N_2O Photochemical Depletion at CeO_{2-x} Surfaces

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Motivation

N_2O together with other nitrogen oxide species (NO, NO_2) is formed in the engine and also in the catalytic converter by the reaction of N_2 with adsorbed oxygen atoms. The destruction of these gases (DeNOx process) via reduction of NO_x to N_2 is of great significance due to their environment and health impact. Especially for nitrous oxide (N_2O) 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 NO_2 have to be firstly converted into N_2O characterized by the high inertness, and then N_2O further liberates oxygen to finally generate environmentally benign N_2, where the latter is the rate determining step of DeNOx process. Reducible oxides, such as TiO_2, CeO_2 and Fe_2O_3, have shown the reactivity to convert N_2O to N_2 presumably at oxygen vacancy sites.

In this study, we monitored the conversion of N_2O to N_2 over the model catalyst oxide support, namely CeO_2 by using photoemission spectroscopy (PES), near edge x-ray absorption fine structure spectroscopy (NEXAFS) and ultra-high-vacuum infra-red reflection absorption spectroscopy (UHV-IRRAS), which also enables us to determine the kinetics of this process.

Experimental

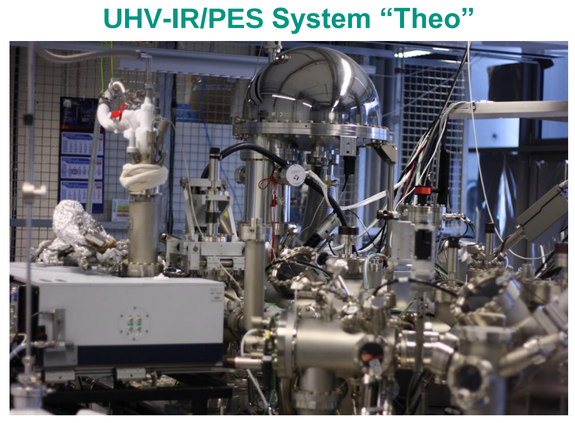
The CeO_2 single crystals were prepared by repeated cycles of sputtering with 1 keV Ar^+ and annealing at 800 K for 15 min in an O_2 atmosphere of 1×10^{-5} mbar for forming stoichiometric surfaces, and then annealed at 800 K to obtain reduced surfaces, i.e., surfaces with oxygen vacancies. The reduced ceria powders were obtained by stepwise annealing from 800 K to 1000 K for 30 min.

NEXAFS and PES measurements were carried out on the HE-SGM beamline at BESSY II. NEXAFS measurements were performed at 120 K after desired Ce oxidation state as judged by PES. Exposure to 50 Langmuirs N_2O was achieved by backfilling the analysis chamber up to 2.6×10^{-7} mbar for 250 seconds. Due to severe charging problems, PES measurements cannot be performed at temperature for N_2O dosing (120 K), but the valence band (VB) spectra were recorded at 150 K to check the change of cerium oxidation state of samples before and after interaction with N_2O.

IRRAS measurements were conducted at ~120K on the other UHV apparatus at KIT. N_2O dosing was achieved by backfilling the IR chamber.The lamp N-8 L (Herolab) with power of 8 W @ λ=365 nm was used for UV-irradiation, which was shed directly on the samples through a quartz-window on IR chamber.

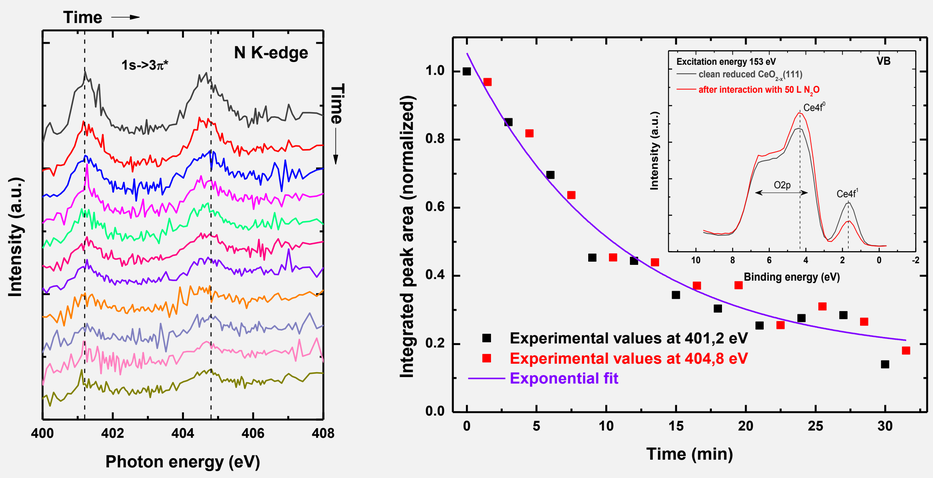
NEXAFS/PES Endstation at HE-SGM Beamline

UHV-IR/PES System "Theo"



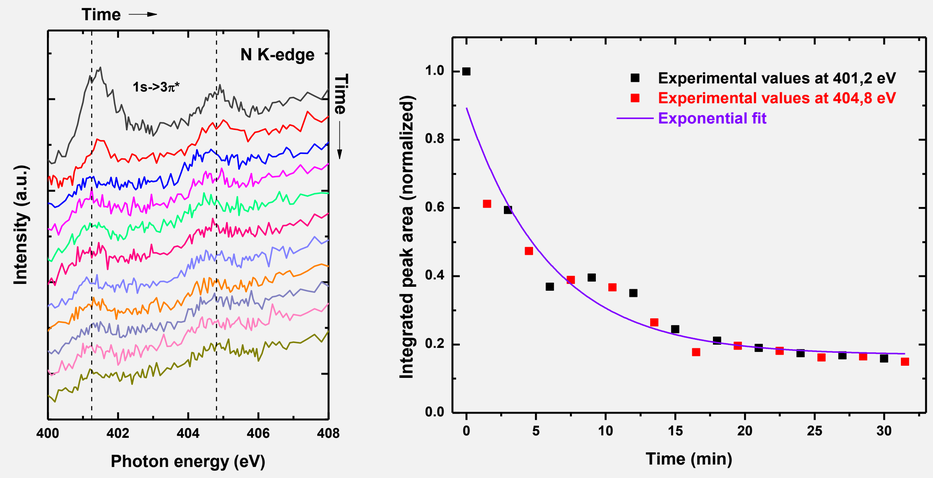
NEXAFS/PES Results

$CeO_{2-x}(111)$



N K-edge NEXAFS spectra of the reduced $CeO_{2-x}(111)$ surface after exposure to 50 Langmuirs N_2O at 120 K are depicted (left). 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 at both photon energies is given in a time dependent plot (right). The measurement time between both signals in one spectrum was estimated to 1.5 min, while between two stacked spectra it was 3 min. Kinetic predictions should be valid under the consideration that both signals have equal peak intensities on a simultaneous time recording scale.
Inset: VB spectra of partially reduced $CeO_{2-x}(111)$ and the $CeO_2(111)$ reoxidized by N_2O photo-decompsotion.

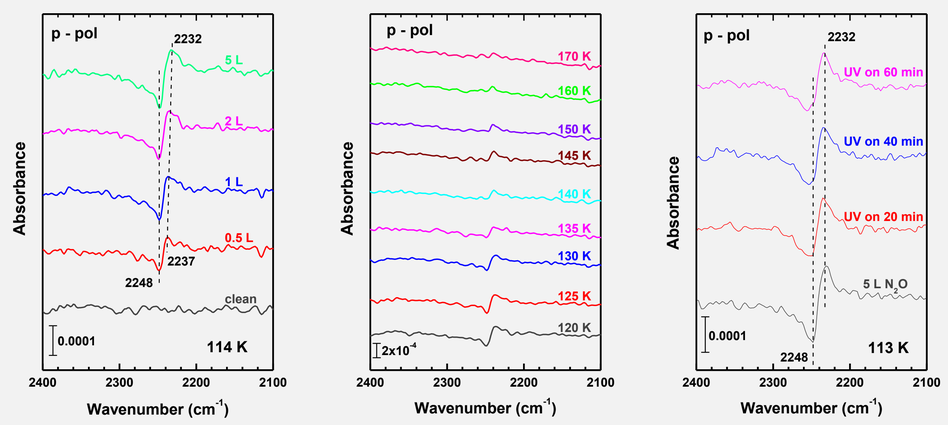
CeO_{2-x} powders



N K-edge NEXAFS spectra of reduced ceria powders were recorded after exposure to 50 Langmuirs N_2O at 120 K (left). The corresponding kinetic profile illustrates the signal decay over time (right). Expontential fitting reveals a first order kinetics for N_2O decompostion over reduced ceria powders.

IRRAS Results

$CeO_{2-x}(111)$

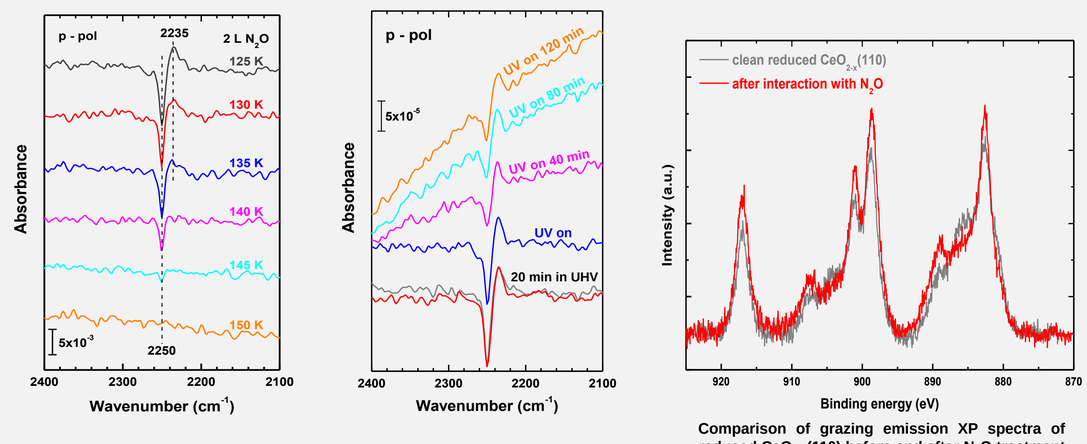


N_2O on reduced $CeO_2(111)$

IRRAS thermal desorption of N_2O on reduced $CeO_{2-x}(111)$

Photochemical depletion of N_2O on reduced $CeO_{2-x}(111)$

$CeO_{2-x}(110)$



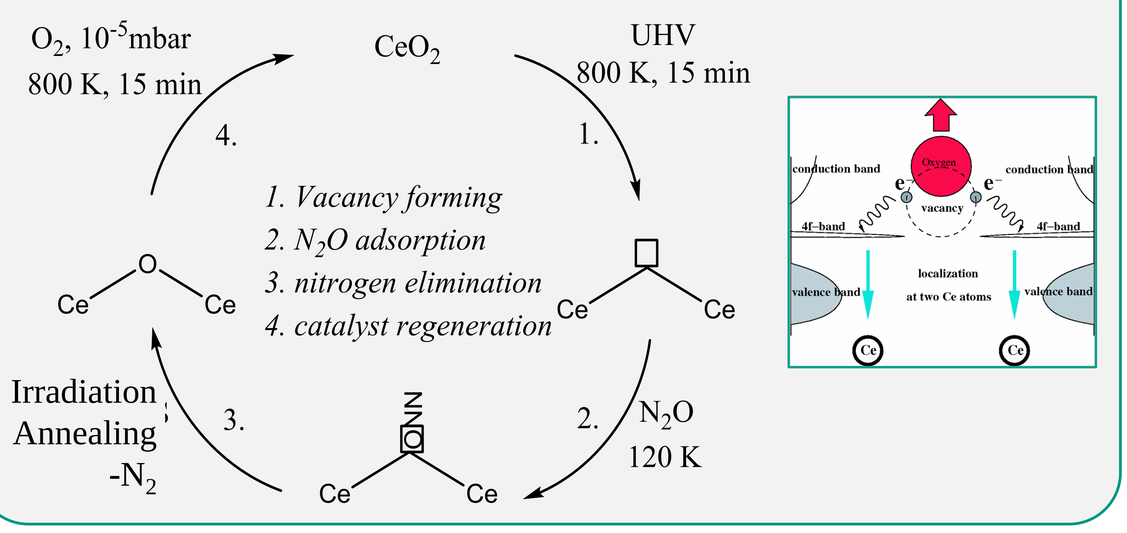
IRRAS thermal desorption of N_2O on reduced $CeO_{2-x}(110)$

Photochemical depletion of N_2O on reduced $CeO_{2-x}(110)$

Comparison of grazing emission XP spectra of reduced $CeO_{2-x}(110)$ before and after N_2O treatment indicates N_2O donated oxygen atom to the oxygen vacancy and re-oxidized the reduced $CeO_{2-x}(110)$.

Mechanisms

Schematic view on N_2O decompostin over nonstoichiometric ceria.



Conclusions

In this work we present NEXAFS and IRRAS results of thermal and photo decomposition of the most inert nitrogen oxide, N_2O, to N_2 over reduced ceria substrates and powers. After exposure of N_2O to reduced $CeO_{2-x}(111)$ and CeO_{2-x} powders at 120 K, two apparent resonances were observed at photon energies of 401,2 eV and 404,8 eV in N K-edge NEXAFS spectra. The tunable excitation energy of X-ray source at synchrotron enabled us to monitor the re-oxidation of reduced ceria samples indicated by the shrink of the Ce4f states signal in valence band (VB) photoemission spectra, which is a direct evidence for replenishing the voids on reduced ceria surfaces with oxygen atoms probably left behind by the decomposition of N_2O to N_2.

IRRAS data corroborate the observations by NEXAFS. After N_2O adsorption on reduced ceria (111) and (110) single crystal surfaces, two IR bands at ~2250 and 2235 cm^{-1} with different signs are observed, which can be ascribed to asymmetric stretching vibration of N_2O adsorbed at O-defect sites and perfect sites, respectively. Both bands shrink with temperature increasing or UV irradiation. Comparison of grazing emission XP spectra of reduced ceria substrates before and after N_2O treatment indicates N_2O donated oxygen atom to the oxygen vacancy and thereby re-oxidized reduced ceria surfaces. This is the first report revealing nonstoichiometric ceria has extraordinary photochemical reactivity for the DeNOx process.

References

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