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SCR - Surface chemical reactions and kinetics

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INTRA-PARTICULAR MOBILITY IN SUPPORTED NANOALLOYS: FROM A METASTABLE TO AN EQUILIBRIUM STRUCTURE

SCR - Surface chemical reactions and kinetics

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The original properties of nanoscale metallic supported particles result from the large fraction of surface atoms and the finite size (3D confinement) effect in terms of electronic structure, magnetic moment, optical response, thermodynamic behavior, etc . Compared to monometallic ones, the addition of one or several metals induces complex behaviors, not always well understood, which give a larger diversity in the structure and morphology of "nanoalloys" and offer an additional degree of freedom to tune their properties. Besides the composition effect, finite matter quantity effects to the nanometer scale lead to original variations of atom arrangement, favoring a segregation behavior by surface and core contraction effects that can be opposed to kinetic trapping effects induced by the growth mode [1]. In our works, atom mobility and structural stability in Ag-based supported nanoalloys (Ag-Co and Ag-Pt) were studied through modeling and experimental in situ investigations of the structure and especially, the formation of core-shell, janus or alloyed configurations. Our idea was to choose two systems AgM (M= Co or Pt) having a strong tendency for phase separation and Ag surface segregation, with a total immiscibility for AgCo and a partial alloying for AgPt, and consequently to study the structural transitions at small size [2, 3]. The goal is to understand the inter- and intra-particular mobility in these supported nanoalloys, through the investigation of their morphological and structural evolution from a metastable to an equilibrium atom arrangement. Preliminarily, this complex behavior requires a determination of the temperature effect and the support effect on pure particle, e.g. in the Ag case [4].

Because the determination of atomic structure in nanoalloys is a complex problem, x-ray methods that probe the chemical or morphological features, are much more powerful when used together. Especially during the growth and annealing processes of these nanoalloys deposited in UHV, X-ray scattering techniques allow the determination of the structural evolution at the atomic scale (at wide angles) by GIWAXS, as well as the morphological evolution at the particle scale (at small angles) by GISAXS, providing highly complementary data, with the support of Monte Carlo simulations [5]. In addition, using anomalous effect [6], segregation or alloying phenomena can be confirmed as in the case of CoAg or PtAg systems supported by high angle annular dark-field (HAADF) and high resolution electron microscopy (HRTEM) [7].

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O1-SCR _245

INVESTIGATING CORE/SHELL PD/AU NANOPARTICLE STRUCTURE BY PROBING CO ADSORPTION WITH SFG

SCR - Surface chemical reactions and kinetics

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Interaction of molecules with nanostructures has become a growing research topic for many applications where the reduction of size and dimensionality is a major tendency: sensors, energy, plasmonics, catalysis and molecular electronics. Binding strength, stability, enhancement of interaction with light are size dependent which influence device functionalities. Probing CO vibrations on nanoparticles (NP), provides a means to understand NP size and structural/composition effects. Surface-sensitive vibrational spectroscopy is a powerful tool to address molecular environment: i.e. molecular-substrate and molecule-molecule couplings [1]. Al_2O_3/Ni_3Al(111) surfaces allow growing high density narrow size distributed NPs [2], particularly well adapted to study small cluster reactivity [3] and promising template for molecular electronic purposes.

Sum Frequency Generation (SFG) experiments have been conducted on CO adsorbed on high-density, narrow size distributed core-shell (Pd/Au) NPs grown on ultrathin Al_2O_3 films on Ni_3Al(111) done in UHV conditions. On bare Pd NPs, CO bind on bridge sites. CO frequency is coverage and NP size-dependant as already observed [1]. For 1 monolayer (ML) thick Au shell at 300 K, a new site is observed at higher frequency and narrower bandwidth, indicating a lower adsorption energy while bridge Pd sites have disappeared. At mbar pressure, CO adsorbs on gold as expected. On 2 ML thick Au shell, almost no CO are observed. The new site is attributed to CO linearly bonded on isolated Pd which migrated from Pd core towards Au shell surface upon CO adsorption [4-5] even at very low CO dose. Pd:Au alloy formation at the core/shell interface is limited to 1-2 ML. Upon CO+O adsorption in the mbar range, NP shell structure is even more modified.

CO-NP interaction varies sensitively with shell thickness. Pd:Au alloy formation is observed but limited to few ML. Au electronic structure is strongly modified by underneath Pd core. Adsorption energies and activation barriers are probably impacted and may affect the catalytic reactivity. SFG spectroscopy of CO on core/shell NPs allows measuring shell thickness with high precision and following structural changes.

Keywords: Core/Shell nanoparticle, alloys, CO, Sum Frequency Generation

Thanks

We would like to thank L. Guillemot for preliminary STM images of Al_2O_3 supported nanoparticles.

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O2-SCR _336

PALLADIUM AND CARBON MONOXIDE OXIDATION AU30PD70(110) UPON OXYGEN AND CARBON MONOXIDE ELEVATED PRESSURE

SCR - Surface chemical reactions and kinetics

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Since supported gold nanoparticles are known to be effective for the low temperature CO oxidation [1], numerous studies has been devoted to gold based catalyst such as Au_XPd_{1-X} alloy to improve the catalytic performance of both elements.

In this context we studied $Au_{30}Pd_{70}$(110) surface from UHV up to near ambient pressure of oxygen and CO as well as reactive condition for CO oxidation (CO + O_2). We coupled in situ structural analysis by GIXRD (Grazing Incidence X-Ray Diffraction) to gas analysis by mass spectroscopy, thanks to an homemade setup [2] . This was completed by chemical analysis by AES for each of the main states of the system.

The (1x1) Au rich surface in UHV, at room temperature, strongly evolves under oxygen when increasing the pressure up to 500 mbar and the temperature up to 200°C. Three main (P,T) domains can be distinguished : (1) oxygen induced (1x2) reconstruction with a Pd enrichment of the outermost surface plane (2) Pd segregation of over several atomic planes without long range order as detected by GIXRD (3) formation of a well-defined PdO(100) film at the surface.

High pressure of CO also induces palladium segregation [3] therefore it appears that under (semi) realistic conditions gold tends to disappear from the $Au_{30}Pd_{70}$(110) surface.

The oxygen induced PdO film is also a very interesting model to study the mechanism of the CO oxidation on pure palladium surface that remains very debated [4]. This PdO(100) film was followed under reactive conditions by adding CO pressure from 0.1 to 10 mbar to the already introduced oxygen (T from RT to 200°C). Reduction and then re-oxidation was observed for a temperature which depends on the CO pressure and the reduced phase was found to give a much lower rate for CO conversion into CO_2. The behavior is quite similar to what was observed for Pd nanoparticles upon CO and oxygen exposure leading to stress the existence of a PdC_X phase in these conditions [5], which could to be the main rate-limiting factor to the CO oxidation rate in semi-realistic conditions.

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O3-SCR _238

EXPERIMENTAL AND THEORETICAL STUDIES ON OXIDATION OF CU-AU ALLOY SURFACES —EFFECT OF BULK AU CONCENTRATION—

SCR - Surface chemical reactions and kinetics

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We report results of our experimental and theoretical studies on the oxidation of Cu-Au alloy surfaces using hyperthermal O_2 molecular beam (HOMB). We determined, both experimentally (HOMB + SR-XPS) and theoretically (DFT-based calculations), the surface Au concentration profile of Cu-Au alloys (viz., Cu_3Au, CuAu, and Au_3Cu) in vacuum. We observed strong Au segregation to the top layer of the corresponding clean (111) surfaces. The degree of segregation strongly depends on the bulk Au components. The richer the Au bulk components, the richer the Au surface segregation. The Au-rich layers form a protective layer against oxidation of the Cu-Au alloys. After exposing the corresponding surfaces to HOMB, we found that surfaces with higher concentrations of Au showed lower susceptibility to oxidation, as determined by the low O sticking probability. Protection again oxidation fails for processes occuring above 300K. At 500 K, Cu segregates on the surface, breaking the protective layer, and oxidation proceeds on the surface, albeit rather slowly as there is still the subsurface. This gives further insight into how we can control the reactivity and robustness of a material, i.e., via the bulk component and the segregation profile. More details will be presented at the conference.

Thanks

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O4-SCR _348

IDENTIFYING THE ADSORPTION CONFIGURATION AND THERMAL DECOMPOSITION MECHANISM OF GUAIACOL ON PT(111): AN INTEGRATED X-RAY PHOTOELECTRON SPECTROSCOPY AND DENSITY FUNCTIONAL THEORY STUDY

SCR - Surface chemical reactions and kinetics

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Guaiacol adsorption on Pt(111) and its thermal decomposition were studied by a combination of density-functional theory (DFT) and in-situ high-resolution x-ray photoelectron spectroscopy (HR-XPS). This organic molecule serves as a model bio-oil compound which is of interest as a renewable source for liquid fuels [1,2]. Time-dependent isothermal adsorption on Pt(111) and temperature-programmed reactions were conducted at beamline U49/2-PGM1 at BESSY II. Calculations of total energies and C 1s and O 1s core-level binding energies of adsorbed species and intermediates were performed using the Vienna Ab-initio Simulation Package.

DFT with van der Waals corrections suggests adsorptions sites whose core-level binding energies are in good agreement with experimental data for C 1s and O 1s levels. The molecule preferentially adsorbs intact in a bridge adsorption site with the molecular plane parallel to the surface at around 230 K (Figure 1a). The decomposition of guaiacol is followed experimentally by temperature-programmed XPS. Figure 2 shows the resulting C 1s evolution. The simulations consider different decomposition mechanisms by stepwise loss of hydrogen atoms or the methyl group, including ring breakage. Two stages are distinguished: in a first stage up to 350 K the methyl group is removed leading to a 1,2-benzoquinone species (Figure 1b). The second step realizes the ring opening and the release of CO up to 450 K (Figure 1c). A quantitative analysis of the data enables cross-checks between the C 1s and O 1s data from both experiment and theory and further supports the suggested dissociation route. Such a combined experimental and theoretical approach is essential for unravelling the elementary reaction mechanism of complicated reaction pathways on metal surfaces which can be used to better guide the development of highly selective catalysts.

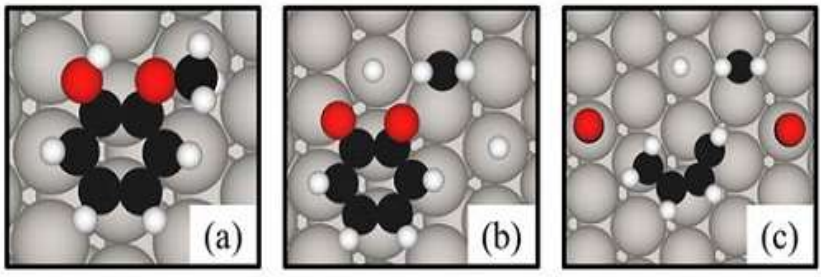

Fig. 1: Calculated geometry of (a) guaiacol adsorbed on Pt(111) for the most stable adsorption site; (b) 1,2-benzoquinone species, and (c) ring opening species from the decomposition of guaiacol on Pt (111).

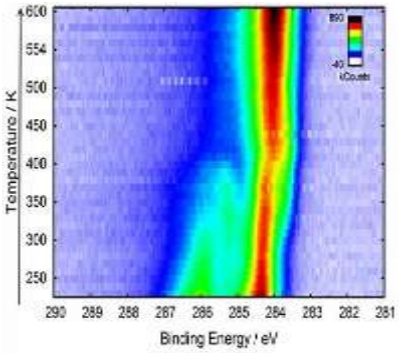

Fig. 2: Color-coded density plot of TP-XPS C 1s data of guaiacol adsorbed at 230 K on Pt(111).

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O5-SCR _149

REACTION DYNAMICS OF FORMATE FORMATION AND DECOMPOSITION ON CU SINGLE CRYSTAL SURFACES

SCR - Surface chemical reactions and kinetics

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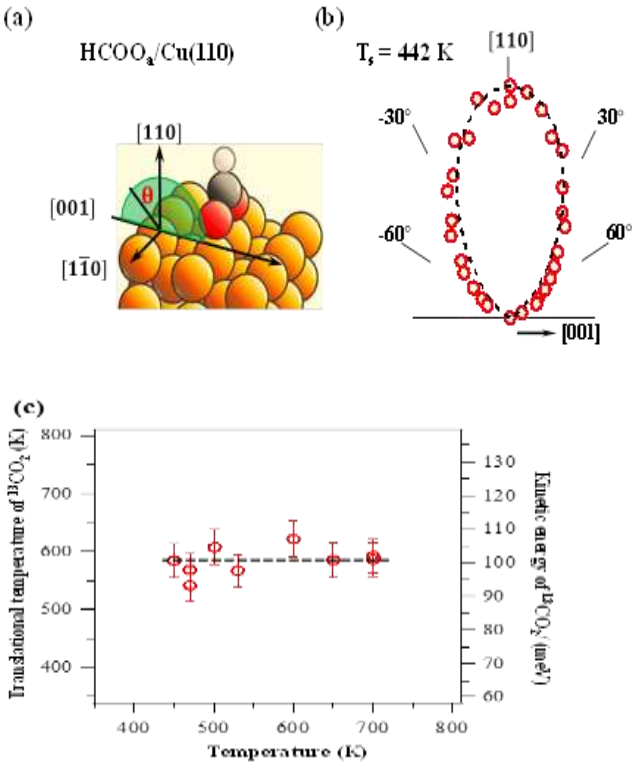
Thermal catalytic reduction of CO_2 to formate (CO_2 + 1/2H_2 → $HCOO_a$) is of an initial and essential step to methanol synthesis over Cu-based catalysts. In this work, we have studied the dynamics of formate formation and decomposition (reverse reaction) on Cu(110), Cu(111) and Cu(100) surfaces by supersonic molecular beam experiments and angle-resolved time-of-flight measurements of product CO_2 emitted from the surface, respectively. For the formate formation reaction, it has been found that CO_2 directly attacks with a hydrogen adatom (H_a) to form formate intermediate on Cu catalysts via an Eley-Rideal (ER)-type mechanism under thermal non-equilibrium through molecular beam experiments. We found that both the translational energy and vibrational energy of CO_2 are indispensable to overcome the reaction barrier of formate formation, whereas the reaction rate is independent of the surface temperature. For the formate decomposition reaction, we have measured angular intensity distribution and translational energy of product CO_2 in a steady state reaction of HCOOH and O_2 on Cu(110). The angular distribution of CO_2 shows a sharp collimation, $\cos^6\theta$, perpendicular to the surface as shown in Fig.1a,b. The translational temperature of CO_2 desorbed perpendicular to the surface is 570 K independent of the surface temperature as shown in Fig.1c. These results clearly indicate that the decomposition of formate is of thermal non-equilibrium. The detail reaction dynamics of both formation and decomposition of formate will be discussed.



Thanks

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O6-SCR _194

XPS AND STM STUDIES OF THE EFFECT OF OXYGEN CONCENTRATION ON HCL REACTION AT CU(100) AND (111) SURFACES

SCR - Surface chemical reactions and kinetics

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Chlorine use in industry is very atom inefficient and has a negative environmental impact, 30% going to waste. As a result there is intense interest in catalytic systems that use or recover chlorine more efficiently. Copper is a common catalyst in these systems and oxygen a common co-reactant but O/Cl reactions at copper surfaces is poorly understood.

We have studied HCl/O(a) at Cu(110) surfaces[1] and shown surface structures consisting of <100> orientated features identified as chlorine covered [210] facets.[2] But how does oxygen facilitate the formation of these facets. Is its role to disrupt the surface of the copper accelerating mass transport of copper to the reconstruction? Or does oxygen provide a pathway for the removal of hydrogen increasing HCl decomposition? Our aim in this paper is to explore how the transition between a submonolayer oxygen state to the beginnings of an oxide affects reactivity at Cu(100) and Cu(111) surfaces both kinetically and structurally, extending a recent study on Cu(100).[3] Reaction of HCl with Cu(100) surfaces is limited to the formation of a monolayer but this barrier is removed in the presence of oxygen leading to the facile formation of multilayer chlorides, Figure 1. A similar effect is observed on Cu(111). We show the surprising reactivity of heavily oxidised surfaces despite the lack of clean copper sites: reaction being initiated with the creation of defective channels in the oxide that subsequently give rise to the development of copper chloride islands.

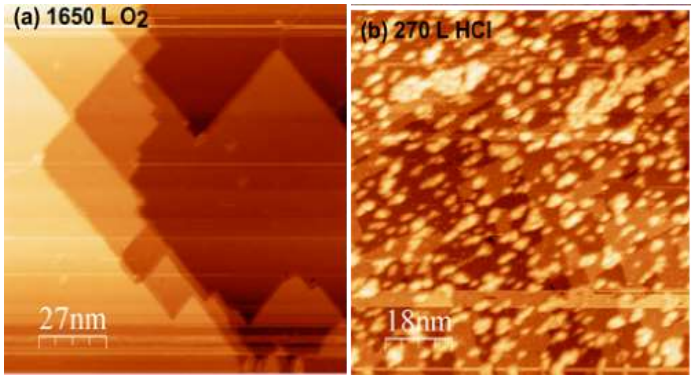

Figure 1: *STM images of (a) Cu(100) surface with σ_O = 1.6x10^{15} cm^{-2} after exposure to O_2 at 523 K. (b) surface in (a) after reaction with HCl at 295 K. CuCl islands are evident on the steps.*

Thanks

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Suadi Arabia for providing a studentship for HA

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O7-SCR_466

OPERANDO CO OXIDATION STUDY OF MGAL2O4(001)-SUPPORTED PT0.33RH0.67 NANOPARTICLES USING SURFACE X-RAY DIFFRACTION

SCR - Surface chemical reactions and kinetics

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Pt-Rh alloy nanoparticles on oxide supports are widely employed in heterogeneous catalysis with applications ranging from chemical industry to automotive exhaust control [1]. To improve the catalyst performance it is essential to grasp the interplay between the oxides forming on the particle facets, the particle size/shape and the sample's catalytic activity [2,3]. Moreover, it is of paramount interest to unravel the underlying mechanisms of particle sintering which is one of the main reasons for catalyst deactivation [4]. This triggers the need for atomic-scale studies of supported nanoparticles during catalytic reactions under realistic pressure and temperature conditions.

Here we present our results on epitaxial $MgAl_2O_4(001)$-supported $Pt_{0.33}Rh_{0.67}$ nanoparticles "at work" during carbon monoxide oxidation obtained in a dedicated in-situ catalysis chamber [5] and by combining surface x-ray diffraction and in-situ mass spectrometry at beamline P09 at the PETRA III storage ring at DESY (E= 11.2 keV).

Our time-resolved gas-switching experiments allowed for monitoring with unprecedented structural resolution at the atomic scale the formation of different surface oxides on the particle facets, and for relating the oxides' emergence to the sample's catalytic activity. The combination of high-resolution reciprocal space mapping (see Fig. 1) and Bragg peak scanning along high symmetry directions facilitated to unravel quantitatively the activity-induced particle shape and size changes, and yielded along with x-ray reflectivity measurements insights into the dramatic mass transport on the sample surface during particle sintering.

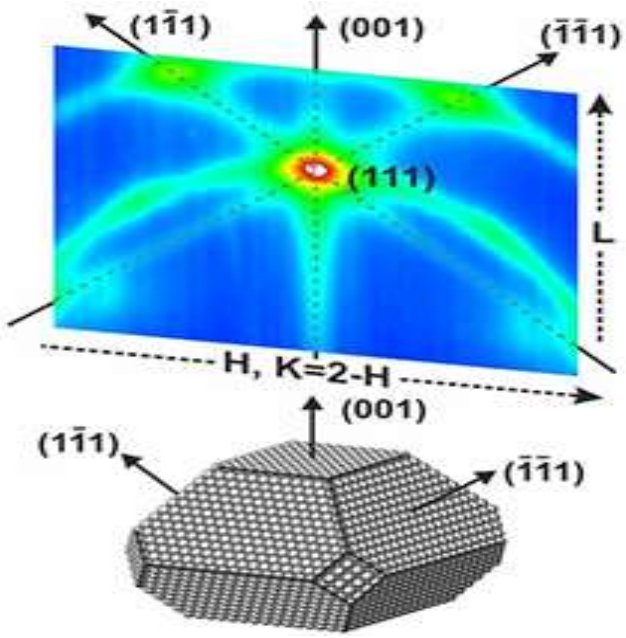

Fig. 1: High resolution reciprocal space map measured under reaction conditions containing signals from (111)- and (100)-facets of the $Pt_{0.33}Rh_{0.67}$ particles.

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O8-SCR _317
ANISE ON PT(111): ADSORPTION AND REACTIVITY

SCR - Surface chemical reactions and kinetics

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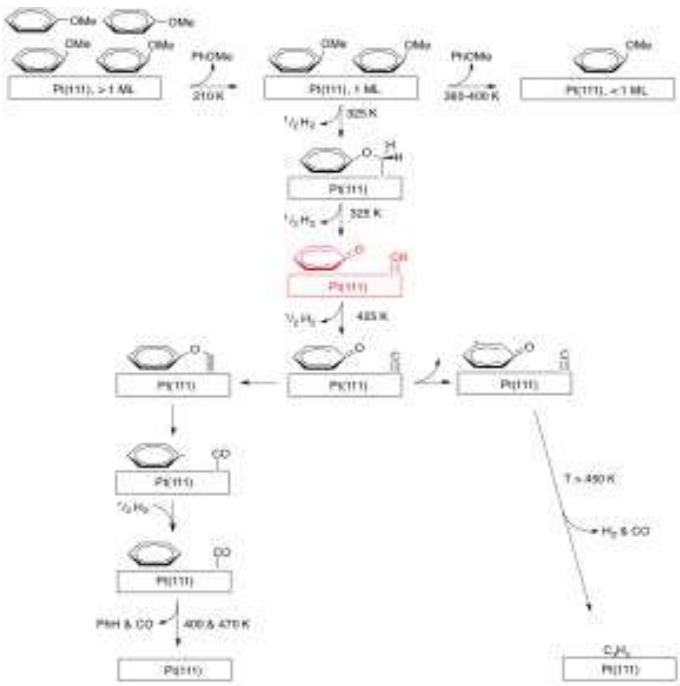
The transformation of biomass into useful chemical compounds with applications in a large range of industries represents the future of a clean and sustainable world. In this study, some fundamental questions regarding the conversion of lignin (primary wood component) into valuable compounds are addressed. We are investigating the reactivity of anisole with Pt metal surfaces in order to compare the facility of the C-H vs. C-O vs. C-C bond cleavage. In the present work, we have chosen a single of Pt(111) to determine the reaction pathways (Figure1).

The adsorption and decomposition of Anisole on clean Pt(111) was studied as a function of temperature and exposure by means of X-ray photoelectron spectroscopy (XPS),Temperature programmed desorption (TPD) and DFT calculations (optPBE functional). Anisole was absorbed on the surface below 120K. TPD and XP spectra revealed that an amount of anisole molecularly desorbs at 260K (83 KJ/mole) for multilayer exposure and DFT is about 61 KJ/mole. For the saturated monolayer part of the anisole molecularly desorbs between 360-400K but it mainly decomposes to produce Benzene, CO and H2. At this point, anisole desorption energy (DFT: 166 kJ/mol) is much higher than the first dehydrogenation barrier (DFT: 108 kJ/mol) suggesting that hydrogen should be produced when anisole decomposition starts. Results will be further discussed broadening our fundamental understanding of catalytic reactions of lignin models on metal surfaces.



O9-SCR_470
ATOMIC-SCALE STUDY OF THE ZIEGLER-NATTA CATALYST

SCR - Surface chemical reactions and kinetics

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The reaction of polymerization of olefin is industrially performed through a catalytic reaction based on the Ziegler-Natta catalyst. Since the first discovery of Ziegler and Natta, the catalyst has undergone different modifications in order to improve the velocity, the yield and the stereoselectivity of the polymerization reaction[1]. Nowadays, the industrially used catalyst consists of a precatalyst composed by a surface of $MgCl_2$ on which the precursor of the active center, $TiCl_4$, is anchored, in presence of a Lewis base. The precatalyst is activated by alkylaluminium[2].

Despite the copious research efforts devoted to the improvement of the activity of the catalyst, its structure at molecular scale and the role of its components are not yet completely understood. An atomic scale understanding of the Ziegler-Natta catalyst is indeed of key importance for the design of more active and selective catalyst.

Our work is focused on the computational study of the Ziegler-Natta catalyst from a molecular point of view. The study is performed at the Density Functional Theory (DFT), in the Generalized Gradient Approximation (GGA) using PBE functional and planewave basis set, as implemented in the VASP package. The model system chosen is a (110) $MgCl_2$ surface, on top of which a $TiCl_4$ unit is adsorbed.

The calculated data are closely related to experiments, and, in order to compare the computed results with the experimental data available, NMR spectra are calculated on the obtained minima.

This work can be divided in two parts. The first part is devoted to the structural characterization of the precatalyst $MgCl_2$/$TiCl_4$/Lewis base, with ethanol as Lewis base. The principal aim of this part is the understanding of the interaction of EtOH with the surface and in particular with the precursor of the active center. The energy variation in EtOH high coverage condition is also taken into account. Several structures are taken into account in order to obtain a wide and realistic view of the precatalyst.

The second part is inherent the activation process, obtained from the interaction with $AlEt_3$. In this case our attention is more focused on the reaction paths bringing to the catalyst.

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O10-SCR _173

SIMULTANEOUS AFM/STM STUDY OF CHIRALITY AND ON-SURFACE CHEMISTRY OF DIBENZO[7]HELICENE DEPOSITED ON AG(111)

SCR - Surface chemical reactions and kinetics

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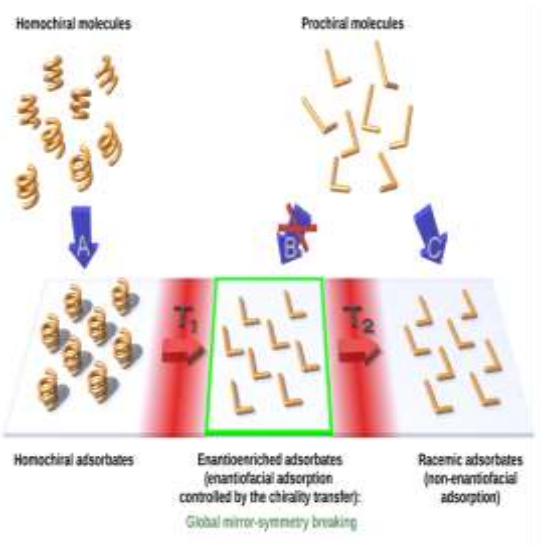
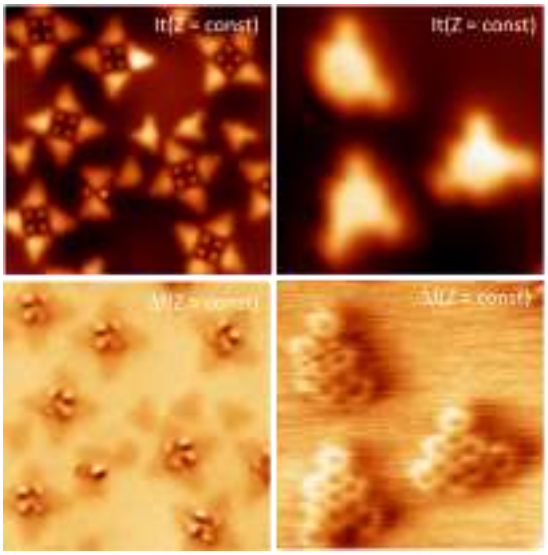
High-resolution AFM images of single molecules brought completely new perspectives in investigation of chemical processes on surfaces. Here we investigated on-surface chemistry of Dibenzo[7]helicene deposited on Ag(111). Annealing above 100C has induced a [4+2] Diels-Alder cycloaddition reaction, which has initiated complex chemical processes on the surface. We have been able to identify an intermediate step and two final products by means of simultaneous AFM/STM measurements with Xe-tip. The intermediate products form complex chiral structures (dimers, trimers and tetramers). To understand the origin of a chiral orientation, we investigated both the racemic mixture and pure (+)-(P) enantiomer of helicene molecules deposited on the Ag(111) surface. We have found that the chiral orientation of the individual molecules as well as their complexes is driven both by chirality of helicene molecules initially deposited on the surface and annealing conditions. We have demonstrated for the first time a chemical control over the final enantiofacial adsorption of non-chiral molecules on the non-chiral metal surface that has resulted in a global mirror-symmetry breaking.





O11-SCR _226

PHTHALIC ACID ON MGO(100) AS A MODEL FOR THE ANCHORING OF CARBOXYLIC ACID FUNCTIONALIZED LARGE ORGANIC MOLECULES

SCR - Surface chemical reactions and kinetics

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The anchoring of large functional organic molecules, such as porphyrins, to oxide surfaces is important in many areas of research. Using high-resolution synchrotron radiation X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure (NEXAFS) and temperature-programmed desorption (TPD), we report on the adsorption of phthalic acid on MgO(100) as a model for the anchoring of carboxylic acid functionalized, large organic molecules. Already below 150 K we find a competition between anhydride and carboxylate formation, and it is not until the surface has been completely covered, and thereby passivated, by carboxylate that we see the growth of intact phthalic acid multilayers. As the surface is heated, phthalic anhydride desorbs at 250 K and phthalic acid at 325 K, leaving a densely-packed carboxylate layer on the surface. NEXAFS confirms the upright standing nature of the carboxylate layer, which is stable up to 600 K for the densely-packed layer. At lower coverages the carboxylate layer is less stable and decomposition occurs already below 500 K.

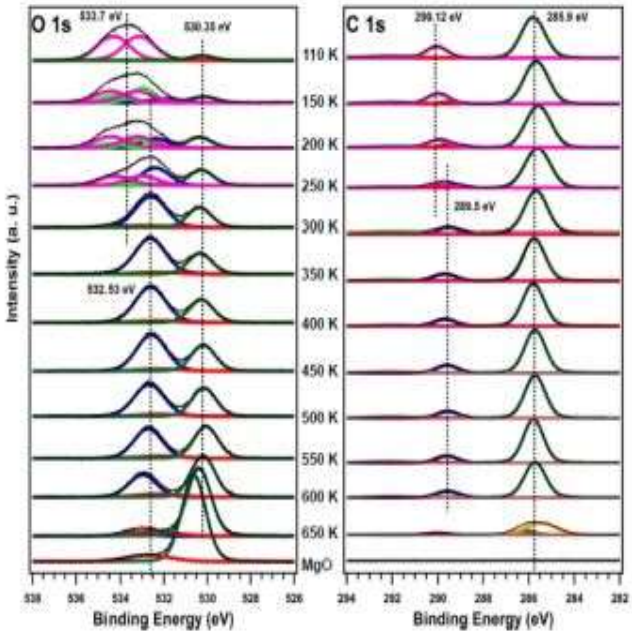

Figure: *O 1s and C 1s X-ray photoemission spectra of 4 ML phthalic acid adsorbed on MgO(100) at 100 K and annealed to the indicated temperatures.*

Thanks

This project is supported by the DFG through FOR 1878 (funCOS).

O12-SCR _221

MECHANISTIC STUDY OF NO REDUCTION BY CR-PHTHALOCYANINE MONOLAYER INVESTIGATED BY DFT CALCULATIONS

SCR - Surface chemical reactions and kinetics

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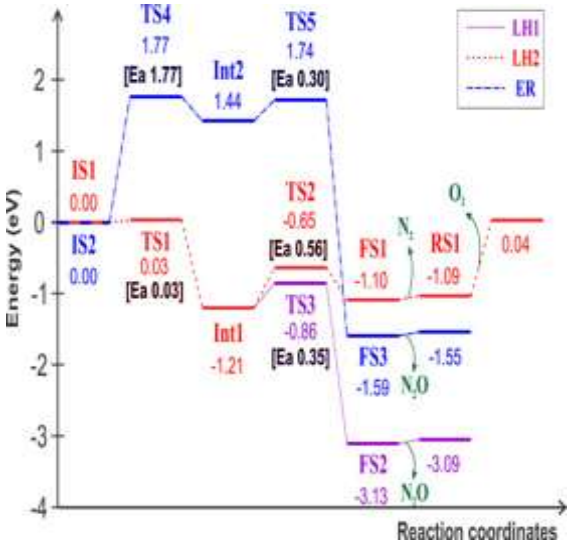
The reaction mechanism of nitric oxide (NO) reduction to nitrous oxide (N_2O) and N_2 catalyzed by Cr-phthalocyanine sheet (CrPc) was investigated by periodic density functional theory (DFT). The results showed that direct NO dissociation on the catalyst is inhibited by large energy barrier owing to the difficulty on the direct cleavage of the strong NO bond. The dimer manner in which the two NO come to play is more preferred via the three competitive mechanistic pathways consisting of two Langmuir-Hinshelwood (LH1 and LH2) and one Eley-Rideal (ER). N_2O is produced from LH1 and ER with the activation barriers (Ea) of 0.35 and 1.17 eV, respectively, while N_2 is a product from LH2 with the Ea of 0.57 eV. All the three pathways are highly exothermic process. Based on the energetic aspect, LH1 is the kinetically and exothermically most favorable pathway (Ea of the rate-determining step is 0.35 eV). Therefore, we predict that NO can be easily reduced by CrPc at mild condition. In environmental implication, CrPc would be a promising catalyst for abatement of NO at low temperature.



Thanks

The authors wish to thank the National Nanotechnology Center (NANOTEC) through “the Flagship Clean Air Program” for financial support.

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O13-SCR _239

ENERGY RELEASE AND SURFACE CHEMISTRY OF THE MOLECULAR SOLAR ENERGY STORAGE SYSTEM NORBORNADIENE / QUADRICYCLANE

SCR - Surface chemical reactions and kinetics

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Fossil fuel-based energy technologies lack a long-term perspective. The further development of existing renewable energy concepts is needed, regarding energy distribution and storage. One possible scenario is the storage and conversion of solar energy by chemical means in the form of strained organic molecules, e.g., the Norbornadiene (NBD) / Quadricyclane (QC) pair: by absorption of light NBD is transformed to the energy rich QC; this can be catalytically transformed back to NBD and thereby release the stored energy.

We investigated the adsorption of the strained multi-cyclic hydrocarbon QC and its strain-released counterpart NBD as well as the conversion of QC to NBD and their decomposition over different catalytically active metal surfaces, in particular Ni(111) and Pt(111). We address this model system with multiple techniques to gain a full understanding of the reaction details. Ultraviolet photoelectron spectroscopy provides characteristic spectra for NBD and QC. By applying heating ramps to the samples, we can observe the thermally-triggered conversion of QC to NBD, except for the Pt(111) surface, where the reaction from QC to NBD is taking place already below 120 K. High-resolution X-ray photoelectron spectra of the adsorption at 120 K and during the heating ramps reflect the different interaction strength between molecules and surface and reveal a fundamentally changed decomposition behavior of NBD at higher temperatures for the different surfaces. Additionally, we will use infrared reflection absorption spectroscopy and DFT calculations to further study the energy release and gain insights to the adsorption mechanisms.

Thanks

We thank the Cluster of Excellence ‘Engineering of Advanced Materials’ and the Helmholtz-Zentrum Berlin for the allocation of synchrotron beamtime.

O14-SCR _206

CHEMICAL BATH DEPOSITION OF MOLYBDENUM DISULFIDE ULTRA-THIN FILMS

SCR - Surface chemical reactions and kinetics

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Transition metal dichalcogenide (TMD) materials are currently widely sought after for their application in semiconductor and nanoelectronic devices. The band gap energies of these materials range from semiconducting to insulating based on the selection of transition metal and chalcogenide.[1] Molybdenum disulfide is a TMD which has applications in nanoelectronic devices due to its tunable bandgap ranging from 1-2 eV. By using templated substrates such as highly oriented pyrolytic graphite (HOPG) and sapphire we have successfully deposited large area ultra-thin molybdenum disulfide films using chemical bath deposition (CBD), a liquid based technique. The CBD method is an ion exchange reaction between a metallic cation and chalcogenide anion under ambient conditions in aqueous solutions. The simplicity of this technique lends itself to be easily adapted to deposit other TMDs of interest such as molybdenum diselenide or tungsten disulfide. By systematically studying reaction conditions and characterizing synthesized materials using XPS, SEM, AFM, Raman, and TOF SIMS a better understanding of the material and CBD technique is found.

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O15-SCR _99

INTERACTION OF IONIC LIQUIDS WITH LITHIUM METAL FILMS STUDIED WITH PHOTOELECTRON SPECTROSCOPY

SCR - Surface chemical reactions and kinetics

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As ionic liquids (ILs) exhibit good ion conductivities, high temperature stability and large electrochemical windows together with a good solubility for lithium salts, they are of potential interest as electrolyte for non flammable Li based batteries, like e.g. lithium/air batteries. To enable good cycle stabilities the interaction of electrolyte and lithium on electrode surfaces has to be investigated carefully.

This can be achieved by disassembling of previously cycled cells and analysis of the electrode surface structure. Recently X-ray Photoelectron (XP) and infrared spectroscopy has been applied to analyze the solid electrolyte interface of a Ge electrode after lithiation/delithiation in the ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide containing (Py1,4]TFSI) 0.5 M lithium bis(trifluoromethylsulfonyl)imide [1] A variety of decomposition products of the ionic liquid prove that an interaction of cations and anions with lithium should have happened.

Due to the low vapor pressure this interaction can be investigated on a fundamental level by preparing thin molecular films of Ionic Liquids in a Physical Vapor Deposition process under ultra-high vacuum conditions on lithium adsorbed on a copper surface. XP spectroscopy applied to the freshly prepared sample exhibit an interaction of the ionic liquid with lithium even at open circuit potential [2]. Thereby, the IL 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([OMIm]TFSI) adsorbed on Li/Cu [2] shows a rather different reaction mechanism compared to the study of [Py1,4]TFSI adsorbed on Li/Cu by Buchner et al. [3].

Thus the interaction of [Py1,4]TFSI, [OMIm]TFSI and 1-butyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide ([Py1,4]FSI) with lithium is analyzed in a comparative study with photoelectron spectroscopy showing reaction products of the ionic liquid and lithium, which give an insight into the individual role of cations and anions in addition.

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O16-SCR _150

FIRST-PRINCIPLES SIMULATIONS OF PLATINUM-ASSISTED WATER ETCHING OF SIC

SCR - Surface chemical reactions and kinetics

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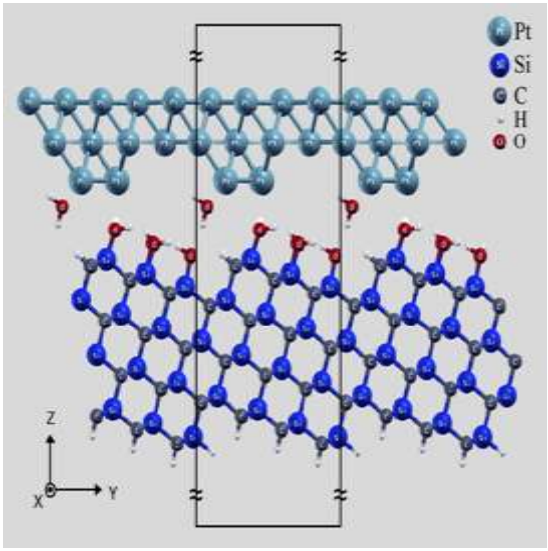
Owing to its excellent physical properties, silicon carbide (SiC) is a promising semiconductor material for electronic applications demanding high-temperature and high-power conditions. Such applications require high-quality and crystally undamaged SiC surfaces. To fulfill the growing demands and requirements of high-accuracy surface processing and low cost fabrication, chemical planarization using a catalyst pad in aqueous solutions, which we term catalyst-referred etching (CARE), has been proposed. This technique was successfully applied to the planarization of SiC wafers using hydrofluoric acid (HF) as the etchant. The obtained surface was atomically smooth with a single bilayer step-and-terrace structure over the entire wafer.

Recently, Isohashi et al. [1,2] reported that CARE performed using Pt and water as the etchant, called water-CARE, could planarize a SiC wafer to a flat surface with a rough-mean-square roughness lower than 0.1 nm. To understand the mechanism, we performed first-principles molecular dynamics calculations using the Simulation Tool for Atom Technology (STATE) program package, which has been successfully applied for investigations on metals, semiconductors, and organic materials. The calculations were based on the DFT within a GGA of PBE. The barrier height was evaluated by means of the climbing image nudged elastic band method. A step-and-terrace 3C–SiC (111) surface of four bilayers and Pt (111) surface layers were used as the calculations model as shown in Fig. 1. The model entails periodically repeated unit cells.



The mechanism is considered a dissociative adsorption of water/HF molecules to the Si–C bonds at the topmost Si surface [2,3]. The results show that the barrier height of the Si–C back bond breaking with Pt as the catalyst is 0.8 eV for HF CARE and 0.75 eV for water-CARE, which are smaller than the values obtained without the Pt catalyst. The gross activation barrier strongly correlates with the stability of the metastable state and is reduced by the formation of Pt–O chemical bonds, leading to an enhancement of the etching reaction.

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I21_SCR_455
SURFACE PROPERTIES OF ELEMENTAL 2D MATERIALS IN AMBIANT CONDITIONS

SCR - Surface chemical reactions and kinetics

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Over the past two decades, elemental nanomaterials, such carbon nanotube, graphene and more recently exfoliated black phosphorus (bP), have been studied for their intriguing low-dimensional semiconducting properties. These works have been largely motivated by the advancement of flexible electronics, but also because of intriguing optical effects induced by 1D and 2D confinement. Here we will first review our work on the surface properties of these nanomaterials and highlight the impact of electronic confinement on their surface chemistry. The common feature that emerges is the presence of ubiquitous charge transfer reactions in air between nanostructures and the water/oxygen redox couple. The reaction was found to induce strong environmental effects, such as p-doping of graphene [1], suppression of electron conduction in carbon nanotubes [2], leak current in Si nanowire field-emitters [3] and photo-induced oxidation of exfoliated black phosphorus layers [4]. A general reaction scheme based on Marcus-Gerischer theory is used to discuss this surface chemistry and to help develop stable interfaces with those materials.

To better highlight this chemistry, we will discuss in more detail the case of bP degradation in air [4]. We took advantage of a procedure carried out in a glove box to acquire the optical and electrical properties of the layers in their pristine states. Mono-, bi- and multilayered bP samples were extensively studied using Raman (See Figure). The degradation of the layers was probed in ambient conditions using TEM-EELS, LEEM, AFM and *in-situ* Raman spectroscopy. The experiments reveal that a combination of oxygen, light and moisture provides the essential ingredients leading to the oxidation of the layers. They also highlight a surprising thickness dependent kinetics of this photo-oxidation reaction, which behavior is consistent with the electron transfer model (redox reaction) influenced by quantum confinement.

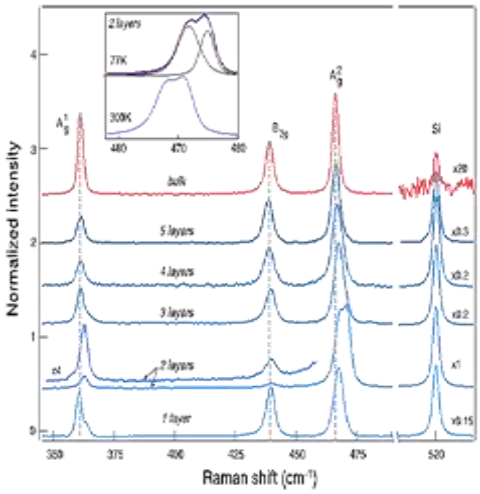

***Figure**: Raman spectra of bP layers. Highlighted (inset) is the splitting of the A^2_g mode for the bilayer, which displays an enhanced Raman intensity.*

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P2-SCR_112
ADSORPTION AND REACTIONS OF BIFUNCTIONAL 2-CHLOROPROPANOIC ACID ON CU(100) AND O/CU(100)

SCR - Surface chemical reactions and kinetics

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Surface chemistry of organic acids on transition metal surfaces, with or without surface modifiers, is of interest to a wide range of applications, such as corrosion inhibition and heterogeneous catalysis [1]. Chemisorbed bifunctional molecules are valuable, potential candidates for surface functionalization [2]. On Cu(100), only a small portion of the adsorbed CH3CHClCOOH molecules undergoes O–H or C–Cl bond scission at 120 K. After the complete O–H bond scission for the adsorbed molecules at 250 K, two intermediates of CH3CH2COO(a) and CH3CHClCOO(a) are generated on the surface. The CH3CHClCOO(a) decreases continuously due to C–Cl bond scission in the temperature range of 250 K~400 K, being transformed into CH3CH2COO(a). At a temperature higher than 400 K, the CH3CH2COO(a) starts to decompose to form H2, H2C=CH2, CO, CO2, which are desorbed between 400 K and 500 K. Other reaction products of HCl and CH3CH=C=O are generated above 710 K. The presence of preadsorbed oxygen promotes O–H bond cleavage of CH3CHClCOOH at 120 K, but suppressing the C–Cl bond dissociation. About a half of the CH3CHClCOOH molecules undergoes O–H scission at 120 K, forming CH3CHClCOO(a), and only a trace amount of the molecules undergoes C–Cl breakage even at 250 K. Upon heating to 380 K, two intermediates of CH3CH2COO(a) and η2-CH3CHCOO(a) are generated, at the sacrifice of CH3CHClCOO(a). On the oxygen-precovered Cu(100), the thermal decomposition products of the chloropropanoic acid are similar to those from the clean surface.

Keywords: chloropropanoic acid, Cu(100), XPS, RAIRS, TPR/D

Thanks

The Ministry of Science and Technology, Republic of China

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P3-SCR_207

GA ON SIO2 AS CATALYST FOR NANOWIRE GROWTH: INVESTIGATION BY X-RAY PHOTOELECTRON SPECTROSCOPY

SCR - Surface chemical reactions and kinetics

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GaAs (NWs) are presently intensively studied because of their potentialities for microelectronics, photonics and energy harvesting. GaAs NWs must be grown using Ga as catalyst (auto-catalyzed growth) in order to avoid Au, which endangers optoelectronic performances. Typically, this auto-catalyzed growth is performed directly on Si substrates without any removal of the native oxide [1-2] or on a SiO_2 layer previously deposited on GaAs wafers [3]. This oxide layer is thought to favor droplet formation with enhanced chemical potential compared to the SiO_2 layer. However, despite this strong interest for the Ga/SiO_2/Si system, the mechanism of the droplet formation and the nature of the chemical interaction between the metal and the substrate is not yet fully understood.

The Ga-Si system is rather different from the Au-Si one. First, unlike gold, gallium is liquid at low temperature (about 30 °C). Second, the eutectic $Ga_{1-x}Si_x$ contains a very small amount of silicon: only 5.10-8 % vs 18.5 % in $Au_{1-x}Si_x$ eutectic. Third, Ga can be easily oxidized and most Ga oxides are stable: for example, thermal and ozone Ga oxides cannot be removed below 582 ± 1 °C and 638 ± 1°C, respectively. However, it has been shown that the removal of native oxides from GaAs wafers can be obtained at lower temperature by converting stable Ga_2O_3 to volatile Ga_2O by exposure to Ga metallic flux.

Using atomic force microscopy and x-ray photoelectron spectroscopy we have studied the effect of the growth temperature (from 50 °C to 700 °C) on the formation of the Ga droplets. Our results show that the size and density of Ga droplet can be controlled by the deposition temperature. This initial configuration of the Ga droplets is of special interest as it determines NWs dimensions and repartition. The evolution of the Si2p, O1s, Ga3d and As3d core levels as a function of the growth temperature allows for displaying interfacial Ga oxides in association with a dewetting phenomenon. Finally, the mechanism of formation of pinholes catalyzed by droplet in the SiO_2 film is discussed.

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P4-SCR_299

THE HYDRATED ELECTRON AT THE ICE SURFACE: INSIGHT INTO DISSOCIATIVE ELECTRON ATTACHMENT TO ADSORBATES

SCR - Surface chemical reactions and kinetics

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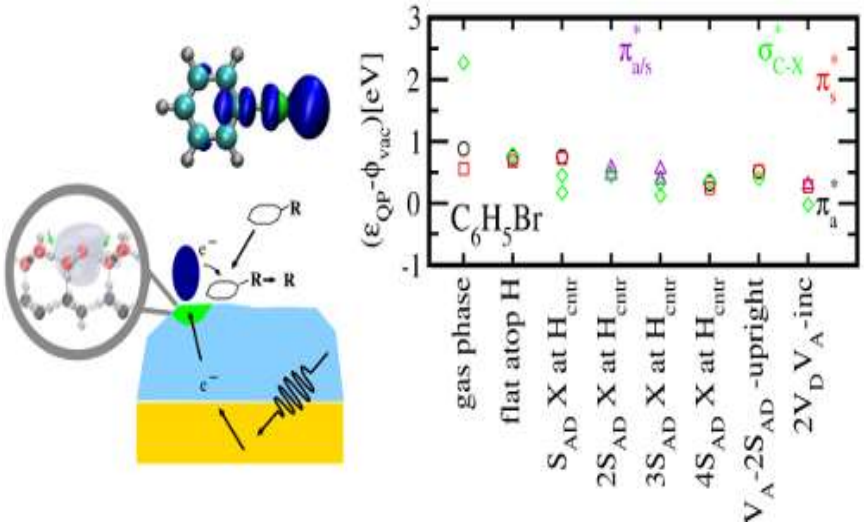
On ice, the solvated electron facilitates electron-induced reactions of adsorbates via dissociative electron attachment (DEA) that for instance take place in atmospheric chemistry. The simultaneous interaction of the electron with the molecule and the ice surface enhances the cross section as compared with the gas phase [1]. The current understanding of the physical mechanisms at work is rather incomplete, in particular a picture on the molecular scale is missing.

In this work we address this probleme within the framework of density functional theory, hybrid DFT, and many body perturbation theory. Prototypical surface electron traps, such as orientational disorder [2], surface vacancies [3], and vacancy clusters are used as a model system. Halogenated hydro carbons favor adsorption sites that are strong electron traps. In the gas phase, their antibonding molecular orbitals are scattering states with negative electron affinity. By the interaction with the trap states the affinity is considerably increased. For molecules adsorbed at strong electron traps the antibonding resonances are located close to the ice conduction band mininum. With a shift as large as 2.0-4eV (cf. the Figure below for X=Cl and Br), the effect is strongest for the antibonding state that is responsible for the dissociation of the halogen. Our results show clear trends across the halogen series F, Cl, and Br.



Thanks

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P5-SCR_304

NACE(WO4)2 MICROSTRUCTURES WITH HIERARCHICAL MORPHOLOGIES: EDTA-ASSISTED HYDROTHERMAL SYNTHESIS , GROWTH MECHANISMS, ELECTRICAL AND PHOTOCATALYTIC PROPERTIES.

SCR - Surface chemical reactions and kinetics

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Since their discovery, the double rare earth tungstates with a scheelite structure have attracted a great attention due to their unique optical[1] and chemical properties[2]. They have a high chemical stability[1] and interesting potential technological applications. Paradoxically, few data are available on the chemistry of these compounds. Recently, we synthesized a novel hierarchical tetragonal structure of $NaCe(WO_4)_2$ via hydrothermal method in the EDTA-mediated process. Different architectures as hierarchical spindles, microflowers and microspheres self-assembled from different building blocks were elaborated. The obtained microstructures were characterized using X-ray diffraction (XRD) combined to Rietveld refinement, scanning electron microscopy (SEM), diffuse reflectance spectra (DRS) and Raman spectroscopy respectively. The results show that the amount of EDTA introduced and the pH of the reaction system modulate the morphology and affect the growth mechanism of the different shapes. The formation mechanisms for different architectures were studied according to a time experiments duration. A scheelite crystallization structure phase is obtained post synthesis, after thermal treatment from 500°C.

The electrical conductivity of different microstructures compacted pellets systems was determined from electrical impedance spectrometry, under air, until 800°C. Finally, photocatalytic and adsorption performance of different morphologies was investigated by monitoring the degradation of Rhodamine B under visible light irradiation within different time intervals at room temperature. The photodecomposition reactivity was discussed as a function of morphology of various hierarchical structures.

Thanks

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