

O 45: Focus Session: Catalysis at Liquid Interfaces

Catalysis at liquid Interfaces has emerged as novel approach to explore the highly dynamic, anisotropic environment of liquid interfaces to create, tailor, and stabilize catalytically active sites with unique reactivity and performance. With this concept, fundamental problems of catalyst science and technology can be addressed to develop novel catalytic materials that combine selectivity, productivity, robustness, and ease of processing at the highest possible level. Thus, the concepts of "Supported Catalytically Active Liquid Metal Solutions" (SCALMS), interface-enhanced "Supported Ionic Liquid Phase" (SILP) and advanced "Solid Catalysts with Ionic Liquid Layer" (SCILL) systems are of particular focus.

Organizers: Marcus Bär (Helmholtz-Zentrum Berlin), Jörg Libuda (FAU Erlangen-Nürnberg), Christian Papp (FAU Erlangen-Nürnberg)

Time: Wednesday 15:00–18:00

Location: H4

Topical Talk O 45.1 Wed 15:00 H4
Addressing Electronic Effects in Catalysis by Intermetallic Compounds — ●MARC ARMBRÜSTER — Chemnitz University of Technology

The catalytic properties of materials are determined by their electronic and geometric structure. A reliable development addresses both influences separately and then combines the ideal electronic and structural properties resulting in superior catalytic materials.

Unfortunately, this is only straightforward on paper. The implementation faces hurdles concerning the control of the materials. E.g. the electronic modification of metallic materials by addition of a second metal with a different electron count can result in substitutional alloys with (in theory) random distribution of the elements. However, the sought-for electronic modification is not reachable due to segregation. Another intrinsic challenge is the geometric and electronic entanglement, i.e. when substituting one element by another, the structure might change and with it, the electronic properties.

A new approach is the partial substitution of main group elements in isostructural intermetallic compounds, enabling excellent electronic control with minimal geometric variation. Taking InPd₂ and substituting In by Sn alters the valence electron count, while the distances are mostly not affected. Tuning the In/Sn ratio allows to address the electronic influence with very high resolution. Results in gas-phase hydrogenation and electrocatalysis are presented as examples of the broadly applicable approach.

O 45.2 Wed 15:30 H4
Gallium droplets on nanostructured surfaces as matrix material for supported liquid metal solutions — ●ANDRÉ HOFER, NICOLA TACCARDI, PETER WASSERSCHIED, and JULIEN BACHMANN — FAU Erlangen, Germany

A large variety of organic compounds are produced industrially using a dehydrogenation reaction which removes H₂ from a molecule and hence converts it into a more reactive and valuable product. Usually, such a reaction is endothermic and needs to be catalysed or performed at elevated temperatures. Our approach for improving the availability of the catalyst is the utilization of supported catalytically active liquid metal solutions (SCALMS). Here, the catalytically active material is dissolved in a dynamic liquid matrix, protecting it from undesired deactivation. Ga is used in our approach as the matrix material due to its outstanding properties. So far, SCALMS catalysis has been performed with very limited control of particle sizes. Here, we present a model system to determine the fundamental kinetic parameters of SCALMS reactions. We fabricate highly ordered, nanostructured substrates by electrochemical anodization of Al, generating indentations in a hexagonal arrangement with a tunable diameter. These substrates are coated with acidic or alkaline metal oxides by ALD to affect the surface tension and wetting behaviour of the Ga droplets. Subsequently, a Ga complex is spin-coated from organic solution on the surfaces and the elementary Ga droplets are obtained upon thermal treatment. Parameters relevant to SCALMS application of the surface fabricated are investigated systematically as they depend on the preparative parameters.

O 45.3 Wed 15:45 H4
Extending the SCALMS catalytic concept to ternary systems — ●MICHAEL MORITZ¹, SVEN MAISEL¹, NARAYANAN RAMAN², HAIKO WITTKÄMPER¹, CHRISTOPH WICHMANN¹, NICOLA TACCARDI², PETER WASSERSCHIED², ANDREAS GÖRLING¹, HANS-PETER STEINRÜCK¹, and CHRISTIAN PAPP¹ — ¹Friedrich-Alexander-Universität Erlangen-Nürnberg, Department Chemie und Pharmazie,

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Over the last few years, supported catalytically active liquid metal solutions (SCALMS) were shown to be remarkably efficient catalysts for alkane dehydrogenation. The active phase of these catalysts consists of a liquid metal matrix, in which catalytically active transition metals are dissolved. So far, only Gallium was used as a liquid matrix material, because of the low toxicity and low melting point. Since extensive research has already been made on Gallium-based SCALMS systems with different catalytically active transition metals, varying the matrix material is the logical next step to further improve the catalyst performance. These efforts are now extended to ternary systems such as GaInPt and GaSnPt. This extension opens up new questions as it increases the complexity, but also brings exciting new properties and insights into the dynamics of liquid SCALMS catalysts. In this talk, the most recent results regarding these ternary systems will be presented, with an emphasis on photoemission studies. Funded by SFB 1452.

O 45.4 Wed 16:00 H4
Investigation of Pt-Ga SCALMS model particles using photoelectron spectroscopy — ●CHRISTOPH WICHMANN¹, HAIKO WITTKÄMPER¹, MICHEAL MORITZ¹, TZUNG-EN HSIEH², JOHANNES FRISCH², MINGJIAN WU³, MARCUS BÄR², ERDMANN SPIECKER³, HANS-PETER STEINRÜCK¹, and CHRISTIAN PAPP¹ — ¹Universität Erlangen, Physikalische Chemie II, Germany — ²Helmholtz-Zentrum Berlin, Germany — ³Universität Erlangen, Lehrstuhl für Werkstoffwissenschaften, Germany

Supported catalytically active liquid metal solutions (SCALMS) recently gained much attention as highly active and stable catalysts for the dehydrogenation of alkanes. SCALMS are metal solutions composed of low amounts of catalytically active transition metals like Rh, Pd, or Pt, alloyed with low melting metals like Ga, which act as matrix. Their stability is attested to a notable resistance against deactivation by coking, which is the prevalent deactivation route for dehydrogenation catalysts. To obtain a fundamental understanding, we make these complex materials systems accessible for a surface science approach. To gain insight in the catalytic properties of such nano-solutions, we work with supported PtGa particle systems. Herein, supported PtGa particle systems with low Pt content were investigated. The influence of the deposition sequence, the effects of annealing, and exposure to oxygen on the alloying and morphology of the resulting particle were studied with XPS using different excitation energies to obtain a depth-profile of the first few layers of the liquid.

Funded by SFB 1452.

Topical Talk O 45.5 Wed 16:15 H4
Understanding liquid metal catalysts for graphene synthesis using machine learning interatomic potentials — ●HENDRIK H. HEENEN — Fritz-Haber-Institut der MPG, Berlin, Germany

High-quality, near defect-free graphene can be synthesized on the levelled and uniform surfaces of liquid metal catalysts. This smoothness on the microscale is sometimes accompanied by seemingly different catalytic properties, the determination of which is, however, ambiguous. Assessing distinct catalytic properties of liquid metal catalysts by first principles atomistic simulations has so far been challenged due to the intractable long length and time scales necessary to model the liquid phase. Using computationally efficient machine learning interatomic potentials (MLIPs) trained to first principles data allows to

extrapolate predictability to necessary scales and opens an avenue for obtaining the desired microscopic insight.

In this talk I will present strategies to train and employ MLIPs for the simulation of graphene synthesis on liquid metal catalysts. I will introduce the data-efficient training of MLIPs via fairly automatic workflows as a tool to extend the predictive accuracy of e.g. density functional theory to larger scales. On basis of these potentials, large-scale simulations can be performed to compute experimental observables and elucidate microscopic processes relevant to graphene synthesis. Further, one can identify trends between different metals and directly compare between the solid and liquid states of a catalyst. Findings based on these simulation approaches shed new light on the role of the liquid state of liquid metal catalysts.

Topical Talk

O 45.6 Wed 16:45 H4

Ionic liquids and deep eutectic solvents - sustainable media for selective molecular recognition and adsorption — ●JAN BLASIUS, LEONARD DICK, and BARBARA KIRCHNER — Mulliken Center for Theoretical Chemistry, University of Bonn, Beringstrasse 4+6, D-53115 Bonn, Germany

The effective reduction of CO₂ emission and chemical waste production are key disciplines on our way towards a more sustainable future. Ionic liquids (ILs) and deep eutectic solvents (DESS) offer new opportunities for addressing these challenges, as their properties can be adjusted in order to fulfill specific purposes. To efficiently optimize their usage for various applications, it is vital to understand the underlying molecular behavior and inherent structuring inside these liquids. Using state-of-the-art theoretical methods, we shed light on molecular adsorption and recognition mechanisms in ILs and DESSs. This enables us to determine the reasons for specific capacities and allows a theoretical design of solvents with precisely tuned geometric, energetic and kinetic parameters in order to enhance the processes of interest. In this presentation, we will highlight our most recent research concerning molecular recognition and adsorption in ILs and DESSs which can support the development of novel chemical processes that pave our way towards a more sustainable future.

O 45.7 Wed 17:15 H4

Surfaces of ionic liquids studied by ARXPS and UHV Pendant Drop — ●ULRIKE PAAP, FLORIAN MAIER, and HANS-PETER STEINRÜCK — Chair of Physical Chemistry II, FAU Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany

Ionic liquids (ILs) are characterized by a low melting point, low vapor pressure and low surface tension. Many ILs exhibit high gas solubility along a high chemical and thermal stability. Such properties are beneficial in many areas such as gas absorbents, refrigerants, lubricants, antistatics and surfactants. In this work, we studied various imidazolium-based ILs with different functional PEG chains attached to the cation using angle-resolved X-ray photoelectron spectroscopy (ARXPS) and a new pendant drop setup, which enables to measure the surface tension also in ultrahigh vacuum (UHV). With ARXPS, we determine the surface composition of the topmost IL nanometers on the molecular level. We combine these results with our surface tensions studies in UHV and atmosphere. Our results allow for a deeper understanding of enrichment and molecular orientation processes at the

outermost surface of these systems in a microscopic and macroscopic range.

This work was supported by the European Research Council (ERC) through an Advanced Investigator Grant (ILID 693398) to HPS and the Collaborative Research Center (CRC) 1452: Catalysis at Liquid Interfaces.

O 45.8 Wed 17:30 H4

Mixed Films of protic and non-protic Ionic Liquids on Metal Surfaces – on-surface metathesis on Ag(111) — ●STEPHEN MASSICOT¹, TOMOYA SASAKI², MATTHIAS LEXO¹, SUNGHWAN SHIN¹, FLORIAN MAIER¹, SUSUMU KUWABATA², and HANS-PETER STEINRÜCK¹ — ¹Lehrstuhl für Physikalische Chemie 2, Friedrich-Alexander-Universität Erlangen-Nürnberg — ²Department of Applied Chemistry, Graduate School of Engineering, Osaka University

Ionic liquids (ILs) are salts that are composed of poorly coordinating ions and thus exhibit melting points typically well below 100°C. Thin films of ILs are of utmost interest in many applications such as in catalysis and electrochemistry. In this context, we investigate mixed ultrathin films of the protic IL diethylmethylammonium trifluoromethanesulfonate ([dema][TfO]) and the aprotic IL 1-methyl-3-octylimidazolium hexafluorophosphate ([C₈C₁Im][PF₆]) on a Ag(111) surface. The films are prepared by *in situ* physical vapor deposition in UHV. The molecular composition of the IL/solid and IL/vacuum interfaces is studied by angle-resolved and temperature-programmed X-ray photoelectron spectroscopy. We observe thermally induced phenomena of ion exchange and preferential enrichment at these interfaces. Furthermore, ions desorb selectively which leads to the on-surface formation of a new IL by metathesis at the IL/metal interface.

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O 45.9 Wed 17:45 H4

SCILL model catalysis - butadiene hydrogenation studied with molecular beam techniques — ●LEONHARD WINTER, STEPHEN MASSICOT, AFRA GEZMIS, FLORIAN MAIER, and HANS-PETER STEINRÜCK — Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Egerlandstr. 3, 91058 Erlangen

Ionic Liquids (ILs) are low temperature melting salts, often liquid even below room temperature. In “Solid Catalyst with Ionic Liquid Layer (SCILL)” systems, IL thin films are used to coat the catalytically active metal and therefore, modify the reactivity and the selectivity of the catalyst. Selectivity is crucial e.g., in the industrially important hydrogenation of 1,3-butadiene to butenes since further hydrogenation to *n*-butane must be suppressed.

We used a supersonic molecular beam to investigate the dynamical details of this reaction in a UHV model study. The method of King and Wells was used to measure sticking coefficients of 1,3-butadiene and 1-butene on bare Pt(111) and Pt(111) coated with ultrathin layers of the IL 1,3-dimethylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([C₁C₁Im][Tf₂N]). The hydrogenation reaction was also modelled by pre-adsorbing and co-feeding hydrogen gas.

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