

CO₂ adsorption on CeO₂(110) surface: NEXAFS and PES 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 CO₂ 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 that can be rapidly formed and eliminated, giving it a high "oxygen storage capacity". It has proven to be a highly active catalyst for CO₂ reduction to methanol recently.² The fundamental research which takes a surface science approach on CO₂ adsorption and reaction at well-defined single crystal surface is really desired for understanding the processes occurring on high surface-area CeO₂ catalysts under reaction conditions.³

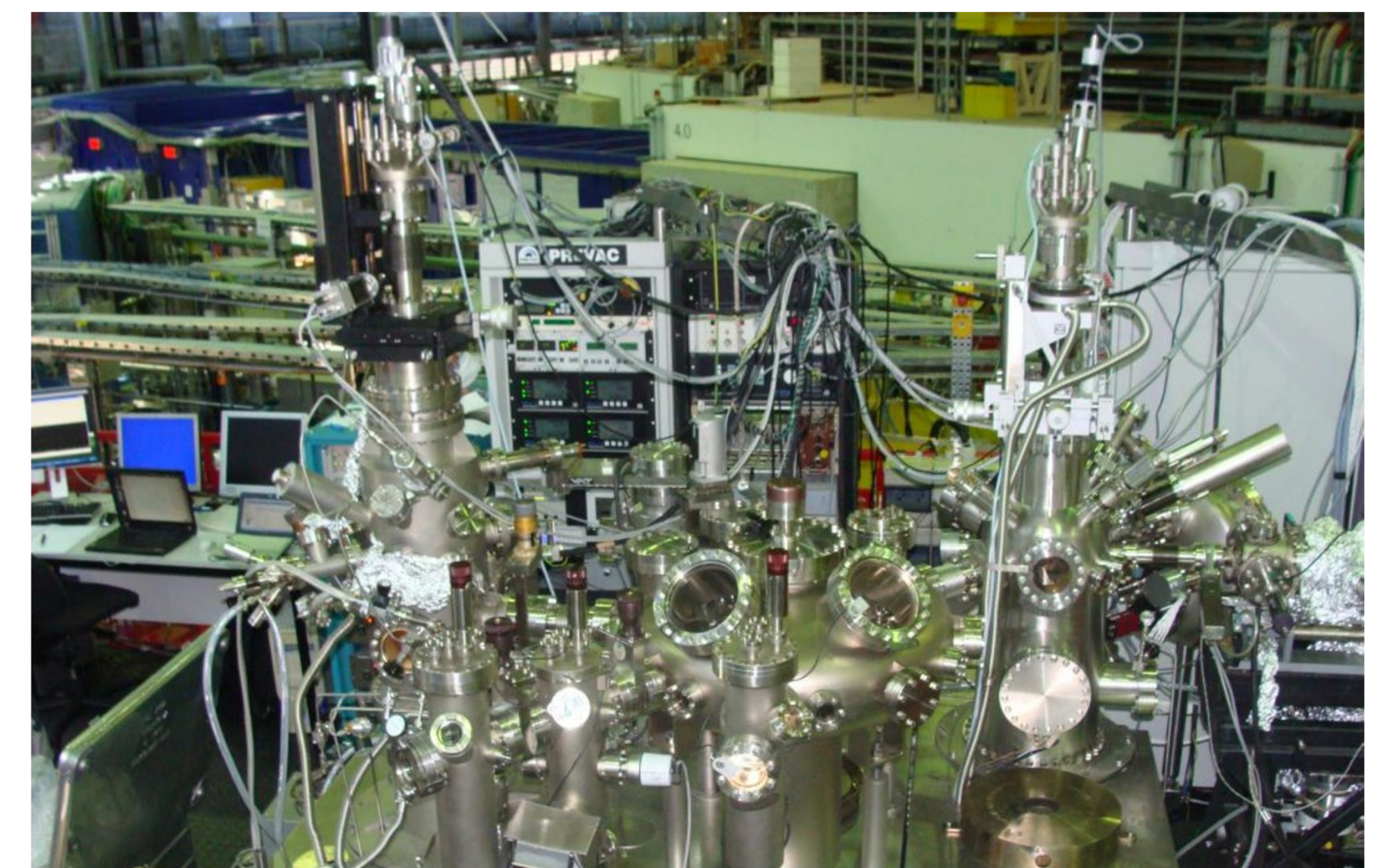
Very recently we succeeded in probing the oxygen vacancies on bulk single crystal CeO₂(111) surface with CO by using UHV-IRRAS.⁴ Here we report the results of CO₂ adsorption onto pristine and defective CeO₂(110) single crystal surfaces, which is more reactive than the CeO₂(111) surface, characterized by using photoelectron spectroscopy (PES) and near edge x-ray absorption fine structure (NEXAFS) spectroscopy, which proves the feasibility of this method to characterize the electronic, structural and chemical properties of surface species of ceria.

Experimental

The NEXAFS and PES measurements were carried out 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(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 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.

NEXAFS measurements only were performed after desired Ce oxidation state as judged by PES. Exposure to 5 Langmuir CO₂ 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 PE spectra were 2 × 10⁻¹⁰ mbar. NEXAFS and PE spectra after CO₂ 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/PES Endstation at HE-SGM Beamline



CO₂ on reduced surface

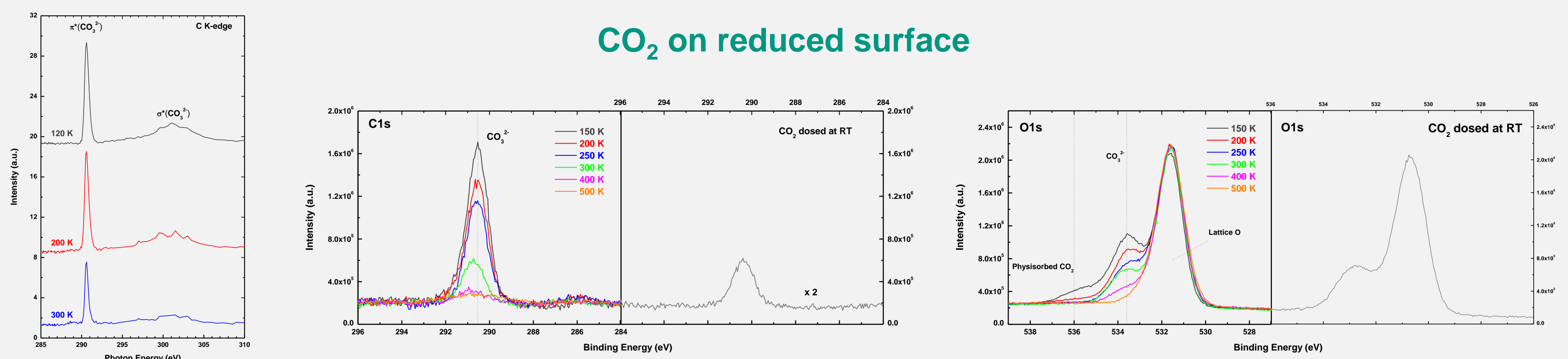


Figure 1. NEXAFS spectra at the C K-edge and C1s, O1s core level PE spectra following the adsorption of 5 Langmuir of CO₂ on reduced CeO₂(110) surface at 120 K and then annealed as indicated as well as after adsorption at RT.

CO₂ on oxidized surface

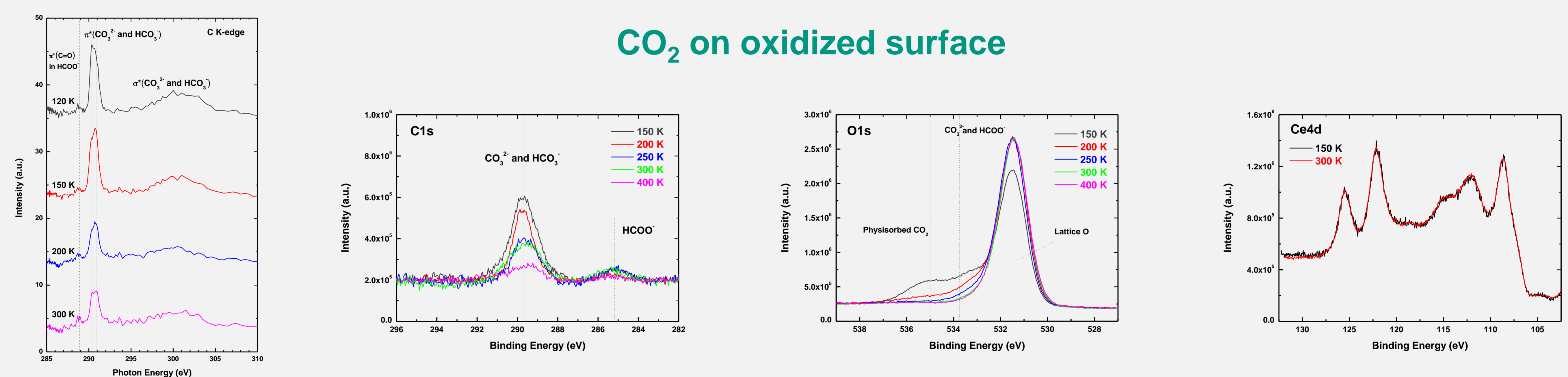


Figure 2. NEXAFS spectra at the C K-edge and C1s, O1s core level PE spectra following the adsorption of 5 Langmuir of CO₂ on oxidized CeO₂(110) surface at 120 K and then annealed as indicated as well as after adsorption at RT.

Reoxidation of reduced CeO₂(110) surface

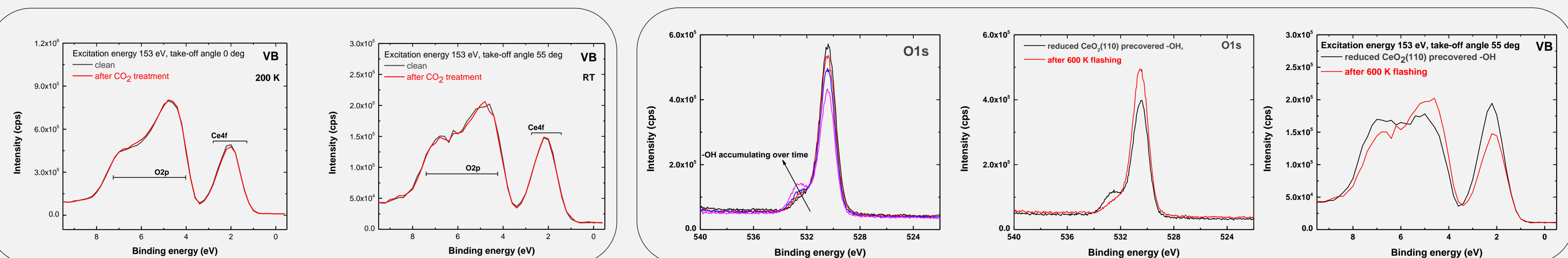


Figure 3. Valence band spectra of clean reduced CeO₂(110) and surfaces precovered CO₂ or after CO₂ desorption.

Figure 4. Evidence for reoxidation of Ce³⁺ via residual water.^[5]

Conclusions

- Below 150 K, CO₂ is adsorbed on the reduced CeO₂(110) surface as carbonate and weakly bound (physisorbed) CO₂, which completely desorbs by 200 K. A carboxylate species was not detected on the reduced surface.
- On the oxidized CeO₂(110) surface, bicarbonate and carboxylate species possibly originating from a reaction of CO₂ with surface hydroxyl groups are detected simultaneously.
- CO₂ can be adsorbed even at room temperature on the reduced surface but cannot act as an oxidizing agent to reoxidize the reduced CeO₂(110). The previous observations of reoxidation might be induced by residual water.

Reference

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