Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room B113 - Session HC+SS-WeM

Origins of Single Atom Catalysis

Moderators: Rachael Farber, University of Kansas, **Gareth Parkinson**, TU Wien

8:00am **HC+SS-WeM-1 Role of Pyridinic Nitrogen in the Mechanism of the Oxygen Reduction Reaction on Carbon Electrocatalysts***, **Kotaro Takeyasu,*** University of Tsukuba, Japan*; S. Singh,* Shiv Nadar University, India*; K. Homma, K. Hayashida,* University of Tsukuba, Japan*; S. Ito, T. Morinaga,* National Institute of Technology, Tsuruoka College, Japan*; Y. Endo, M. Furukawa,* University of Tsukuba, Japan*; T. Mori,* National Institute for Materials Sciences (NIMS), Japan*; H. Ogasawara,* SLAC National Laboratory*; J. Nakamura,* International Institute for Carbon-Neutral Energy Research, Kyushu University, Japan

Nitrogen doped carbon catalysts are promising Pt-free catalysts for the oxygen reduction reaction (ORR) in polymer electrolyte fuel cells owing to the high durability and the high activity in alkaline media. The primary active site in N-doped carbon catalysts is the pyridinic nitrogen (pyri-N), which is bound to two carbon atoms with negative charge.[1] However, a large barrier of N-doped carbon catalysts for the commercial usage is the decreased activity in acidic media. Hence, we investigated this deactivation phenomenon to widen the applicability of N-doped carbon catalysts. In acidic media, the protonation of pyri-N (pyri-NH+) occurs as the first step owing to the basicity of pyri-N.

$\text{pyri-N} + H^+ \rightarrow \text{pyri-NH}^+$ (1)

As the following process, we have demonstrated the electrochemical reduction of pyri-NH+ coupled with thermal O2 adsorption on carbon atoms near pyri-NH+ using model catalysts:

$O_2 + \text{pyri-NH}^+ + e^- \rightarrow O_{2a} + \text{pyri-NH}$ (2)

In this reaction, the thermal adsorption of O2 let the electrochemical reduction of pyri-NH+ to pyri-NH thermodynamically favorable due to the adsorption energy of O2. Although the formation of pyri-NH+ is a cause of the decrease in ORR activity, but pyri-NH+ itself is essential for the formation of pyri-NH and the adsorption of O2. A key point is that a dope electron into π* orbital of π-conjugative system near pyri-NH promotes the adsorption of O2. However, the hydration of pyri-NH+ forming pyri-NH+・(H2O)n causes a lower shift in the redox potential and consequently, Eq. 2 becomes the rate-determining step (RDS). Therefore, we consider that the hydration of pyri-NH+ is the main cause of the decrease in ORR activity in acid electrolytes.[2] Thus, we hypothesize an enhanced ORR activity by the introduction of hydrophobicity in the vicinity of pyri-NH+, suppressing the extent of hydration.

Introducing the hydrophobic cavity prevented the hydration of pyri-NH+ but inhibited the proton transport. We then increased proton conductivity in the hydrophobic cavity by introducing SiO2 particles coated with ionic liquid polymer/Nafion® which kept the high onset potentials with an increased current density even in acidic media.[3]

References

[1] D. Guo, J. Nakamura et al., Science, 2016, 351, 361-365.

[2] K. Takeyasu, J. Nakamura et al., Angew. Chem. Int. Ed. 60, 5121 (2021).

[3] S. K. Singh, K. Takeyasu, J. Nakamura et al., Angew. Chem. Int. Ed. 61, e202212506 (2022).

8:20am **HC+SS-WeM-2 Atomic-Level Studies of Mono-Carbonly and Gem-Dicarbonyl Formation on Rh-Decorated Fe_3O_4(001)***, **Panukorn Sombut**, C. Wang, L. Puntscher, M. Meier, J. Pavelec, Z. Jakub, M. Schmid, U. Diebold,* TU Wien, Austria*; C. Franchini,* University of Vienna, Austria*; G. Parkinson,* TU Wien, Austria

Understanding the interaction between reactant molecules and "single atom" active sites is important for comprehending the evolution of single-atom catalysts in reactive atmospheres. Here, we study how Fe_3O_4(001)-supported[1] Rh_1 monomers and Rh_2 dimer species interact with CO using density functional theory (DFT), combined with temperature-programmed desorption, x-ray photoelectron spectroscopy, and in-situ scanning tunneling microscopy techniques. Our results show that stable $Rh_1(CO)_1$ monocarbonyls are the exclusive product of CO adsorption at both 2-fold and 5-fold coordinated Rh_1 sites, but the different coordination environment leads to different adsorption energies. The DFT calculations reveal that the $Rh_1(CO)_1$ formed at the 5-fold coordinated Rh_1 site adopts an octahedral structure, while the $Rh_1(CO)_1$ formed at the 2-fold coordinated Rh_1 site forms an additional bond to a subsurface oxygen atom of the support, leading to a pseudo-square planar structure. The direct addition of a second CO molecule to $Rh_1(CO_1)$ at the 2-fold coordinated Rh_1 site to form a $Rh_1(CO)_2$ gem-dicarbonyl is energetically favorable according to DFT; however, this process is not observed in experiments under UHV conditions. Instead, we observe the formation of limited $Rh_1(CO)_2$ exclusively via the CO-induced breakup of Rh_2 dimers, in agreement with DFT results, which suggest an unstable $Rh_2(CO)_3$ intermediate.

1. Bliem, R. *et al.* Subsurface cation vacancy stabilization of the magnetite (001) surface. *Science* **346**, 1215–1218 (2014).

8:40am **HC+SS-WeM-3 A Few Questions About Single Atom Catalysts: When Theory Helps***, **Gianfranco Pacchioni,*** University of Milano-Bicocca, Italy **INVITED**

In the past, single atom catalysts (SACs) could not be clearly visualized and characterized due to the limitations associated with instrumental resolution. Today this is a new frontier in heterogeneous catalysis due to the high activity and selectivity of SACs for various catalytic reactions. This has opened various questions for theory. One is where are the atoms and what is the stability of SACs in working conditions. In order to address these questions, we will discuss the nature of isolated metal species deposited on oxide surfaces (TiO_2 and ZrO_2 in particular). These systems have been characterized experimentally using high-resolution scanning transmission electron microscopy (STEM), Fourier transform infrared spectroscopy (FTIR), and temperature programmed desorption (TPD) spectra of adsorbed CO probe molecules. Combining these data with extensive Density Functional Theory (DFT) calculations one can provide an unambiguous identification of the stable single-atom species present on these supports and of their dynamic behavior.

The other question that can be addressed by theory is the prediction of the behavior of SACs in electrocatalytic processes such as the oxygen reduction (ORR), the oxygen evolution (OER) and the hydrogen evolution (HER) reactions. In this context we assist to a rapidly growing number of DFT studies and of proposals of universal descriptors that should provide a guide to the experimentalist for the synthesis of new catalysts, in particular related to graphene-based SACs. We will critically analyze some of the current problems connected with these DFT predictions: accuracy of the calculations, neglect of important contributions in the models used, physical meaning of the proposed descriptors, inaccurate data sets used to train machine learning algorithms, not to mention some severe problems of reproducibility. It follows that the "rational design" of a catalyst based on some of the proposed universal descriptors or on the DFT screening of large number of structures should be considered with some caution.

9:20am **HC+SS-WeM-5 A Multi-Technique Study Of Ethylene and H2 Adsorption on Rh_1/Fe_3O_4***, **Gareth Parkinson**, C. Wang, P. Sombut, L. Puntscher,* TU Wien, Austria

The hydroformylation of alkenes has emerged as one of the most interesting applications of "single-atom" catalysis. Nevertheless, there have been relatively few fundamental studies into how the reactants (CO, alkene, and H_2) bind at the active site. In this talk I will show STM, XPS, TPD and DFT results to illustrate how C_2H_4 and H_2 interact with a Rh_1/Fe_3O_4(001) model catalyst. Ethylene binds strongly at the Rh_1 sites, but there is very little evidence for the formation of di-ethylene species under UHV conditions. H_2 adsorbs as a dihydride at the Rh_1 sites, and desorbs close to room temperature in TPD experiments without spilling over onto the oxide support. Evidence for the co-adsorption of the different reactants will be discussed in the context of the hydroformylation reaction.

9:40am **HC+SS-WeM-6 Remote Activation of H–H bonds by Platinum in Single-Atom Alloy Catalysts*, Francisco Zaera,*** University of California Riverside

With heterogeneous catalysts, chemical promotion takes place at their surfaces. Even in the case of single-atom alloys (SAA), where a reactive metal is atomically dispersed in small quantities within the main host, it is assumed that both elements are exposed and available to bond with the reactants. Here we show, on the basis of *in situ* x-ray absorption spectroscopy data, that the Pt atoms in Cu-Pt SAA catalysts are located at the inner interface between the metal nanoparticles and the silica support instead. Kinetic experiments indicated that these catalysts still display better selectivity for the hydrogenation of unsaturated aldehydes to unsaturated alcohols than the pure metals. Quantum mechanics calculations not only corroborated the particular stability of Pt at the metal-support interface, but also explained the catalytic performance improvement as due to a remote lowering of the activation barrier for the scission of the H–H bond in molecular hydrogen at Cu sites by the internal Pt atoms.

11:00am **HC+SS-WeM-10 Electrifying Industrial Chemistry at the Molecular Level: Controlling the Electrocatalytic Transformation of Alcohols and Alkanes to Valuable Products*, Marcel Schreier,*** University of Wisconsin-Madison **INVITED**

Producing fuels and chemicals using renewable electricity holds the promise to enable a truly sustainable circular economy based on sustainably produced carriers of electrical energy and sustainably produced chemicals. To date, the vast majority of electrocatalytic reactions are limited to the transformation of small inorganic molecules such as CO_2, H_2O, N_2, as well as the oxidation and reduction of alcohols. However, comprehensive electrification of the chemical industry will require electrocatalytic reactions that can promote the transformations of C(sp^3)-H and C(sp^3)-C(sp^3) bonds, which are central to today's industry.

In this presentation, I will show how fundamental understanding of the interfacial processes occurring in electrocatalytic reactions can be exploited to expand the reaction scope of electrocatalysis to the transformation of complex substrates involving the controlled activation of C-H and C-C bonds. In a first step, I will show how this approach allows us to transform ethanol to ethylene oxide, an important plastic precursor. Subsequently, I will discuss methods to electrocatalytically transform inert alkanes such as methane and ethane at room temperature.

11:40am **HC+SS-WeM-12 Probing Elementary Steps and Catalyst Structure Evolution: Insights into Formic Acid Conversion on Rh/Fe_3O_4(001) Model Catalysts*, Zdenek Dohnalek,*** Pacific Northwest National Laboratory

Single-atom catalysis represents an exciting area of research due to the potential to qualitatively transform the activity and selectivity of supported metal catalysts. However, our fundamental understanding of their stability under reaction conditions is limited. To address this gap, we employed scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and temperature programmed desorption (TPD). We prepared well-characterized model Rh/Fe_3O_4(001) catalysts with distinct types of Rh single-atom sites. In model catalytic studies, we investigated the effect of reactants on the structure and activity of such Rh/Fe_3O_4(001) catalysts. Formic acid, which deprotonates to surface formate and hydroxyl species, is employed as a model to follow the fate of dehydration and dehydrogenation reaction channels. We demonstrate that small amounts of Rh adatoms induce a shift from the dehydration pathway yielding CO on bare Fe_3O_4(001) to dehydrogenation yielding CO_2 on Rh_{ad}-Fe_3O_4(001). Multiple turnovers are achieved on each Rh_{ad} during the single TPD sweep. As Rh adatoms are highly unstable, we further studied the Rh stabilized in octahedral iron sites within the Fe_3O_4(001) surfaces that are stable on high surface area Rh/Fe_3O_4 catalysts. A similar shift from dehydration to dehydrogenation is observed, but much higher coverages of Rh are required. We showed that adsorbed species transiently destabilize Rh_{oct} and lead to the formation of Rh_{ad}, which is only present during the reaction. Independent studies of hydroxylated surfaces reveal that surface OHs are responsible for the Rh_{oct} destabilization and conversion to active Rhad species. Studies of elementary reaction steps and catalyst dynamics on well-defined model systems are critical for the future design of catalysts with maximum activity and selectivity.

12:00pm **HC+SS-WeM-13 Hydrogen and Hydrocarbon Reactions on Single-Atom RhCu(100)*, Laurin Joseph,*** *M. Powers, J. Rosenstein, A. Utz,* Tufts University

A class of catalysts called single-atom alloys allow for the combination of a more reactive, more expensive dopant metal dispersed within a less active, more selective, and cheaper base metal. These catalysts have been well characterized and studied using techniques such as temperature programmed desorption (TPD), scanning tunneling microscopy (STM), and reflection absorption infrared spectroscopy (RAIRS). However, the detailed, molecular-level bond activation energetics and kinetics have not yet been experimentally interrogated for high-barrier reactions on these catalysts—a region where more efficient catalysts are most sorely needed.

We will present recent results that first characterize the dissociation and spillover of H resulting from both atomic and molecular H2 adsorption on base Cu(100) and RhCu(100) single atom alloy, and then describe results from energy resolved molecular beam studies of CH4 dissociation that quantify reaction probability as a function of energy distribution among reactant and surface degrees of freedom. We expect these studies will reveal new insights into the molecular mechanism for an important class of heterogeneously catalyzed reactions and provide new benchmarks for computational studies of single atom catalysts.

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