# $CO_2$ adsorption on $CeO_2$(110) single crystal surface

Chengwu Yang,[1,2] Alexei Nefedov,[1] Fabian Bebensee,[1] Jun Chen,[1] Christof Wöll[1]

[1]Institute of Functional Interfaces
[2]Helmholtz Research School „Energy-related catalysis“

## 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.

**References**

[1] M. Aresta (Ed.), Carbon Dioxide as Chemical Feedstock, Wiley-VCH, New York, **2010**.
[2] J. Graciani, *et al.*, Science, **2014**, 345, 546.
[3] U. Burghaus, Progress in Surface Science, **2014**, 89, 161.
[4] C. Yang, L. Yin, F. Bebensee, M. Buchholz, H. Sezen, S. Heissler, J. Chen, A. Nefedov, H. Idriss, X. Gong, C. Wöll, Physical Chemistry Chemical Physics, **2014**, 16, 24165.

## 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 $1\times10^{-5}$ 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 $2\times10^{-10}$ 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.

## Stoichiometric $CeO_2$(110) Surface

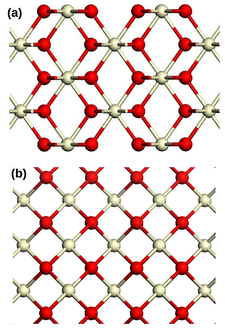
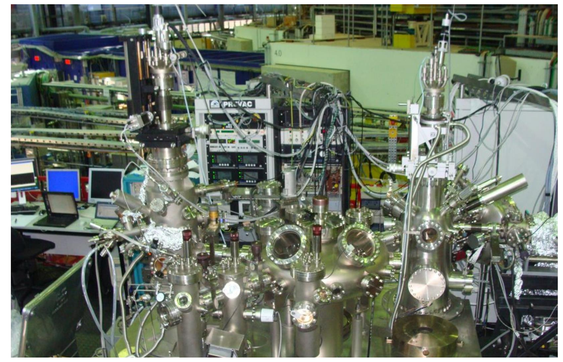



**Figure 1.** Ball-and-stick model of the $CeO_2$(110) surface (a) side view and (b) top view, red – oxygen, white – cerium.

## NEXAFS/XPS Endstation at HE-SGM Beamline.



## $CO_2$ on Reduced Surface

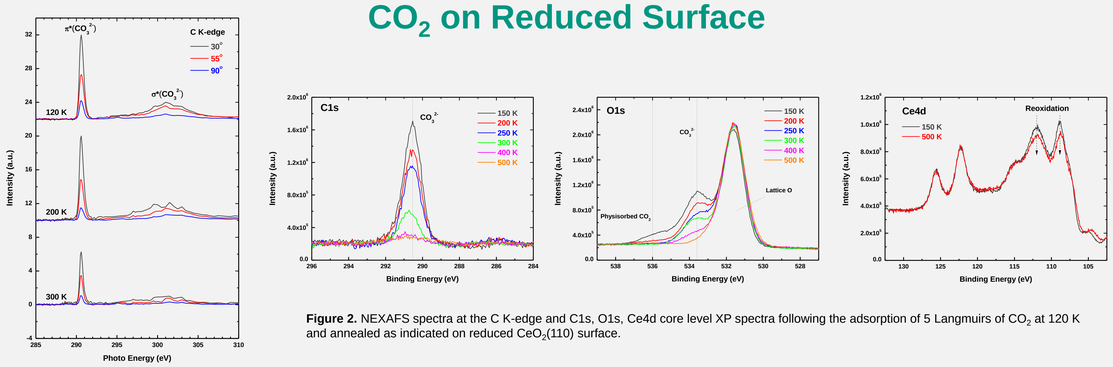



**Figure 2.** NEXAFS spectra at the C K-edge and C1s, O1s, Ce4d core level XP spectra following the adsorption of 5 Langmuirs of $CO_2$ at 120 K and annealed as indicated on reduced $CeO_2$(110) surface.

## $CO_2$ dosed at RT on Reduced Surface

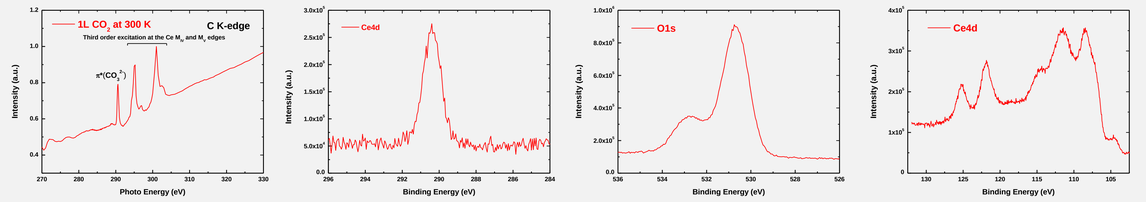



**Figure 3.** Raw NEXAFS spectrum at the C K-edge and C1s, O1s, Ce4d XP spectra following the adsorption of 1 Langmuir of $CO_2$ at room temperature on reduced $CeO_2$(110) surface.

## $CO_2$ on Oxidized Surface

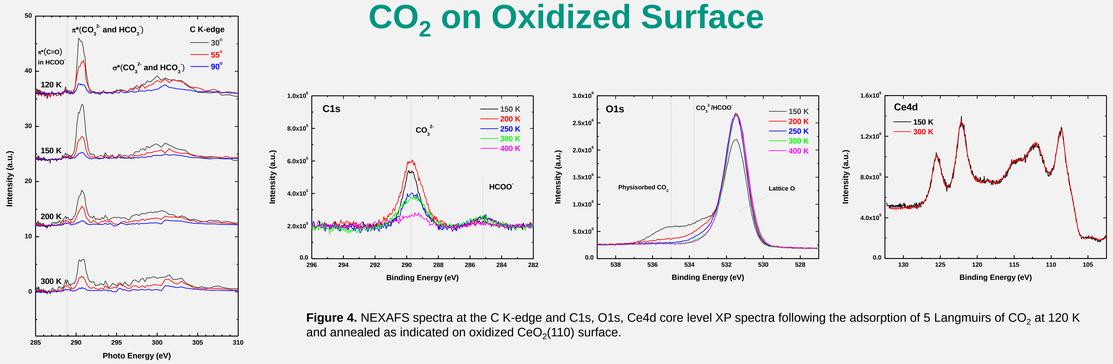



**Figure 4.** NEXAFS spectra at the C K-edge and C1s, O1s, Ce4d core level XP spectra following the adsorption of 5 Langmuirs of $CO_2$ at 120 K and annealed as indicated on oxidized $CeO_2$(110) surface.

## Conclusions

- $CO_2$ adsorbs on reduced $CeO_2$(110) surface mainly as carbonate and weakly bound physisorbed $CO_2$ below 150 K. The formation of a carboxylate intermediate is not really evident. The physisorbed $CO_2$ completely desorbs by 200 K.
- However, on oxidized $CeO_2$(110) surface carboxylate and bicarbonate were detected, which possibly originate from $CO_2$ react with surface hydroxylate group and adsorbed atomic hydrogen.
- $CO_2$ even can be adsorbed at room temperature on reduced surface and act as an oxidizing agent to partially reoxidized the reduced $CeO_2$(110) surface.

Contact: Christof Wöll, Institute of Functional Interfaces (IFG), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany. Christof.woell@kit.edu. Chengwu Yang would like to gratefully acknowledge the Helmholtz Research School Energy-Related Catalysis for financial support.