



Sebastian Dahle<sup>1</sup>, Florian Voigts<sup>1</sup>, Kai Volgmann<sup>1</sup>, Fabian Bebensee<sup>2</sup>  
and Wolfgang Maus-Friedrichs<sup>1</sup>

<sup>1</sup>Institut für Physik und Physikalische Technologien, TU Clausthal, Leibnizstrasse 4, 38678 Clausthal-Zellerfeld, Germany

<sup>2</sup>Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstrasse 3, 91058 Erlangen, Germany

## Introduction

The adsorption of different atmospheric molecules on metals is both of fundamental and technological interest that arises from several applications. Ca is used to enhance the performance of high temperature oxygen sensors based on SrTiO<sub>3</sub>, as a promoter in many catalytic reactions and as metal electrode in different organic or polymeric semiconductor components. A lot of studies of the effect of Ca on different catalysts neglect the interaction of Ca itself with different gases, although this might contribute to the role of Ca as a promoter in catalysis. This poster shows Metastable Induced Electron Spectroscopy (MIES), Ultraviolet Photoelectron Spectroscopy (UPS) and X-ray Photoelectron Spectroscopy (XPS) results on the interaction of Ca and CaO films with CO<sub>2</sub> and CO.

## Experimental

For probing the surface density of states (SDOS) we applied Metastable Induced Electron Spectroscopy using a hemispherical analyzer (VSW HA100) combined with a source for metastable helium atoms (mainly He<sup>+</sup> 3S<sub>1</sub>) and ultraviolet photons (He). Additional information for chemical analysis was obtained by XPS utilizing a commercial non-monochromatic X-ray source (Specs RQ20/38C). All XPS spectra presented are recorded with a resolution of 1.1 eV using Al K<sub>α</sub> at a photon energy of 1486.7 eV.

Ca films with a thickness of about 4 nm were prepared on a cleaned Si(100) target using an Omicron EFM3 e-beam evaporator charged with calcium pieces (Sigma-Aldrich, 99%).

CaO films with a thickness of about 7 nm were prepared evaporating Ca in an oxygen atmosphere at pressure of 6.7x10<sup>-7</sup> mbar and at target temperature of 670 K.

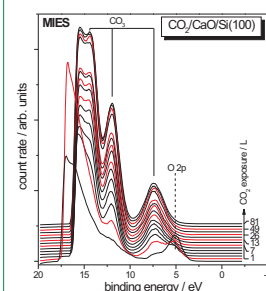
CO (Linde Gas, 99.97%) and CO<sub>2</sub> (Linde Gas, 99.995%) were offered via backfilling using a bakeable leak valve, controlled by a quadrupole mass spectrometer (Balzers QMS 112 A).

## CO<sub>2</sub> / CaO

MIES spectra are displayed using waterfall offset, starting at the bottom with the pure CaO film. CO<sub>2</sub> induced changes are:

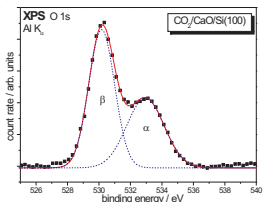
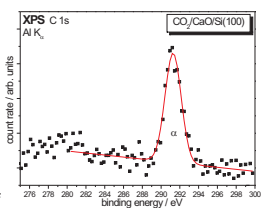
- decrease of O 2p intensity at 5.1 eV representing CaO bulk oxide
- emission of CO<sub>2</sub><sup>-</sup>-MOs at 7.6 eV, 12.1 eV and 14.3 eV
- increase of work function

XPS measurements after exposure are shown in detail beside.

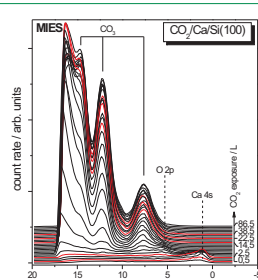


The single peak (α) in the C 1s region at 291.2 eV has a FWHM of about 2 eV. This peak belongs to carbonate groups.

The O 1s region contains contributions from bulk CaO at 530.8 eV (β) and an additional peak at 533.5 eV (α) corresponding to the CO<sub>3</sub><sup>2-</sup> groups. Low doses are sufficient to complete the reaction, saturation is achieved after a dosage of 3 L CO<sub>2</sub>. Afterwards only the top layer of the surface consists of CO<sub>3</sub><sup>2-</sup> groups while the bulk remains CaO.



## CO<sub>2</sub> / Ca



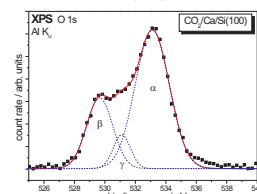
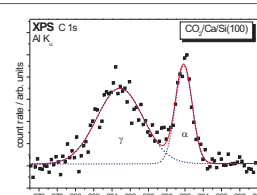
Chemisorbed oxygen develops as intermediate state before the carbonation during exposure of metallic Ca to CO<sub>2</sub>.

Further exposure leads to subsequent carbonation of the chemisorbed oxygen as also observable on CaO.

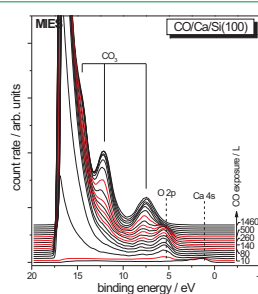
XPS spectra after CO<sub>2</sub> dosage show additional peaks compared to clean CaO. In the C 1s region, there is a peak (γ) caused by carbon atoms from complete CO<sub>2</sub> dissociation incorporated into the surface.

The O 1s structure consists of the following:

- a carbonate peak (α)
- a bulk oxide peak (β), though at much smaller intensity compared to CaO films. In consequence there must be an amount of oxide remaining underneath the carbonate.
- a peak induced by chemisorbed oxygen atoms (γ)



## CO / Ca



The MIES spectra show:

- chemisorption of oxygen on the metal surface as transitional state
- carbonation of the chemisorbed oxygen by impinging CO molecules

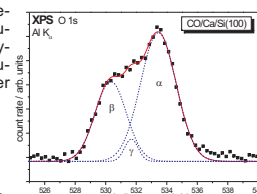
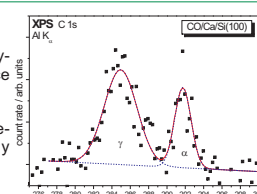
This oxidation requires dissociation of CO molecules. Influences of impurities of the CO as analyzed by QMS can be excluded, as discussed later on.

XPS shows the following peaks in the O 1s region:

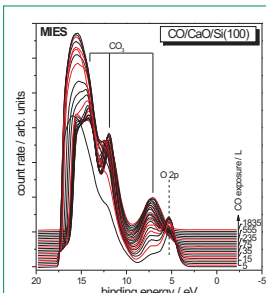
- oxygen in carbonate groups (α)
- bulk CaO (β)
- chemisorbed oxygen (γ), as found offering CO<sub>2</sub> at Ca surfaces, though with smaller relative intensity for chemisorbed oxygen at CO dosage.

In the C 1s region are the following structures:

- a peak (α) due to surface carbonate
- a peak of carbon incorporated into the surface (γ), pointing out complete dissociation of CO



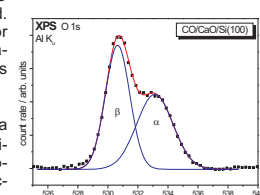
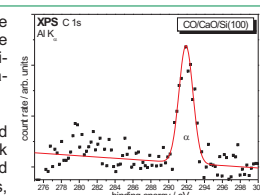
## CO / CaO



CO offer produces the same effect of surface carbonation, but requires much higher dosages than offering CO<sub>2</sub>.

MIES peak heights and the evolution of the work function are displayed over the exposure. Thus, the behaviour for CO offer can be recognized. The dosage needed for a saturation of the surface with CO<sub>3</sub><sup>2-</sup> groups is about 500 L.

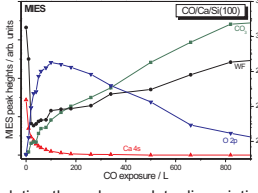
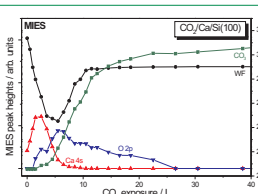
XPS spectra show a peak (α) in the C 1s region due to surface carbonate. Further on, characteristic structures for surface carbonate in the O 1s region were found, where a bulk oxide state (β) beside a carbonate state (α) is visible.



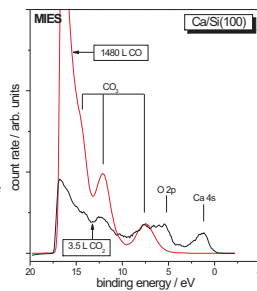
## Discussion

Surface oxidation through dissociation of CO<sub>2</sub> on Ca surfaces and subsequent carbonation of the surface oxide has been observed. The evolution of peak heights in MIES and the work function are displayed over exposure.

Carbonation was also observed while offering pure CO, though requiring much higher dosage. The assumption that the reaction is due to unavoidable CO<sub>2</sub> contamination can be excluded as can be deduced from comparing a MIES spectrum of saturated CO exposure with one of CO<sub>2</sub> exposure at a dosage representing the contamination of the offered CO.



Thus, an interaction of CO with Ca surfaces is observed. Surface oxidation through complete dissociation of the CO molecule is the rate limiting step, since carbonation of CaO through CO afterwards works much faster.



## References

[1] F. Voigts, F. Bebensee, S. Dahle, K. Volgmann and W. Maus-Friedrichs: *The adsorption of CO<sub>2</sub> and CO on Ca and CaO films studied with MIES, UPS and XPS*, Surface Science 603 (2009) 40-49

## Acknowledgements

We are thankful for the technical assistance of Benjamin Eggers and Christiane Lehmann.

