The adsorption of CO₂ and CO on Ca and CaO films studied with MIES, UPS and XPS

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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 sensors based on SrTiO₃, 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 and CO₂.

Introduction

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Experimental

For probing the surface density of states (BDOS) we applied Metastable Induced Electron Spectroscopy using a hemispherical analyzer (VSW HA100) combined with a source for metastable helium atoms (mainly He⁺) and ultraviolet photons (HeI). 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 Kα at a photon energy of 1486.7 eV.

Co/Ca

Chemisorbed oxygen develops as intermediate state before the carbonation during exposure of metallic Ca to CO₂.

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

CO / CaO

CO₃²⁻/Ca²⁺

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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 (u)
- bulk CaO (j)
- chemisorbed oxygen (i), as found following CO₂ at CaO surfaces, though with smaller relative intensity for chemisorbed oxygen at CaO-dosage.

In the C 1s region the following structures:
- a peak (s) due to surface carbonate
- a peak of carbon incorporated into the surface (v), pointing out complete dissociation of CO.

Discussion

Surface oxidation through dissociation of CO₂ 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 CO₂ contamination can be excluded as can be deduced from comparing a MIES spectrum of saturated CO₂ exposure with one of CO. Thus, a saturation 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


Acknowledgements

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