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CO_2 adsorption on CeO_2 (110) surface: NEXAFS and XPS study

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Motivation

Carbon dioxide studies were motivated by not only the mitigation of this greenhouse gas but also the potential utilization of CO_2 as a feedstock for the chemical industry.[1] Ceria, as one of the most reducible metal oxide, provides the basis for extensive catalytic applications due to oxygen vacancy defects can be rapidly formed and eliminated, giving it a high "oxygen storage capacity". It has proven to be a highly active catalyst for CO_2 reduction to methanol recently.[2] The fundamental research which take a surface science approach on CO_2 adsorption and reaction at well-defined single crystal surface is really desired for understanding the processes occurring on high surface-area CeO_2 catalysts under reaction conditions.[3]

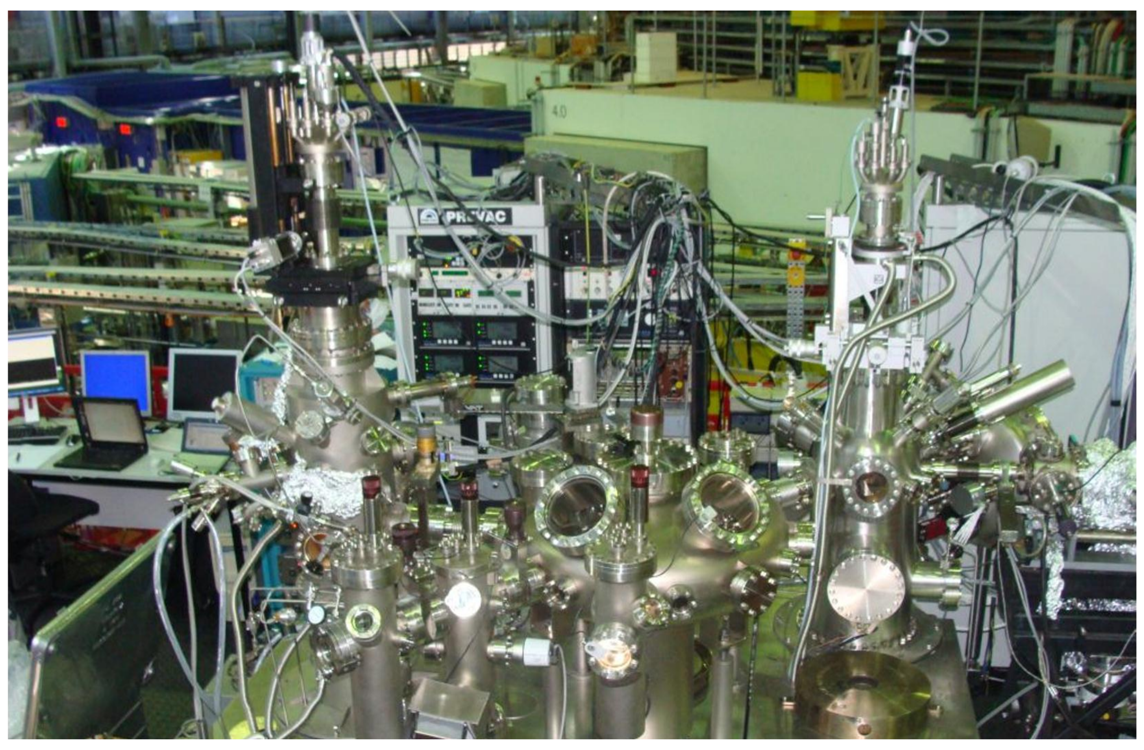
Very recently we succeeded in probing the oxygen vacancies on bulk single crystal CeO_2(111) surface with CO by using UHV-IRRAS.[4] Here we report the results of CO_2 adsorption onto pristine and defective CeO_2(110) single crystal surfaces, which is more reactive than the CeO_2(111) surface, characterized by using x-ray photoelectron spectroscopy (XPS) and near edge x-ray absorption fine structure spectroscopy (NEXAFS), which proves the feasibility of this method to characterize the electronic, structural and chemical properties of surface species of ceria.

Experimental

The NEXAFS and XPS measurements were carried out in our own UHV-apparatus on the HE-SGM beamline at BESSY II. CeO_2 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 CeO_2(110) single crystal surface was 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 a stoichiometric surface, or alternately without O_2 to create a reduced one. For temperature monitoring, a K-type thermocouple was directly attached on the sample surface.

NEXAFS measurements only were performed after desired Ce oxidation state as judged by XPS. Exposure to 5 Langmuir CO_2 at sample temperatures typically below 120 K was achieved by backfilling the analysis chamber up to 10^{-9} mbar. Typical base pressures during acquisition of NEXAFS and XP spectra were 2×10^{-10} mbar. NEXAFS and XP spectra after CO_2 exposure were firstly recorded at low temperature. And then the sample temperature was elevated to a set of given temperatures and acquire the spectra there to monitor their evolution during thermal desorption process.

NEXAFS/XPS Endstation at HE-SGM Beamline



CO_2 on reduced surface

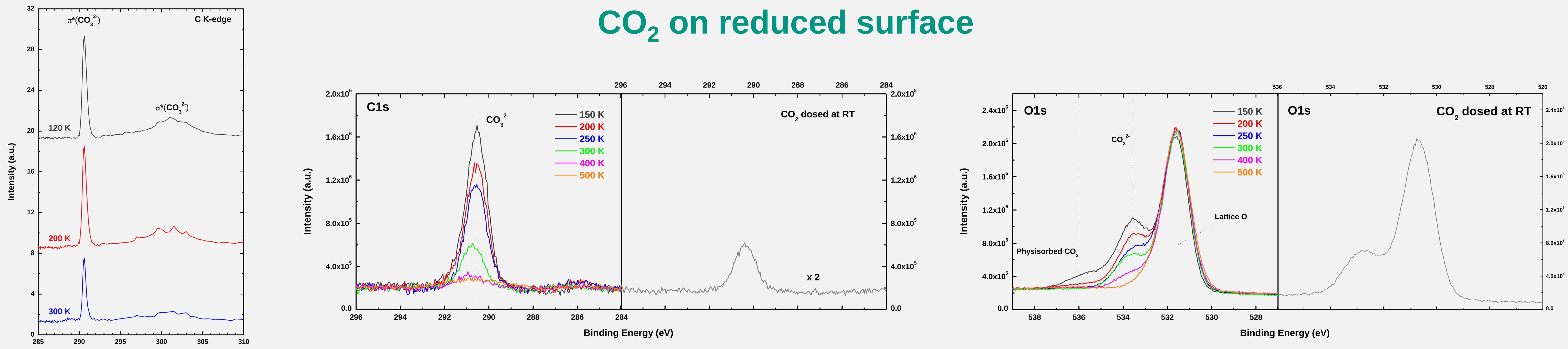
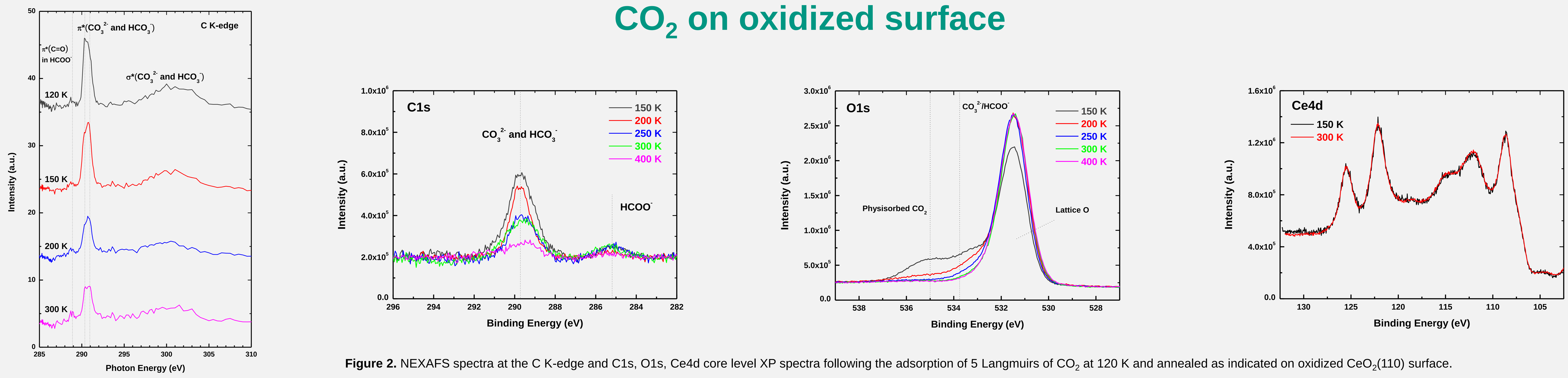


Figure 1. NEXAFS spectra at the C K-edge and C1s, O1s core level XP spectra following the adsorption of 5 Langmuirs of CO_2 at RT and 120 K then annealed as indicated on reduced CeO_2(110) surface.

CO_2 on oxidized surface



Two resonances resolved at around 291 eV are assigned π resonances of CO_3^{2-} and HCO_3^-.

Figure 2. NEXAFS spectra at the C K-edge and C1s, O1s, Ce4d core level XP spectra following the adsorption of 5 Langmuirs of CO_2 at 120 K and annealed as indicated on oxidized CeO_2(110) surface.

Reoxidation of reduced CeO_2(110) surface

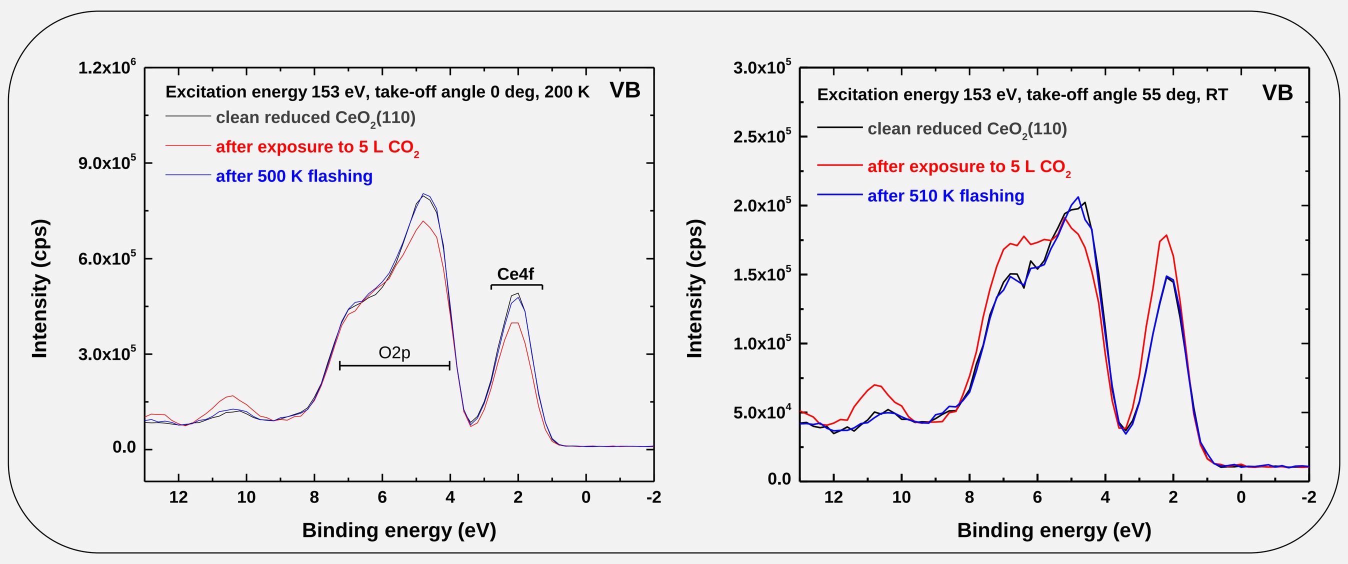


Figure 3. Valence band XP spectra of clean reduced CeO_2(110) and surfaces precovered CO_2 or after CO_2 desorption.

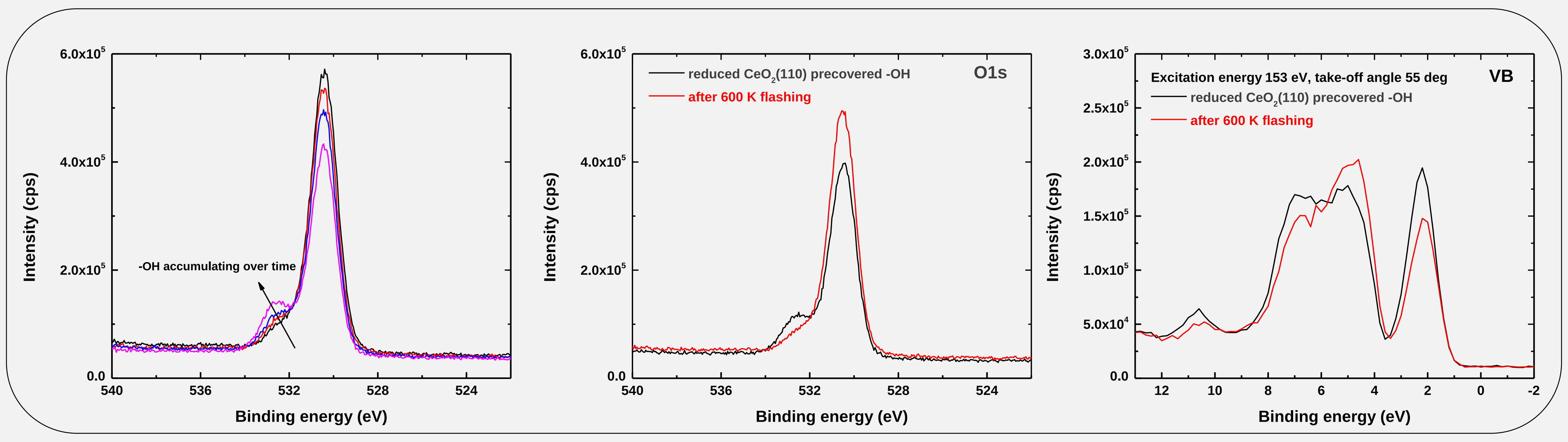


Figure 4. Evidence for reoxidation of Ce^{3+} via residual water.[5]

Conclusions

- Below 150 K, CO_2 is adsorbed on the reduced CeO_2(110) surface as carbonate and weakly bound (physisorbed) CO_2, which completely desorbs by 200 K. A carboxylate species was not detected on the reduced surface.
- On the oxidized CeO_2(110) surface, bicarbonate and carboxylate species possibly originating from a reaction of CO_2 with surface hydroxyl groups are detected simultaneously.
- CO_2 can be adsorbed even at room temperature on the reduced surface but cannot act as an oxidizing agent to reoxidized the reduced CeO_2(110). The previous observations of reoxidation might be induced by residual water.

Reference

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