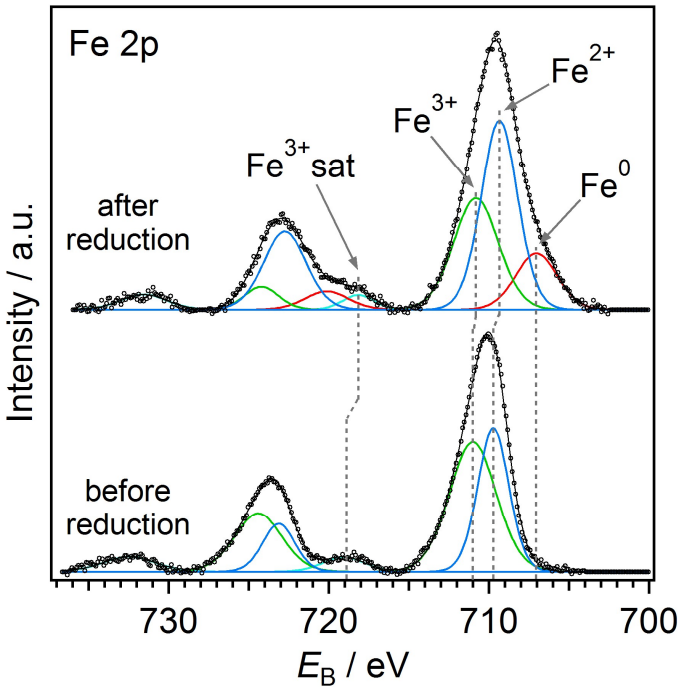

Figure S1. XPS spectra of $Nd_{0.6}Ca_{0.4}FeO_3$ prior and after reductive treatment. Fe 2p spectra clearly display the formation of metallic Fe at 707.0 eV upon nanoparticle exsolution.

4. In situ NAP-XPS analysis of cobalt nanoparticle exsolution from $Nd_{0.6}Ca_{0.4}Fe_{0.9}Co_{0.1}O_3$

For the experiments, the same parameters (H_2/H_2O ratio) as for the TEM measurements were chosen. The total pressure during *in situ* NAP-XPS experiments was ~1 mbar.

Unfortunately, when using a lab-based NAP-XPS system with Al Kα radiation an overlap between the cobalt 2p signal and the Nd MNN Auger signal is present. This makes peak fitting and data interpretation rather complex. Nevertheless, we managed to detect the formation of the metallic cobalt phase with a signal at ~776 eV, which corresponds to cobalt nanoparticle exsolution. For better spectra and also a more accurate XPS analysis (qualitative and quantitative) synchrotron based measurements would be needed.

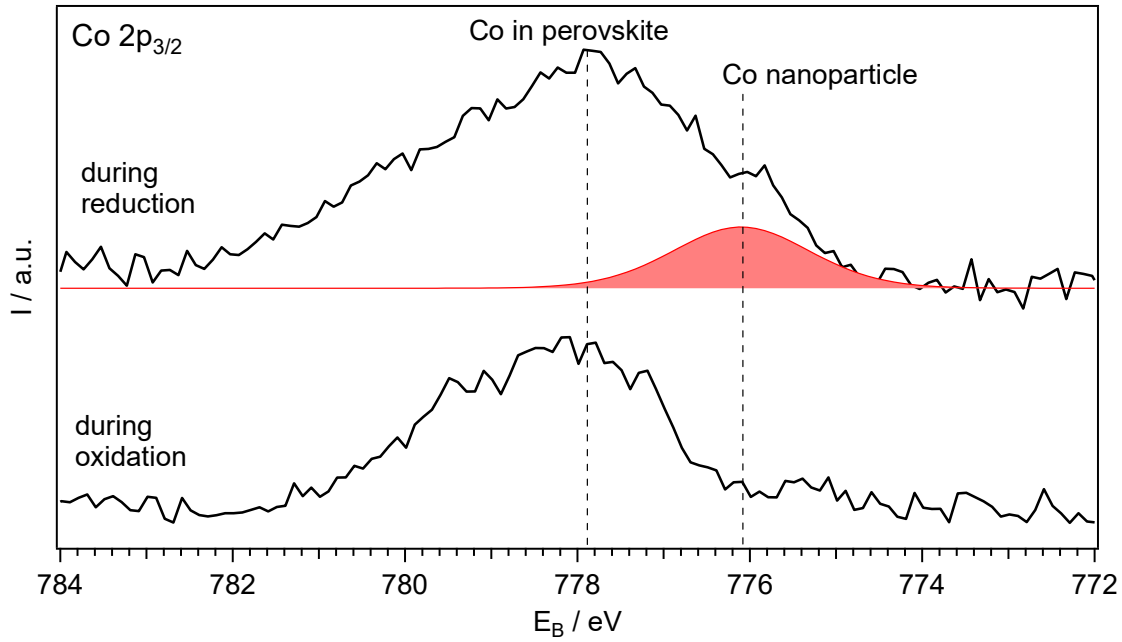

Figure S2. Co 2p XPS spectra of $Nd_{0.6}Ca_{0.4}Fe_{0.9}Co_{0.1}O_3$ recorded during oxidation (in ~1 mbar O_2 at 473 K) and during reduction in H_2/H_2O at 873 K. In reducing atmosphere the appearance of a signal at ~776 eV could be observed, which corresponds to metallic cobalt from the nanoparticle exsolution.

5. DFT calculations

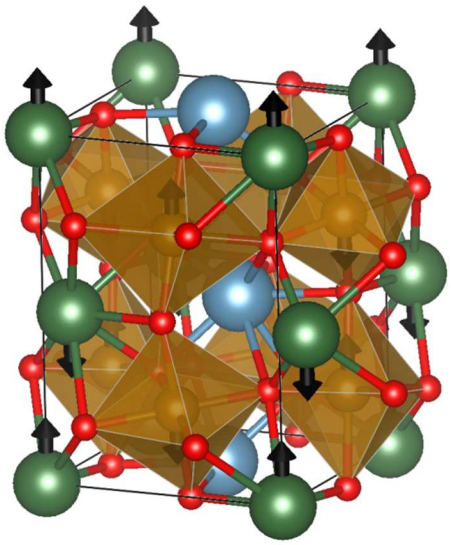

Figure S3. DFT structure of $Nd_{0.5}Ca_{0.5}FeO_3$ in an orthorhombic cell after optimization of the atomic positions. Atom colors: Nd – green, Ca – blue, Fe – brown, O – red. Distorted Fe-O-octahedra are also shown in brown. The black arrows indicate the relative orientation of spins of the Nd and Fe sublattice respectively.