

NEXAFS studies of N₂O conversion on reduced ceria surface

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Motivation

N₂O together with other nitrogen oxide species (NO, NO₂) is formed in the engine and also in the catalytic converter by the reaction of N₂ with adsorbed oxygen atoms. The destruction of these gases (DeNOx process) via reduction of NO_x to N₂ is of great significance due to their environment and health impact. Especially for nitrous oxide (N₂O) has been considered as the single most important ozone-depleting substance emitted and is expected to remain the largest throughout the 21st century. Specifically, NO and NO₂ have to be firstly converted into N₂O characterized by the high inertness, and then N₂O further liberates oxygen to finally generate environmentally benign N₂, where the latter is the rate determining step of DeNOx process. Reducible oxides, such as TiO₂, CeO₂ and Fe₂O₃, have shown the reactivity to convert N₂O to N₂ presumably at oxygen vacancy sites.

In this study, we monitor the conversion of N₂O to N₂ over the model catalyst oxide support, namely CeO₂(111), and ceria powders by using photoemission spectroscopy (PES) and near edge x-ray absorption fine structure spectroscopy (NEXAFS), which also enables us to determine the kinetics of this process.

Experimental

The NEXAFS and PES measurements were carried out with a synchrotron radiation source in our own UHV-apparatus on the HE-SGM beamline at BESSY II. CeO₂ single crystal was mounted on the sample holder with electron beam heating. Cooling was made with copper braids connected to the sample holder and a liquid helium cryostat. The CeO₂(111) single crystal surface was prepared by repeated cycles of sputtering with 1 keV Ar⁺ and annealing at 800 K for 15 min in an O₂ atmosphere of 1×10⁻⁵ mbar for forming a stoichiometric surface, or alternately without O₂ to create a reduced one. For temperature monitoring, a K-type thermocouple was directly attached on the sample surface. For preparation of ceria powders, the sample was annealed stepwise from 800 K to 1000 K for 30 min.

NEXAFS measurements only were performed after desired Ce oxidation state as judged by PES. Exposure to 50 Langmuir N₂O at sample temperatures at 120 K was achieved by backfilling the analysis chamber up to 2.6 × 10⁻⁷ mbar for 250 seconds. Typical base pressures during acquisition of NEXAFS and valence band (VB) spectra were 2 × 10⁻¹⁰ mbar. After N₂O exposure NEXAFS spectra were recorded at 120 K. Due to strong grounding effects, PES measurements cannot be performed at that low temperature. For that reason the temperature was elevated to a given set of temperatures. The VB data were gathered for evaluation of the ceria oxidation state.

NEXAFS/PES Endstation at HE-SGM Beamline



N₂O dosing experiments on CeO_{2-x}(111)

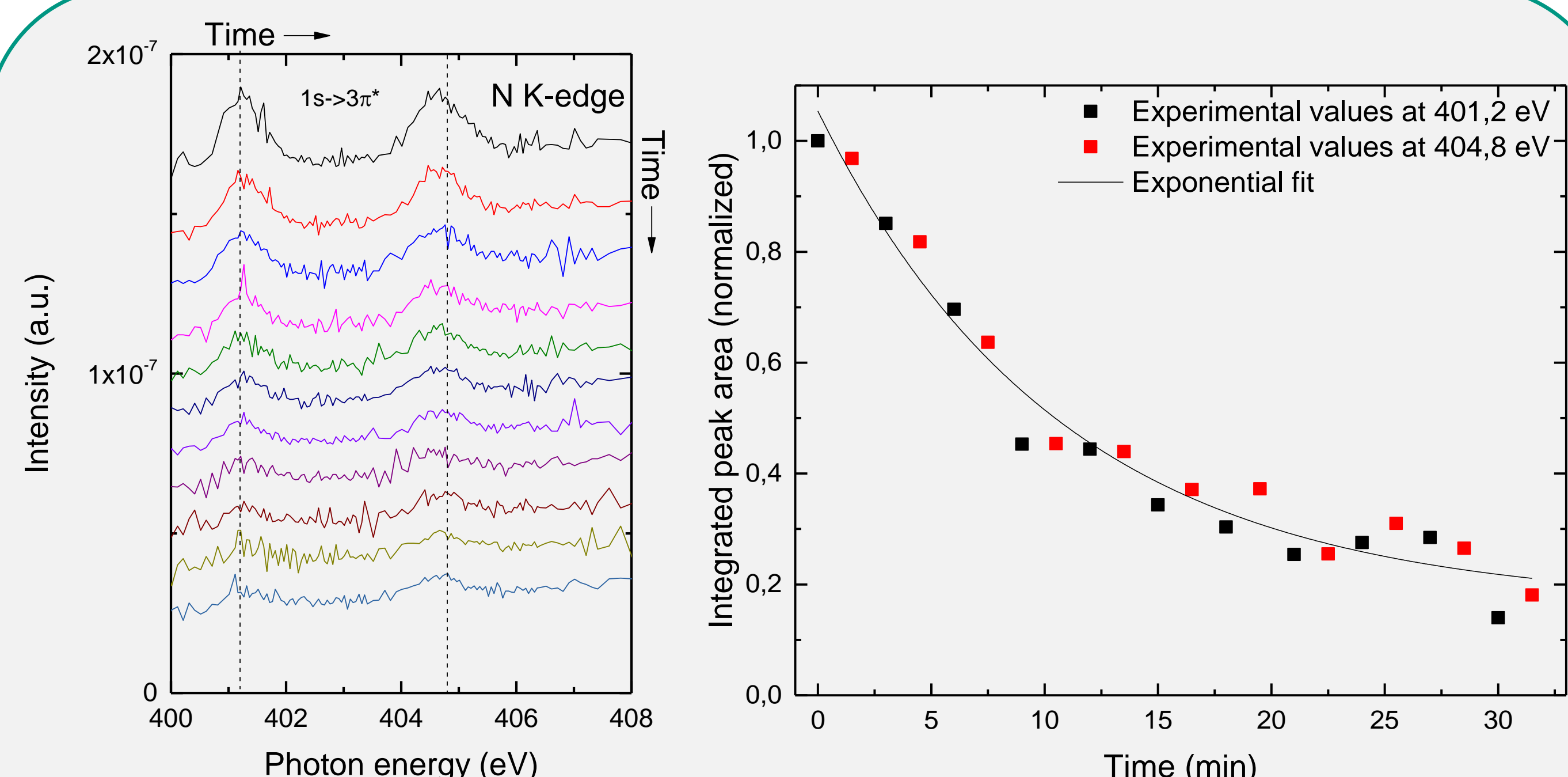


Figure 1: N K-edge NEXAFS spectra after dosing 50 Langmuir N₂O on a reduced CeO₂(111) surface (left) at 120 K are depicted. Two X-ray resonances at 401.2 eV (Ce-O-N-N) and 404.8 eV (Ce-O-N-N) were observed. The signal decay for both photon energies is given in a time dependent plot (right). The measuring time between both signals in one spectrum was estimated to 1.5 min, between stacked spectra it was set to 3 min. Kinetic predictions should be valid under the consideration that both signals have equal peak areas on a simultaneous time recording scale.

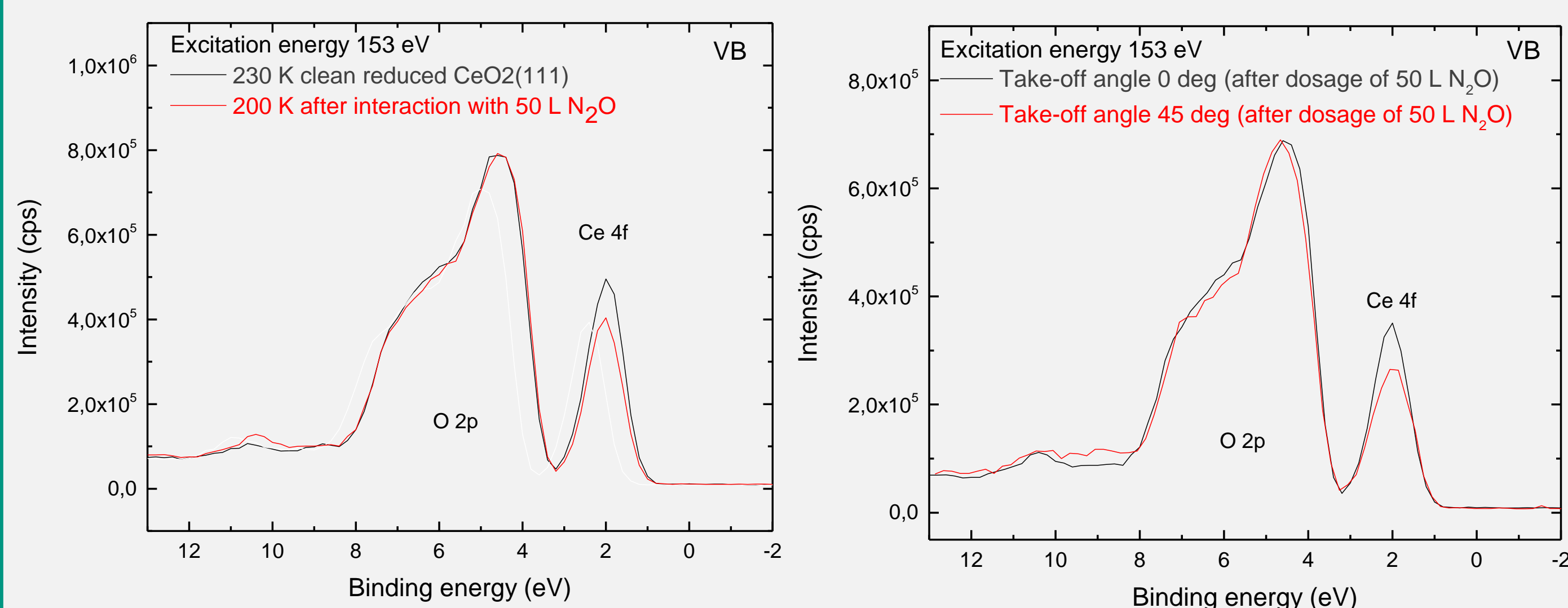


Figure 2: Valence band spectra on partial reduced ceria and photorelated ceria reoxidation by N₂O (left). Angle-resolved -PES measurements exhibit the oxidation process close to the surface (right).

N₂O dosing experiments on CeO_{2-x} powder

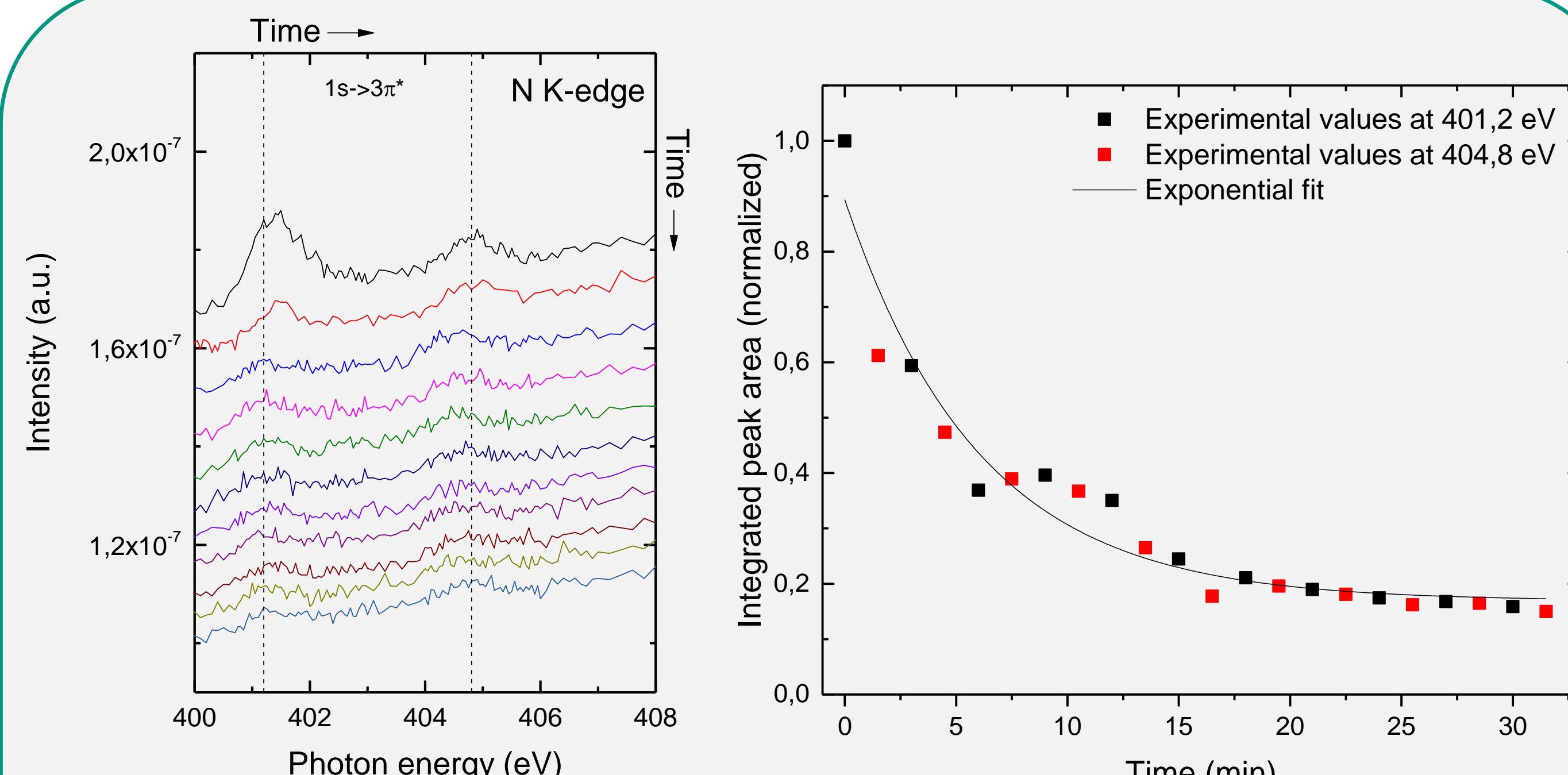


Figure 3: NEXAFS spectra were recorded in the N K-edge region after interaction with 50 L N₂O on reduced ceria powder at an ambient temperature of 120 K. The corresponding kinetic profile is illustrating the signal decay over time (right). Exponential fitting reveals a first order kinetic for N₂O splitting on reduced ceria.

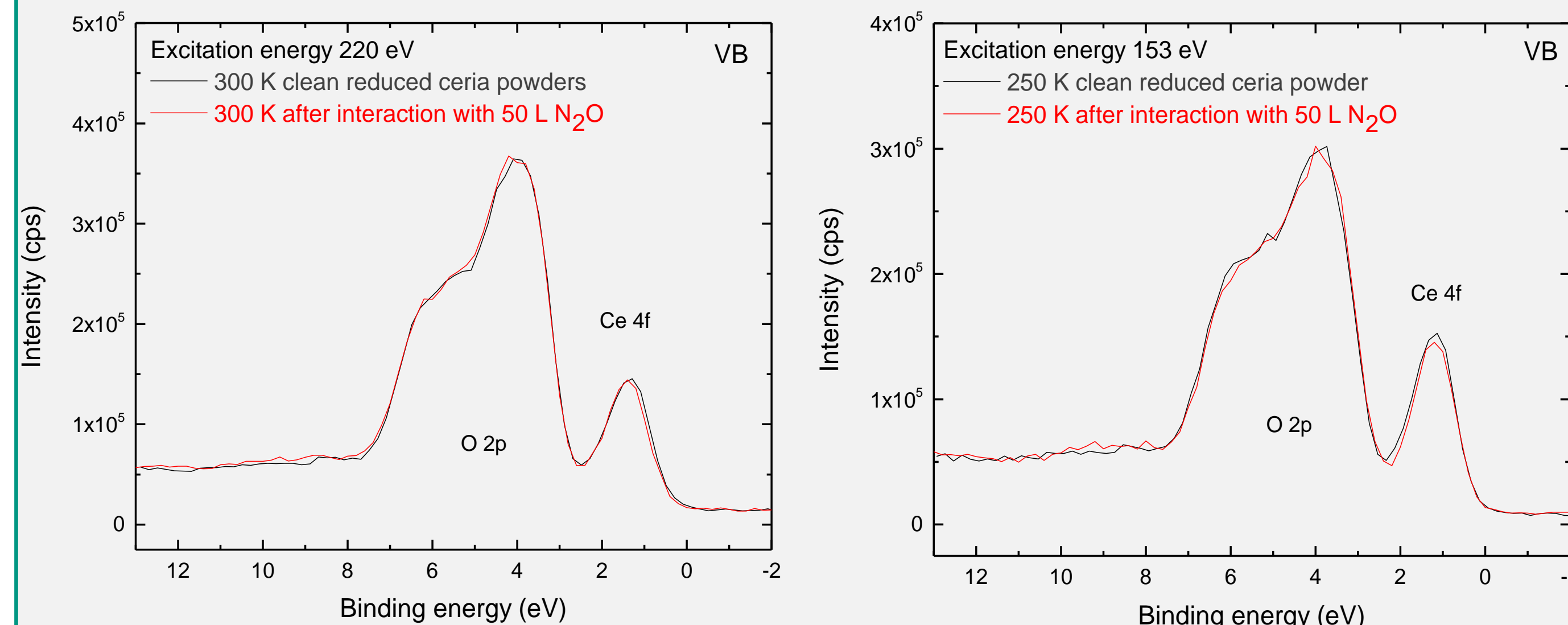


Figure 4: PES-VB measurements before and after the dosage of 50 L N₂O on reduced ceria powder for different excitation energies. For powders, ceria reoxidation is not observable by means of valence band spectra. Lowering the excitation energy will result in a more surface sensitive measurement, which can be derived from the higher ratio between Ce4f and O2p peak (right).

Proposed mechanism

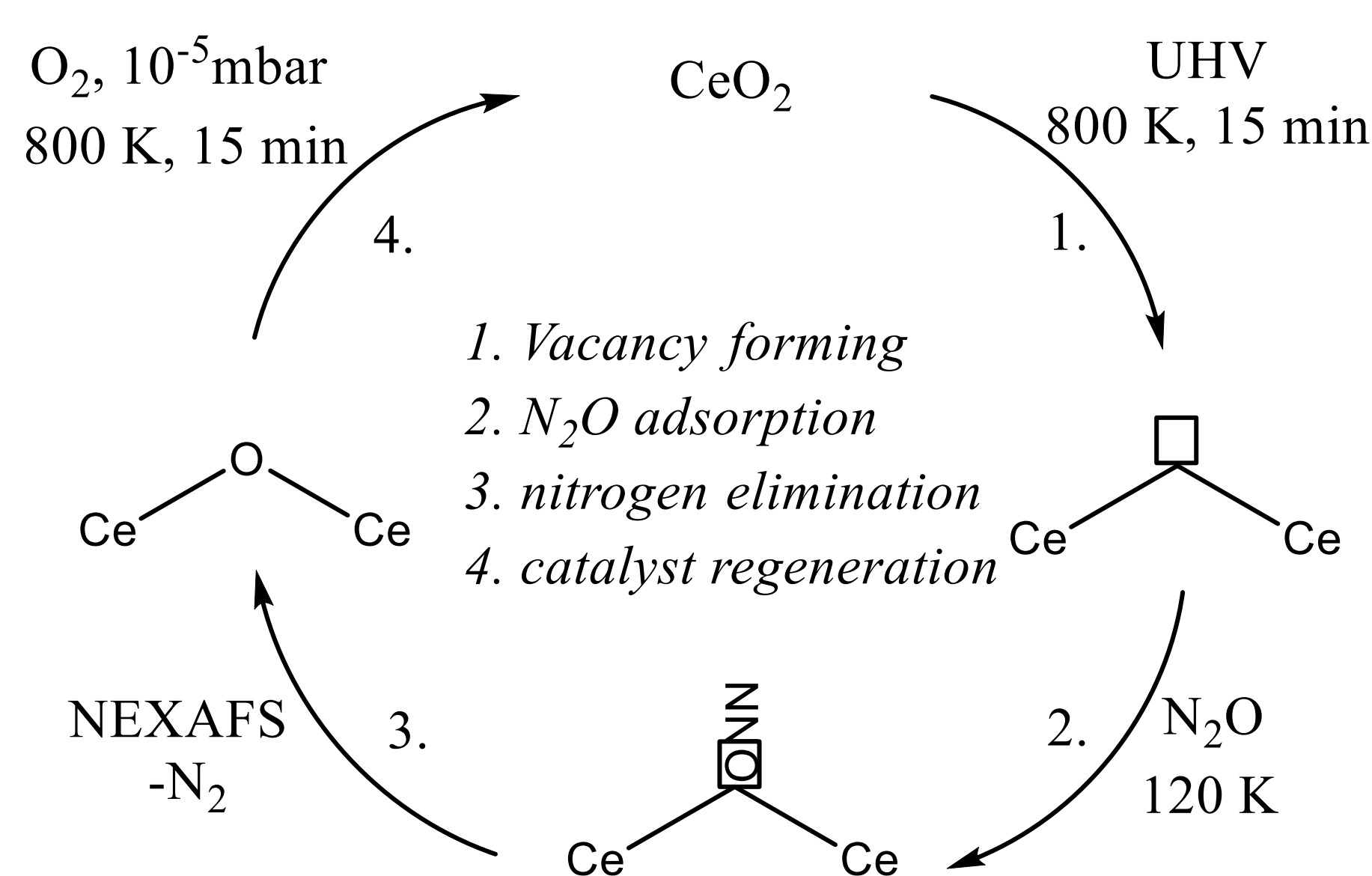


Figure 5: Schematic view on N₂O conversion for ceria and preparation conditions.

Conclusions

In this work we presented the *in-situ* reaction monitoring of laughing gas (N₂O) to N₂ on reduced ceria substrates by NEXAFS and PES experiments. After deposition of 50 L N₂O at 120 K, two apparent signals were observed for photon energies of 401.2 eV and 404.8 eV in NEXAFS spectra inside the N K-edge region on CeO_{2-x}(111) and CeO_{2-x} powder, respectively. For the single crystal surface the oxidation process could be directly followed by the shrink of the Ce4f shell signal in valence band photoemission spectra, which is a clear indication for replenishing the voids on reduced surfaces with atomic oxygen. Hence the chemical conversion from N₂O to molecular nitrogen can be assumed. In comparison to ceria powder the situation seems to be more complicated, because the reoxidation is concealed in VB measurements. The amount of adsorbed N₂O molecules on powders is much higher than on single crystals, which can be read out in the kinetic profiles. The nitrogen signal decay in NEXAFS occurs much more rapid than for single crystals, so the conversion seems to be more effective on powders for multilayer dosages due to much higher surface area. This is the reason why we cannot detect the reoxidation via PES, because the number of unoccupied adsorption sites (vacancies) on reduced ceria powder is vast referring the „small“ gas dosage of 50 L.

References

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