

O 111: Oxides and Insulators: Adsorption II

Time: Friday 10:30–12:30

Location: MA 041

O 111.1 Fri 10:30 MA 041

New Insights into the Catalytic Activity of Solid Solutions: Carbon Dioxide Activation on NiMgO — ●ALIAKSEI MAZHEIKA, MARIE-MATHILDE MILLET, SABINE WRABETZ, ELIAS FREI, ROBERT SCHLÖGL, and SERGEY V. LEVCHENKO — Fritz-Haber-Institut der MPG, Berlin 14195, Germany

$\text{Ni}_x\text{Mg}_{1-x}\text{O}$ solid solutions are stable and active catalysts for dry reforming of CH_4 and CO_2 hydrogenation. Despite numerous experimental investigations, the structure of NiMgO surfaces at realistic conditions was unclear. We present a combined hybrid DFT/experimental study of CO_2 adsorption at NiMgO surfaces. The DFT calculations are performed with the HSE(α) functional, where the fraction of exact exchange α is set to 0.3 based on a comparison of the HSE(α) and CCSD(T) embedded-cluster calculations. The periodic calculations reveal that NiMg defects prefer to occupy low-coordinated sites (corners and steps) at the MgO (100) surface [1]. Thus, Ni doping promotes formation of such sites during synthesis of the solid solution. Indeed, IR experiments showed that the number of undercoordinated O sites at NiMgO surfaces is significantly increased compared to pristine MgO samples. The stabilization of (110) and reconstructed octopolar (111) surfaces by Ni doping reconciles theoretical results with microcalorimetry measurements of CO_2 adsorption energies. The presence of Ni at steps and corners considerably decreases CO_2 adsorption energies compared to pure MgO which prevents the carbonation and allows further chemical transformations of CO_2 .

[1] A. Mazheika and S.V. Levchenko, JPCC **120**, 26934 (2016)

O 111.2 Fri 10:45 MA 041

Electronic and Surface Chemical Properties of the Interface Diethyl Carbonate/Zirconia — ●MARKUS FRERICKS, NATALIA SCHULZ, THOMAS SPÄTH, WOLFRAM JAEGERMANN, and RENÉ HAUSBRAND — Oberflächenforschung, FB 11, TU Darmstadt, Deutschland

Interface phenomena and related reaction layers play a crucial role in the performance and stability of lithium ion batteries (LIB). Besides the study of naturally formed solid electrolyte interface (SEI) layers, artificial protection layers are investigated on their potential to improve the stability of interfaces in LIBs. Among several candidates, zirconia (ZrO_2) was found to improve the cycle stability when used as thin film coating for cathode materials such as lithium cobalt oxide (LiCoO_2). While previous studies focused on the discussion of the high fracture toughness of ZrO_2 and thus mainly mechanical properties, we investigated the electronic and surface chemical properties of zirconia coated model electrodes by solvent adsorption.

The experiment was performed at the beam line UE56_PGM-1 at the photon source BESSY II in Berlin. Diethyl Carbonate (DEC), a commonly used solvent in the electrolyte of LIBs, was adsorbed in consecutive steps on a cooled sample of a thin ZrO_2 layer on a Ti substrate. The steps were monitored by X-ray photoelectron spectroscopy, yielding the electronic and chemical structure at the interface. Compared to the adsorption on pristine LiCoO_2 , less reactions are observed. The results will also be discussed with respect to electron transfer through the layer system $\text{LiCoO}_2/\text{ZrO}_2/\text{DEC}$, evaluating the possibility for improved passivation by zirconia.

O 111.3 Fri 11:00 MA 041

Corrosion mechanism in lead-free materials for the electronic industry — ●GABRIELE SALEH and STEFANO SANVITO — Trinity College Dublin, College Green, Dublin 2, Ireland

Silver and tin constitute the major components (>99%) of alloys adopted to assemble printed circuit boards, ever since many countries have severely restricted the use of lead due to its toxicity. However, those alloys tend to suffer from corrosion issues, which represent an economic burden for the electronic industry. Although Ag-Sn surfaces play the main role in the corrosion process, their structure, composition and reactivity have never been investigated at the atomic level. In this contribution, we show how we bridged this gap by means of extensive ab initio simulations [Saleh et al., PCCP, submitted]. We investigated more than 70 surfaces (including non-stoichiometric ones) for all the known Ag-Sn alloys, thereby establishing which surfaces are most stable and will form in a real sample. Moreover, we systematically studied O and S chemisorption, and contextualized the results in the framework of corrosion tendency. The observed trends are ratio-

nalized in terms of structural and electronic features. Calculations on suitable model systems were performed to confirm the proposed rationale. On top of that, we present our preliminary results on molecular dynamics simulations ('ReaxFF' approach) to address what we call 'silver paradox', that is the experimentally observed preferable formation of silver sulphide over silver oxide despite O and S having almost identical chemisorption energies on Ag and Ag_2S and Ag_2O formation energies being almost identical.

O 111.4 Fri 11:15 MA 041

Temperature dependent initial sticking probability of Mg atoms on H:Si and SiO₂ surfaces — ●MIRIAM FRITSCHER¹, ULRICH HAGEMANN², and HERMANN NIENHAUS¹ — ¹Faculty of Physics and CENIDE, University of Duisburg-Essen, Duisburg — ²Interdisciplinary center for analytics on the nanoscale (ICAN), CENIDE, Duisburg

The temperature dependence of the initial sticking probability of magnesium atoms evaporated from a Knudsen-cell onto hydrogen passivated silicon (H:Si(111)) and silicon dioxide (SiO_2) substrates is investigated. Mg is evaporated stepwise onto both surfaces simultaneously and X-ray photoelectron spectra are recorded after each step to determine the growth rate of the Mg film. This is done at variable substrate temperatures between 140 K and room temperature. It was found that the sticking probability of Mg atoms is approximately the same for both surfaces at low temperatures ($T < 210$ K), whereas for room temperature it reaches zero for the SiO_2 substrate. The temperature dependence of the sticking probability on Si surfaces is significantly smaller. Furthermore, the reduction of the sticking probability on SiO_2 at room temperature is not dependent on the thickness of the SiO_2 film. Experiments indicate that a single monolayer of SiO_2 on Si results already in the dramatic decrease of the sticking probability. Once Mg atoms are sticking to the substrate they form islands and do not desorb again. A simple precursor mediated sticking-desorption model is applied to explain the findings.

O 111.5 Fri 11:30 MA 041

Interaction of an Ionic Liquid Adlayer with Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Influence of 1 Post- and Predeposited Lithium — ●JIHYUN KIM¹, FLORIAN BUCHNER^{1,2}, and R. JÜRGEN BEHM^{1,2} — ¹Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany — ²Helmholtz-Institute Ulm (HIU) Electrochemical Energy Storage, D-89081 Ulm, Germany

In this model study, we aimed toward a detailed understanding of the interaction of the battery-relevant ionic liquid 1-butyl-1-methylpyrrolidinium bis-(tri-fluoro-methyl-sulfonyl)-imide ([BMP][TFSI]) with well-defined spinel lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (111), which is a promising anode material for a lithium-ion batteries, employing X-ray photoelectron spectroscopy (XPS) in ultrahigh vacuum (UHV). Furthermore, the influence of pre- and post-deposited Li on the IL adlayer was investigated. First of all, [BMP][TFSI] mainly adsorbs as intact ion pairs on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at 300 K, except a negligible amount of decomposition products (LiF , Li_xS , Li_xSO_y , SO_x and LiN_3), which increases moderately after post-deposition of 1 ML of Li, i.e. most of the Li most likely diffuses through the IL adlayer and subsequently into the bulk of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. At 80 K, in contrast, a small amount of Li^+ remains in the near-surface regime, forming a Li-rich $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ ($x \sim 0.3$) phase. Due to the remaining Li in the near surface, the subsequent deposition of the IL results in a significant decomposition of the adlayer, which demonstrates the reactive interaction of Li with the IL adlayer even at 80 K.

O 111.6 Fri 11:45 MA 041

Measuring Heats of Adsorption of Porphyrins on Oxide Single-Crystal Surfaces — ●OLE LYTKEN, QURATULAIN TARIQ, DANIEL WECHSLER, MATTHIAS FRANKE, and HANS-PETER STEINRÜCK — Universität Erlangen-Nürnberg, Germany

Porphyrins are large organometallic complexes interesting for a variety of applications such as organic electronics and solar cells. For many of these applications the interface between the porphyrins and the substrate they are deposited on is particularly interesting. However, determining the heats of adsorption of porphyrins on surfaces is not straight forward: theoretical calculations have to include van

der Waals interactions, and experimental measurements have to consider decomposition of the monolayer simultaneous with desorption. In this study we present temperature-programmed desorption (TPD) measurements of three porphyrins, CoTPP, ZnTPP and MgTPP, from an MgO(100) surface. To reduce the influence of decomposition, which may affect the shape of the desorption peak, we use simple Redhead analysis. The accuracy of Redhead analysis depends critically on the chosen prefactor, and we use the prefactor derived from desorption of multilayers.

O 111.7 Fri 12:00 MA 041

Reversible and Efficient Photo-Switching of Azobenzene Derivatives on an Insulator Surface — •SIMON JAEKEL¹, AN-TJE RICHTER², ROBERT LINDNER², CHRISTOPHE NACCI¹, ANGELIKA KÜHNLE², STEFAN HECHT³, and LEONHARD GRILL¹ — ¹Department of Physical Chemistry, Karl-Franzens University of Graz, Austria — ²Institute for Physical Chemistry, Johannes-Gutenberg University Mainz, Germany — ³Department of Chemistry, Humboldt-University Berlin, Germany

Studying single molecular switches is of interest for a better understanding of fundamental physical and chemical processes, but also in view of their possible use in smart materials and molecular nanotechnology. Azobenzene is a prototypical molecular switch, which changes between trans and cis isomers at the central N=N bond upon an external stimulus. Adsorption on solid substrates allows to study their properties on the single-molecule scale. However, the mostly used metallic substrates can strongly influence the switching properties. Therefore, and also in view of potential electronic applications, the use of non-metallic substrates is desired. Here, we report non-contact atomic force microscopy (nc-AFM) results on the first switching of individual azobenzene molecules on an insulating calcite surface. Surprisingly,

cis isomers appear on the surface already directly after preparation, indicating kinetic trapping. It is demonstrated that unlike on metals the molecules retain their efficient photoisomerization properties known from solution. Furthermore, the photoisomerization is shown to be reversible and selective, depending on the excitation wavelength.

O 111.8 Fri 12:15 MA 041

C₆₀ adsorption on a two-dimensional oxide quasicrystal — •EVA MARIA ZOLLNER¹, STEFAN FÖRSTER¹, and WOLF WIDDRA^{1,2} — ¹Martin-Luther-Universität Halle-Wittenberg, Halle, Germany — ²Max-Planck-Institut für Mikrostrukturphysik, Halle, Germany

The recent observation of a two-dimensional oxide quasicrystal (OQC) derived from ultrathin films of BaTiO₃ on Pt(111) demonstrates that quasicrystalline structures can emerge in the heteroepitaxial growth of conventional periodic materials [1]. Due to the complexity of QCs, studies on the relation between aperiodic order and physical properties are challenging. Therefore, QC surfaces have been tested as templates for the growth of two-dimensional single element QCs formed by molecular adsorbates [2]. Here we report the first adsorption studies on the BaTiO₃-derived OQC using C₆₀ molecules. Different coverages of C₆₀ have been deposited on the OQC at different temperatures and characterized by LEED and STM. At room temperature C₆₀ molecules form hexagonal islands at the OQC surface with preferential adsorption at step edges, which indicates a weak interaction with the OQC substrate. At temperatures below 150 K the diffusion of individual C₆₀ molecules is strongly suppressed and small C₆₀ islands are formed upon adsorption. Besides local hexagonal C₆₀ arrangements, we find local C₆₀ structure with quadratic arrangement. The latter being combined into local triangle-square tilings.

[1] S. Förster et al., Nature 502, 215 (2013).

[2] J. A. Smerdon et al., Nano Lett. 14, 1184 (2014).