

"Chirality and Molecular Recognition at Surfaces" (Chir@Surf)
CECAM Workshop, Lyon, October 1st-3rd 2007

(last update 14/09/2007)

Program

Monday, October 1st

8:30 – 8:50	<i>Registration</i>	
8:50 – 9:00	Philippe Sautet	Welcome & workshop opening
	Chiral molecules at surfaces	<i>Chair Rasmita Raval</i>
9:00 – 9:55	Pr F. Zaera	"Bestowing Chirality on Solid Surfaces"
9:55 – 10:10	<i>Coffee break</i>	
10:10 – 11:05	Dr B. Hammer	"Adsorption of an Amino Acid on a Chiral Surface: Cys/Au(111)"
11:05 – 12:00	Dr A. Vargas	"DFT Studies towards the Understanding of Catalytic Chiral Surfaces: the Adsorption of Highly Flexible Molecules on Platinum"
12:00 – 14:00	<i>Lunch</i>	
	Chiral molecules at surfaces	<i>Chair Francisco Zaera</i>
14:00 – 14:55	Pr R. Raval	"Creating Chiral Surfaces: From Nanoscale Control to Macroscale Amplification"
14:55 – 15:50	Pr D. Sholl	"First-Principles Studies of Chiral Adsorption on Metal Surfaces"
15:50 – 16:05	<i>Coffee break</i>	
16:05 – 17:00	Dr S. Jenkins	"Structure, Symmetry and Chirality of bcc and hcp Surfaces"
17:00 – 17:45	Pr K.-H. Ernst	"Amplification of chirality and conglomerate formation at crystal surfaces"
17:45 – 18:30	Dr S. Irrera	"Study of Organic-Inorganic Interface on Metal Surfaces"

Tuesday, October 2nd

	Asymmetric heterogeneous and homogeneous catalysis	<i>Chair Bjørk Hammer</i>
8:15 – 9:00	Dr P. McBreen	"Rate-Acceleration and Stereoselection in Heterogeneous Chiral Catalysis"
9:00 – 9:55	Pr M. Lemaire	"Heterogenous asymmetric catalysis"
9:55 – 10:10	<i>Coffee break</i>	
10:10 – 11:05	Pr W. Thiel	"Density Functional Studies on Asymmetric Homogeneous Catalysis: Rh-Catalyzed Olefin Hydrogenation"
11:05 – 12:00	Pr G. Attard	"Elucidation of Active Sites and Mechanism during Enantioselective Hydrogenation of Ethyl Pyruvate"
12:00 – 14:00	<i>Lunch</i>	
	Self-assembly systems and chirality	<i>Chair Philippe Sautet</i>
14:00 – 14:55	Dr T. Linderoth	"Chiral switching and chiral recognition for organic molecules on surfaces studied by UHV-STM"
14:55 – 15:50	Dr T. Bürgi	"Chiral Gold Nanoparticles: Preparation, size-selection and chiroptical properties"
15:50 – 16:05	<i>Coffee break</i>	
16:05 – 17:00	Dr A. P. J. Jansen	"Monte Carlo Studies of Segregation of Enantiomers and Induction of Chirality in Adlayers of Tartrate and Succinate"
20:00	<i>Conference dinner</i>	

Wednesday, October 3rd

	Molecular recognition and selectivity at surfaces	<i>Chair Thomas Bürgi</i>
8:15 – 9:00	C. Dupont	"Recent Advances in PROX: Vibrational Characterization and Reactivity on the Pt ₃ Sn(111) Surface"
9:00 – 9:55	Dr C. Becker	"Identifying Complex Molecular Adsorbates Using a Combined Experimental and Theoretical Approach"
9:55 – 10:10	<i>Coffee break</i>	
10:10 – 11:05	Dr L. Piccolo	"Why Pd-Au is More Selective than Pd in the Catalytic Hydrogenation of 1,3-butadiene : a Surface-Science Study"
11:05 – 12:00	Dr S. Cristol	"Modelling the Adsorption of Thiophene and Benzene on MoS ₂ : on the Importance of a Good Surface Description"
12:00		Workshop closure

List of abstracts

Bestowing Chirality on Solid Surfaces

Francisco Zaera

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It has been shown that heterogeneous hydrogenation catalysts such as platinum and nickel can be made enantioselective by the use of molecular modifiers. Two mechanisms have been proposed for this based on the formation of one-to-one complexes between the modifier and the reactant and on the chiral templating of the surface via the formation of ordered adsorbate suprastructures. Both mechanisms have been explored in our laboratory using surface sensitive techniques. The adsorption of cinchona alkaloids from solution onto platinum surfaces, the prototypical example of the first, has been detailed using reflection-absorption infrared spectroscopy (RAIRS) in-situ at the liquid-solid interface. Parameters such as adsorption geometry, reversibility of adsorption, and the effect of gases and solvents were investigated. Correlations were identified between the catalytic performance of the cinchona modifiers and their adsorption properties, and between the latter and the structural parameters of those molecules. For the second mechanism, the templating of Pt(111) surfaces with chiral 2-butanol, 2-methylbutanoic acid, and 1-(1-naphthyl)ethylamine adsorbates has been probed under vacuum using enantiopure propylene oxide as a probe. Evidence for both one-to-one complexation and suprastructure ordering was obtained in the latter two cases. The relative importance of each mechanism in all these examples will be discussed.

Adsorption of an Amino Acid on a Chiral Surface: Cys/Au(17 11 9)

Bjørk Hammer

University of Aarhus, Denmark

The adsorption of cysteine on a kinked gold surface, Au(17 11 9), has been investigated with X-ray photoelectron diffraction (XPD), X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT). The equilibrium adsorption forms of the L- and D-cysteine enantiomers are found with XPD to be non-mirror-symmetric [1]. This is confirmed with DFT which further shows a 140 meV preference for the adsorption configurations adopted by the L-cysteine[1]. Studying with XPS the temporal evolution towards the equilibrium adsorption forms, the D-cysteine is found to evolve more slowly [2]. This is explained with DFT in terms of a higher barrier for a deprotonation step (identified in the XPS) involving the amine group of the D-cysteine[2]. The implications of the results for the possible development of asymmetric heterogeneous catalysts are discussed.

[1] T. Greber, Z. Sljivancanin, R. Schillinger, J. Wider, and B. Hammer, PRL 96, 056103 (2006).

[2] R.Schillinger, Z.Sljivancanin, B. Hammer, and T. Greber, PRL 98, 136102 (2007).

DFT Studies towards the Understanding of Catalytic Chiral Surfaces: the Adsorption of Highly Flexible Molecules on Platinum

Angelo Vargas and Alfons Baiker

ETH Zurich Institute for Chemical and Bioengineering, Switzerland

Modification of transition metal catalysts by means of chiral molecules is an efficient and elegant method for the preparation of solid materials possessing enantioselective properties. The basis of the modification process is the adsorption of the chiral modifier to the metal surface to form chiral sites, within which the critical asymmetric interactions occur. The work here presented shows the recent advances in determining the topology of surface chiral sites obtained by adsorption of natural and substituted cinchona alkaloids on platinum, and their role as hydrogen transfer mediators. The mentioned alkaloids have a remarkable conformational complexity and the deriving structural flexibility is of fundamental importance for the understanding of the mechanisms of surface chiral recognition. The role of cinchona alkaloids surface conformations will therefore be discussed in relation to the enantioselectivity achieved during the asymmetric hydrogenation of activated ketones.

- Reflections on chiral metal surfaces and their potential for catalysis A. Baiker *Catal. Today* 100 (2005) 159
- Controlling the sense of enantioselection on surfaces by conformational changes of the adsorbed modifiers. A.Vargas, D. Ferri, N. Bonalumi, T. Mallat, A. Baiker, *Angew. Chem. Int. Ed.* 46 (2007) 3905
- Catalytic Chiral Metal Surfaces Generated by Adsorption of O-phenyl Derivatives of Cinchonidine N. Bonalumi, A. Vargas, D. Ferri, A. Baiker *J. Phys. Chem. C.* In press

Creating Chiral Surfaces: From Nanoscale Control to Macroscale Amplification

Rasmita Raval

Surface Science Research Centre, Department of Chemistry, University of Liverpool, UK

One of the most versatile ways of introducing the property of chirality to a high symmetry surface is via the introduction of organic molecules [1-4]. This talk will illustrate the manifestation, transfer and amplification of chirality from the nanoscale to the macroscale at such surfaces - from the creation of local chiral sites, to macroscopic extended chiral arrays. Pertinent examples, chosen from the adsorption of bicarboxylic acids and amino acids at metal surfaces, will show that a variety of mechanisms from supramolecular assemblies, to chiral reconstructions, to chiral electronic perturbations, enable the property of chirality to be introduced and propagated at surfaces. It will also be demonstrated that chiral molecular assemblies at surfaces are capable of incredibly complex and dynamic behaviour, spawning versatile interfaces that can display multifunctional polymorphic organisations. In addition, their susceptibility to small nanoscale perturbations leads to highly dynamic responses at the global level, and drives important characteristics like self-adaptive behaviour, 2-D chiral resolution, chiral recognition at the single-molecule level, and global amplification of chirality.

[1] 'Extended Surface Chirality from Supramolecular Assemblies of Adsorbed Chiral Molecules', M.Ortega-Lorenzo, C.J.Baddeley, C.Muryn, R.Raval, *Nature*, 404 (2000) 376.

[2] 'Complex Organic Molecules at Metal Surfaces: Bonding, Organisation and Chirality', S. Barlow and R.Raval, *Surface Science Reports*, 50 (2003) 201.

[3] 'From Local Adsorption Stresses to Chiral Surfaces: (R,R)-Tartaric Acid on Ni(110)', V.Humblot, S. Haq, C. Muryn, W.A.Hofer, R.Raval, *J. Am. Chem. Soc.*, 124 (2002) 503.

[4] Local and Global Chirality at Surfaces: Succinic Acid versus Tartaric Acid on Cu(110)', V.Humblot, M.Ortega Lorenzo, C.J.Baddeley, S.Haq and R.Raval, *J. Am. Chem. Soc.* 126 (2004) 6460.

First-Principles Studies of Chiral Adsorption on Metal Surfaces

David Sholl

Department of Chemical Engineering Carnegie Mellon University, United States

Density functional theory (DFT) calculations are a useful complement to experimental methods for understanding the chemisorption of molecules on well defined metal surfaces. I will present DFT calculations that have probed several aspects of chiral adsorption on metal surfaces. First, I will discuss the structure of enantiopure and racemic alanine adlayers adsorbed on Cu(100) and Cu(110). A good deal is known about these adlayers, but several important features related to their chiral behavior have been clarified using DFT calculations. We have also used DFT to understand the structure of alanine on Cu(3,1,17), an intrinsically chiral surface. These calculations provide detailed information on the experimentally observed reconstruction of Cu(100) by adsorbed alanine that leads to creation of chiral facets of Cu(3,1,17). Second, we have used DFT to examine a range of small chiral molecules adsorbing on a range of intrinsically chiral Cu surface. The outcomes from these calculations allow several hypotheses regarding the enantiospecificity of chemisorption on these surfaces to be tested and give suggestions for selecting adsorbate/surface combinations that will have highly enantiospecific adsorption. Finally, I will show how DFT calculations have been used to examine strategies for tuning the chemical functionality of chiral metal surfaces by doping these surfaces with low coverages of additive metals.

Structure, Symmetry and Chirality of bcc and hcp Surfaces

S.J. Jenkins and S.J. Pratt

Department of Chemistry, University of Cambridge, Cambridge, UK

The intrinsic chirality of certain high-index surfaces of fcc metals has been recognised for some time, and has generally been described in terms of the structural details associated with low-coordination kink sites [1, 2, 3]. One major deficiency in this approach, however, is that it is far from clear how surface chirality relates to surface structure when considering non-fcc materials. Indeed, we recently pointed out [4] that there exists a class of bcc surface that is indisputably chiral despite possessing no kink sites whatsoever. In order to describe the relationship between the symmetry and structure of general high-index surfaces more appropriately, therefore, we have developed a new conceptual framework that is applicable to the surfaces of any crystal structure [5]. Examining the surfaces of bcc and hcp materials within this framework, we can identify well-defined surface structure and symmetry categories, and make definitive statements about the combinations of these that may arise. For example, all bcc surfaces fall into one of three structure categories (flat, stepped or kinked) and one of five symmetry categories (chiral, singly-, doubly-, triply- or quadruply-reflexive), but certain combinations can never arise (e.g. chiral and flat, or doubly-reflexive and stepped). In the more complex hcp case, we identify precisely six distinct structure categories and nine distinct symmetry categories. Amongst the notable surface types that are permissible for hcp materials, we find a class having intrinsic glide symmetry, another displaying an intrinsic racemic quality, and yet another featuring double-chirality akin to that found in the phenomenon of molecular diastereoisomerism. Our approach furthermore allows these different surface properties to be deduced directly from knowledge of the Miller indices, rather than painstakingly obtained by inspection of the surface atomic coordinates.

[1] C.F. McFadden, P.S. Cremer and A.J. Gellman, *Langmuir* 12, 2483 (1996)

[2] A. Ahmadi, G.A. Attard, J. Feliu and A. Rodes, *Langmuir* 15, 2420 (1999)

[3] G.A. Attard, *J. Phys. Chem. B* 105, 3158 (2001)

[4] S.J. Pratt and S.J. Jenkins, *Surf. Sci. Lett.* 585, L159 (2005)

[5] S.J. Jenkins and S.J. Pratt, *Surf. Sci. Reports* (invited, accepted)

Amplification of Chirality and Conglomerate Formation at Crystal Surfaces

Karl-Heinz Ernst, Roman Fasel, Manfred Parschau

Empa- Swiss Federal Laboratories for Materials Testing and Research, Dübendorf, Switzerland

In his famous experiment Pasteur manually separated enantiomorphous ammonium sodium tartrate crystals and observed opposite optical activity for their aqueous solutions. His insight that enantiomorphism is based on molecular structure laid the foundation of modern structural organic chemistry. Two aspects in his experiment allowed the manual separation: i) Handedness was transferred from molecular structure into the macroscopic shape of the crystal (hemihedrism), and ii) the enantiomers precipitated into a conglomerate of homochiral crystals allowing manual separation. Up to date, both processes are still poorly understood. We are neither able to predict the shape of a crystal based on the molecular structure nor do we understand why racemic mixtures crystallize sometimes into conglomerates. A promising approach to answer these questions is studying two-dimensional (2D) crystallization phenomena on well-defined surfaces via scanning tunneling microscopy (STM). Here we present studies on different two-dimensional chiral systems and discuss their tendency to undergo enantiomeric separation. A special surface enantiomorphism is observed via STM after adsorption of the enantiomers of a helical aromatic hydrocarbon on Cu(111). Instead of crystallization into homochiral 2D domains on the surface, racemic mirror domains are observed. In this situation, a small excess of one enantiomer is sufficient to create domains possessing single handedness throughout the entire surface layer. [1] The induction of homochirality by chiral doping has also been observed for succinic acid [2] and achiral (R,S)-tartaric acid. Our findings are explained by cooperative interactions between many chiral units, similar to the mechanism of chiral amplification observed in helical polymers coined as "Sergeant and Soldiers" principle. The homochiral crystal templates have implications of this 2D chiral amplification for bulk crystallization and separation of enantiomers will be discussed. *The work was supported by the Schweizerischer Nationalfonds.*

[1] R. Fasel, M. Parschau, K.-H. Ernst, Nature 2006 439, 449.

[2] M. Parschau, S. Romer, K.-H. Ernst, J Am Chem Soc 2004 126, 15398

Study of Organic-Inorganic Interface on Metal Surfaces

Simona Irrera, Dominique Costa

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Chirality is the symmetry property of objects which exist in two mirror-like forms and the importance of such property is addressed by the fact that life is based on chiral biomolecules; an attractive area is the study of chiral surfaces which can act as heterogeneous catalysts and sensors. This work reports about the study of chemisorption of an aminoalcohol (alaninol) on a metal substrate, Cu (100). This system has been investigated systematically by using the Vienna Ab-initio Simulation Package (VASP) which performs periodical density functional theory (DFT) calculations. This approach is focused on obtaining a final chemisorption model and new insight at the photoelectron spectra providing core electrons binding energies to be compared with the experimental data (XPS). The fruitful interchange between experimental and theoretical investigations is crucial to elucidate the interplay between geometric structure and electronic response for oriented systems. At the first stage, considering the high range of possible structures, a selection has been made on the base of the experimental values of XPS and UPS finally indicating three possible connectivities that is through the Hydroxylic group, the Amino group or both; XPS spectroscopic responses of those three possible adsorption modes have been evaluated and compared with experimental data.

Rate-Acceleration and Stereoselection in Heterogeneous Chiral Catalysis

Peter H. McBreen

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The Orito reaction describes the enantioselective hydrogenation of activated ketones such as alpha-ketoesters on cinchona-modified Pt catalysts. There is a consensus in the literature that the reaction proceeds through the formation of 1:1 chiral modifier-substrate complexes. One of the most interesting facets of the reaction is the observation of rate-enhancement on the chirally-modified surface with respect to the rate of the racemic reaction on the non-modified surface. For example, ethyl pyruvate displays significant rate-enhancement of the enantioselective reaction. However, several groups have also reported results for substrates that display negligible rate-enhancement. In this presentation, we assume that there is a real rate-enhancement effect for ethyl pyruvate under typical operating conditions. In support of a rate-enhancement effect, STM and RAIRS data show that clustering of methyl pyruvate on Pt(111) arises from enol formation, a reversible process. Studies of a range of substrates on Pt(111) will be presented and the results will be discussed within the context of literature data for rate-acceleration and enantioselection.

Heterogeneous Asymmetric Catalysis

Marc Lemaire

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More than thirty years after the discovery of practical asymmetric catalysis by Knowles and Kagan, the number of industrial processes using asymmetric catalysis is relatively small. This is mainly due to the high cost and often high toxicity of the organometallic complexes used as catalysts in homogeneous asymmetric catalytic processes. In most cases, the separation and the recycling of homogeneous catalysts from the bulk of the reaction are very difficult, if not impossible. Indeed, catalysis is largely used in production of chemicals where heterogeneous ones are generally preferred and 75% of these products (in weight) are synthesized via heterogeneous catalysis. Preparation and evaluation of heterogeneous asymmetric catalysts as efficient and selective as their homogeneous counter parts, began almost immediately after the discovery of practical asymmetric catalysis. We have used methodologies such as homogeneous supported catalysis and biphasic liquid-liquid catalysis, as well as ionic liquids and supercritical CO₂ in order to obtain efficient asymmetric catalysts which are both easy to separate and recycle. Bisoxazoline is one of the most useful ligands in asymmetric catalysis. Over the last few years, we have developed new materials based on bisoxazoline ligands grafted onto inorganic supports, such as silica. Control of the metal precursor and the surface (catalyst loading and silanol protection, etc.) allows the formation of catalysts with efficiency and selectivity similar to those obtained in solution. In addition, these catalysts can be recycled without decreasing either the conversion or the enantiomeric excess. Binap also has a wide range of applications, and are now produced on a hundred kilogram scale. Nevertheless, the modification of binap in order to make the separation and the recycling of the catalyst easier at the end of the reaction should improve the use of the catalyst prepared with this ligand. We have synthesized modified binap as selective as the binap itself, but included in a polymer main chain or soluble in water, an ionic liquid or supercritical CO₂. All these new processes show in our opinion that organic synthesis is not only the tool to create new useful molecules but may also contribute to solving actual environmental problems.

Density Functional Studies on Asymmetric Homogeneous Catalysis: Rh-catalyzed Olefin Hydrogenation

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For the title reaction, rhodium catalysts with chiral monodentate phosphorous ligands have become an interesting alternative to those with their bidentate counterparts. While maintaining high efficiency and enantioselectivity, they are more easily tunable to various types of substrates. The enantioselectivity of Rh-complexes with chelating P-ligands has been described by Halpern [1] using an "anti lock and key" principle according to which the major enantiomer of the product is formed from the less stable of the two diastereomeric pro-chiral catalyst-substrate complexes. While subsequent calculations [2] have confirmed these findings, it has been shown recently that Rh-catalysts containing chiral monodentate P-ligands [3] follow the "lock and key" principle. We present detailed DFT investigations of the enantioselective hydrogenation of itaconic acid using a chiral Rh(phosponite)₂ catalyst, combined with kinetic simulations, to explain these differences [4]. This case study illustrates the use of density functional theory in mechanistic work on asymmetric homogeneous catalysis.

[1] A. S. C. Chan, J. J. Pluth, J. Halpern, *J. Am. Chem. Soc.* 1980, 102, 5952-5954.

[2] C. R. Landis, J. Halpern, *J. Am. Chem. Soc.* 1987, 109, 1746-1754.

[3] M. T. Reetz, A. Meiswinkel, G. Mehler, K. Angermund, M. Graf, W. Thiel, R. Mynott, D. G. Blackmond, *J. Am. Chem. Soc.* 2005, 127, 10305-10313.

[4] K. Angermund, M. Graf, W. Thiel, to be published.

Elucidation of Active Sites and Mechanism during Enantioselective Hydrogenation of Ethyl Pyruvate

Gary Attard

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The enantioselective hydrogenation of ethyl pyruvate using supported Pt modified by cinchona alkaloids is one of the most remarkable of all heterogeneous catalytic reactions and continues to provide a benchmark by which our understanding of surface chirality at catalyst surfaces may be measured. A key factor necessary for the optimisation of the performance of such catalysts is the identification of the active surface site giving rise to the greatest value of enantioselective excess (ee) in the final product mixture. One surface sensitive technique that has proved most fruitful in helping identify the different adsorption sites present at a supported Pt catalyst is cyclic voltammetry. Using a mixture of thermal and chemical treatments of the supported Pt catalyst, including selectively decorating the various Pt surface sites (steps or terraces) with inert or reactive adatoms, it is possible to correlate variations in catalyst activity and enantioselectivity with particular adsorption sites. Our conclusion from these electrochemical and hydrogenation studies is that edge sites (possibly chiral corner kinks) at the metal-support boundary are crucial to the achievement of optimal values of ee. Furthermore, it is demonstrated that ethyl pyruvate hydrogenation on extended Pt{100} terraces leads to a reduction in overall ee. It is suggested that in order to account for these observations, Pt{100} terrace sites present at the catalyst surface must either be giving rise to purely racemic reaction or, more likely, inversion of ee. Prospects for future catalyst design in the light of these findings will be discussed.

Chiral Switching and Chiral Recognition for Organic Molecules on Surfaces Studied by UHV-STM

Trolle Linderoth

Interdisciplinary Nanoscience Center (iNANO) and Department of Physics and Astronomy

High-resolution Scanning Tunneling Microscopy under ultra-high vacuum conditions allows direct and detailed exploration of chiral adsorption and organisation for organic molecules on surfaces, including time-resolved studies of dynamic processes. Adsorption studies for the chiral amino acid cysteine on the Au(110)-(1x2) surface will be reviewed with focus on intermolecular chiral recognition in cysteine dimerisation [1] and clustering [2] as well as molecule-surface chiral recognition upon cysteine binding to chiral kink sites [3]. Secondly, recent results for the chiral ordering of a class of oligo-phenylene-ethynylenes on the Au(111) surface will be discussed [4,5]. These prochiral compounds can adsorb as both chiral and achiral surface conformers, and are surprisingly shown to be able to switch between these forms through thermally activated conformational changes after adsorption. The molecular tiling pattern is strongly correlated to the conformational chirality of the molecular constituents, and the chiral switching enables an efficient channel for chiral ordering on surfaces, termed chiral accommodation. The effects of varying molecular geometry and end-group chemistry have been systematically explored.

[1] *Chiral recognition in dimerization of adsorbed cysteine observed by scanning tunnelling microscopy*, A. Kühnle, T. R. Linderoth, B. Hammer, and F. Besenbacher *NATURE* **415**, 891 (2002).

[2] *Self-assembly of Monodispersed, chiral nanoclusters of cysteine on the Au(110)-(1x2) surface*, A. Kühnle, T.R. Linderoth and F. Besenbacher, *Journ. Am. Chem. Soc.*, **125** 14680 (2003)

[3] *Enantiospecific adsorption of cysteine at chiral kink sites on Au(110)-(1x2)* A. Kühnle, T.R. Linderoth, and F. Besenbacher *Journ. Am. Chem. Soc.* **128** 1176 (2006)

[3] *Chiral switching by spontaneous conformational change in adsorbed organic molecules*, S. Weigelt, C. Busse, L. Petersen, E. Rauls, B. Hammer, K.V. Gothelf, F. Besenbacher, and T.R. Linderoth *Nature Materials*, **5** 11 (2006)

[4] *Chiral ordering and conformational dynamics for a class of oligo-phenylene-ethynylenes on Au(111)*, C. Busse, S. Weigelt, L. Petersen, A. H. Thomsen, M. Nielsen, K. V. Gothelf, E. Lægsgaard, F. Besenbacher, and T. R. Linderoth, *J. Phys. Chem. B*, 111 5850 (2007)

Chiral Gold Nanoparticles: Preparation, Size-Selection and Chiroptical Properties

Thomas Bürgi

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Attempts are described that aim at bestowing chirality onto metal nanoparticles. The latter can be viewed as the nanometer size analogues of extended metal surfaces. The solubility of these particles allows the application of chiroptical techniques such as circular dichroism (CD) and vibrational circular dichroism (VCD), i.e. the differential absorption of left- and right-circularly polarized light. The latter technique yields, in combination with quantum chemical calculations, information on the structure of the adsorbed molecules. The former technique probes electronic transitions that might be located in the metal core. Gold nanoparticles covered by chiral thiols that were separated into well-defined compounds by gel electrophoresis show circular dichroism in metal-based electronic transitions. Possible origins for this observation are discussed.

Monte Carlo Studies of Segregation of Enantiomers and Induction of Chirality in Adlayers of Tartrate and Succinate

C.G.M. Hermse and A.P.J. Jansen

Schuit Institute of Catalysis SKA, Eindhoven University of Technology, Eindhoven, The Netherlands

We have used Density-Functional Theory to determine the nature and the strengths of the lateral interactions in tartrate layers on Cu(110). The results show that the chirality in (R,R)-tartrate is due to steric repulsion between OH groups, whereas hydrogen bonds are only formed intramolecularly. The trough in the (9 0, 1 2) structure is caused by adsorbate-induced stress in the surface along the rows of Cu atoms. The steric repulsion seems to be the more important factor to explain the structures of adlayers of tartrate and similar molecules. So we have made some simpler models without stress and with hard sphere interactions modeling the other interactions. We have used these models in (kinetic) Monte Carlo simulations to study the induction of chirality in adlayers of succinate by tartrate, and to study the segregation of (R,R)- and (S,S)-tartrate. The segregation is a consequence of close-packing in these models. The induction of chirality in succinate depends on the adsorption mode of the succinate. If the succinate adsorbs to four Cu atoms forming a rectangle, as does tartrate, then little or no chiral induction is found. If the four Cu atoms form a skewed parallelogram, then chiral induction is possible provided the succinate can change between the two orientations that are possible for that adsorption mode.

Recent Advances in PROX: Vibrational Characterization and Reactivity on the Pt₃Sn(111) Surface

C. Dupont, Y. Jugnet, F. Delbecq and D. Loffreda

University of Lyon, Institute of Chemistry, Ecole Normale Supérieure de Lyon, Lyon, France and Institut de Recherches sur la Catalyse et l'Environnement de Lyon, Villeurbanne, France

Fuel cells are well-known conversion systems for producing electricity from chemical energy. The hydrogen combustible usually contains traces of carbon monoxide (CO), which is known to be a catalyst poison. Among the technological solutions proposed for the CO removal, the selective oxidation in a hydrogen-rich environment (PROX: PReferential OXidation) has retained much attention during the last few years. The bimetallic catalysts exhibit an enhanced activity and selectivity towards PROX. In fact, the presence of a second metal, such as Ru or Sn(1-2), has already provided a remarkable improvement of CO tolerance.

In this talk, the PROX reaction is investigated on the Pt₃Sn(111)-(2x2) surface from both theoretical and experimental approaches. The first necessary step concerns the adsorption of the different species playing a part in the reaction. Hence the adsorption of all reactants and products is studied by Density Functional Theory (DFT) using the VASP code. Vibrational spectra are simulated allowing molecular recognition and a systematic comparison with HREELS spectra.

In a second part, we study the reactivity. We first focus on the key step: CO oxidation. In fact, we have to be sure that PtSn surfaces are more efficient for CO oxidation than pure platinum. DFT calculations have been performed (3) in comparison with PM-IRRAS and QMS spectra. This dual theoretical and experimental study shows a higher efficiency of PtSn alloy regarding CO oxidation. Finally, we will examine the theoretical aspect of the main other elementary steps involved in PROX mechanism such as oxygen and hydrogen dissociation, OH or H₂O formation.

(1) H.A. Gasteiger, N. Markovic, P.N. Ross and E.J. Cairns, *J. Phys. Chem*, 98 (1994) 617.

(2) M.M. Schubert, M.J. Kahlich, G. Feldmeyer, M. Huttner, S. Hackenberg, H.A. Gasteiger and R.J. Behm, *Phys. Chem. Chem. Phys.* 3 (2001) 1123.

(3) C. Dupont, Y. Jugnet and D. Loffreda, *J. Am. Chem. Soc.* 128 (2006) 9129.

Identifying Complex Molecular Adsorbates Using a Combined Experimental and Theoretical Approach

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The investigation of reaction mechanisms, selectivities or activities in catalytic processes requires a profound understanding of the interactions of the reactants, intermediates and products with the catalyst itself. Since the surface structures of industrial catalysts are usually highly complex, model systems with defined surface structures have to be used to perform such investigations. Besides using mono- and bimetallic single-crystalline samples, also alloying the surface of a monometallic substrate with a second metal can be used to create well-defined model catalyst surfaces. We employ high-resolution electron energy loss spectroscopy (HREELS) in conjunction with density functional theory (DFT) to gain deeper insights into molecule-surface interactions, surface processes and modifications by alloying effects. For simple systems (e.g. cyclopentene on Pt(111)) for which only a single adsorption mode exist on the surface this approach yields the atomic structure of the surface molecule complex [1]. When multifunctional molecules such as alpha,beta-unsaturated aldehydes (e.g. prenal and crotonaldehyde) are considered not only the vibrational spectra are by far more complex but also the number of possible adsorption configurations is multiplied [2]. This requires an additional effort in the calculations of the stable adsorption configurations and vibrational spectra. Our approach is to calculate all possible adsorption configurations of the molecules in question using DFT and comparing the derived theoretical vibrational spectra to the experimental ones. This allows us to identify the molecular species actually present on the surface. By comparing the adsorption on Pt(111) to that on two ordered Pt-Sn surface alloys the role of alloying on the adsorption of multifunctional molecules is derived. For alpha,beta-unsaturated aldehydes important changes in the bonding modes of the most stable adsorption complexes are found. The knowledge of the initially present adsorption modes on the surfaces open also the route to a complete thermodynamic description of the decomposition pathways.

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Why Pd-Au is more Selective than Pd in the Catalytic Hydrogenation of 1,3-butadiene: a Surface-Science Study

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Mixed gold/platinum group metal supported catalysts have recently demonstrated their efficiency for catalyzing various reactions [1]. Moreover, Pd-Au is presently the sole gold-based catalyst used in a large-scale chemical process, namely the production of vinyl acetate monomer.

In this study, a Pd₇₀Au₃₀(111) single-crystal surface has been used as a model catalytic system. From low energy electron diffraction, Auger electron spectroscopy and low energy ion scattering spectroscopy, this surface was found unreconstructed and its first atomic layer composed of 75 at.% Au [2]. The reactivity of Pd and Pd-Au surfaces was investigated in a static reaction cell (pressures up to 100 Torr) coupled to an ultra-high vacuum preparation setup. In the case of the CO oxidation reaction, gold has a negative effect on the Pd activity, by lowering the probability of oxygen chemisorption [3]. Besides, a study of the H₂+O₂ reaction reveals that the activity and stability differences between Pd and Pd-Au crystals also arise from their different abilities to absorb hydrogen and form surface hydrides [4].

From a practical point of view, the most interesting effect of the addition of Au to Pd was observed for the hydrogenation of 1,3-butadiene (C₄H₆). The presence of gold is seen to increase the selectivity toward butenes (C₄H₈) up to almost 100% over the whole range of butadiene conversions, and to significantly lower the rate of (unwanted) n-butane (C₄H₁₀) formation from butene hydrogenation [2]. On the basis of density functional theory calculations (VASP program), the adsorption structures of butadiene and its partially hydrogenated products (butenes) have been modeled on various Pd₃Au(111) surfaces, in order to rationalize these results. In realistic conditions of temperature and pressure, the DFT calculations indicate that the adsorption of butenes is more destabilized by the increased surface content of gold than the adsorption of butadiene. Hence, the change of selectivity has been associated with the higher ability of Pd-Au surfaces to desorb the partially hydrogenated products, hence lowering the butene hydrogenation rate.

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Modelling the Adsorption of Thiophene and Benzene on MoS₂: on the Importance of a Good Surface Description

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Hydrodesulfurization (HDS) is a key step of the petroleum industry that consists in the removal the heteroatoms through a high temperature treatment of the feedstock under a high hydrogen pressure. The mechanism of this reaction is still under debate, even if it is widely accepted that the reaction takes place on the edges of the molybdenum sulfide nanoparticles. First theoretical studies have focused on the adsorption of the reactive molecules on the perfect surfaces, some of which presenting highly unsaturated metallic atoms. On the chemical point of view though, such surfaces are very unlikely to be present on the edges of the active phase as H₂S present in the gas phase will react with the unsaturated metal atoms. We have therefore undertaken a systematic study of thiophene and benzene adsorption both on the perfect surfaces and on more realistic surfaces that take into account the surrounding gas phase (1). As far as thiophene is concerned, on the perfect surface the adsorption takes place in a flat eta5 mode in which all the atoms of the cycle are interacting with surface metal atoms.

On the other hand, on more realistic surfaces, the adsorption mainly takes place in a eta1 mode, only the sulphur atom interacting with the surface. Comparisons between computed vibrational frequencies and the FTIR spectroscopy shows that this adsorption mode is indeed the most favoured. Such an adsorption mode can only be explained by a complete saturation of the surface of the active phase with sulphur atoms and confirms the importance of a good surface description in the catalytic conditions. Such adsorption is impossible for benzene and we tested its adsorption of different sites. Some of them allow the adsorption in eta2 or eta5 mode but require the departure of one sulphur atom from the stable surface that is highly unfavourable. The question of the hydrogenation site in HDT catalysts is then still open although it has been proposed recently (2) that this reaction could take place on the basal plane of the MoS₂ crystallites.

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