

O 79: Surface Reactions and Heterogeneous Catalysis 3

Time: Friday 10:30–12:45

Location: H4

Topical Talk

O 79.1 Fri 10:30 H4

Exploitation of Heterocycles for N-doped Graphene Nanomaterials — RÉMY PAWLAK¹, ULRICH ASCHAUER², SILVIO DECURTINS², JASCHA REPP³, PAVEL JELÍNEK⁴, ERNST MEYER¹, LAERTE L. PATERA⁵, and SHI-XIA LIU² — ¹Department of Physics, University of Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland — ²Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, 3012 Bern, Switzerland — ³Institute of Experimental and Applied Physics, University of Regensburg, 93053 Regensburg, Germany — ⁴Institute of Physics of Czech Academy of Sciences, 16200 Prague, Czech Republic — ⁵Department of Chemistry and Catalysis Research Center, Technical University of Munich, 85748 Garching, Germany

On-surface chemical reactions have been intensively investigated in order to obtain carbon-based functional nanomaterials which very often cannot be synthesized by wet chemistry. Thus, tailored heterocyclic precursors are becoming increasingly important for the development of highly symmetric 2D-conjugated porous architectures and 1D N-doped graphene nanoribbons (GNRs) with desired functions due to their intrinsic electronic properties. This presentation will focus on our collaborative work on C-C coupling reactions on various surfaces leading to the formation of a range of nanostructures, including molecular wires, fully fused porphyrin-GNR hybrids, as well as 1D- and 2D-conjugated porous networks. All of these atomically precise nanostructures can be directly visualized by STM and AFM. The fine-tuned electronic properties by chemical modification are discussed.

O 79.2 Fri 11:00 H4

On-surface cyclomerization of oxygen heterocycles: Controlling the ring size by tuning the molecule-surface interaction — ●ANDREAS DÖRR¹, NEMANJA KOCIC¹, LUKAS FROMM², VLADIMIR AKHMETOV³, KONSTANTIN Y. AMSHAROV³, ANDREAS GÖRLING², and SABINE MAIER¹ — ¹Department of Physics, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen (Germany) — ²Department of Chemistry and Pharmacy, Chair of Theoretical Chemistry, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen (Germany) — ³Institute for Chemistry, Martin-Luther-University Halle-Wittenberg, 06099 Halle (Germany)

Heterocycles with nitrogen, oxygen, or sulfur atoms are the basic units that incorporate chemical functionalization into carbon scaffolds. For oxygen-doped nanographenes, furan and pyran, having five- and six-membered rings, respectively, are the most common ones. However, their on-surface synthesis via cyclomerization reactions has so far been elusive. Here, we present a low-temperature scanning tunneling microscopy study combined with density functional theory calculations to understand the on-surface synthesis of furan and pyran derivatives from ketone-functionalized precursors on metal surfaces. We first discuss the self-assemblies of the precursors, which are strongly influenced by molecule-surface interactions. Upon annealing, the different intermolecular binding motifs resulted in selective cyclomerization reactions toward furan and pyran moieties.

O 79.3 Fri 11:15 H4

Proximity-induced superconductivity in atomically precise nanographene — ●JUNG-CHING LIU¹, RÉMY PAWLAK¹, XING WANG², PHILIPP D'ASTOLFO¹, CARL DRECHSEL¹, PING ZHOU², HONGYEN CHEN³, SILVIO DECURTINS², ULRICH ASCHAUER², SHI-XIA LIU², WULF WULFHEKEL³, and ERNST MEYER¹ — ¹Department of Physics, University of Basel, Klingelbergstrasse 82, CH-4056 Basel — ²Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Freiestrasse 3, CH-3012 Bern — ³Physikalisches Institut, Karlsruhe Institute of Technology, Wolfgang-Gaede-Str. 1, D-76131 Karlsruhe

Atomically precise nanographenes (NGs) can be efficiently synthesized through on-surface reactions. On such designed NGs, topological superconductivity could be fostered via proximity to a s-wave superconductor. However, on-surface synthesis of NGs is still missing on superconducting surfaces [1-3]. To fill the gap, we first fabricate a Ag buffer layer on the Nb(110) superconductor [4], and grow atomically precise NGs on the Ag/Nb substrate using DBBA as the precursor. Through the investigation of low temperature STM/AFM, we demonstrate successful synthesis of polymeric chains and NGs on the superconducting Ag/Nb(110) substrate. We believe our method provides a promising

platform for studying the role of topology in the interaction between carbon magnetism and superconductivity [5]. [1]Cai et al., Nature 466, 470-473 (2010) [2]K. A. Simonov et al., Sci. Rep. 8, 3506 (2018) [3]M. Kolmer et al., Science 369, 571-575 (2020) [4]T. Tomanic et al., Phys. Rev. B 94, 220503 (2016) [5]J.-C. Liu et al., arXiv:2202.00460

O 79.4 Fri 11:30 H4

Real-space Imaging of Unprecedented Phenyl Group Migration Reaction on Metal Surfaces — ●ZILIN RUAN^{1,2}, BAIJIN LI², SHIJIE SUN², YONG ZHANG², LEI GAO³, JIANCHEN LU², MICHAEL GOTTFRIED¹, and JINMING CAI² — ¹Department of Chemistry, Philipps University Marburg, Hans-Meerwein-Straße 4, 35037 Marburg (Germany) — ²Faculty of Materials Science and Engineering, Kunming University of Science and Technology, Kunming, Yunnan 650093 (China) — ³Department of Chemistry, Philipps University Marburg, Hans-Meerwein-Straße 4, 35037 Marburg (Germany)

We report on-surface identification and visualization of an unprecedented and universal phenyl group migration reaction of 1,4-dimethyl-2,3,5,6-tetraphenyl benzene (DMTPB) a precursor on Au(111), Cu(111) and Ag(110) substrates by a combination of bond-resolved scanning tunneling microscopy (BR-STM) and density functional theory (DFT) calculations. The phenyl group migration reaction of DMTPB precursor results in formations of variously unprecedented polycyclic aromatic hydrocarbons on the substrates. DFT calculations reveal that the multiple-steps phenyl group migration reactions are facilitated by the radical attack and rearomatization of the DMTPB precursor. Our study provides unprecedented insights into complex surface reaction mechanisms at the single molecule level, which may guide the design of chemical species.

O 79.5 Fri 11:45 H4

Deciphering the intramolecular C-C coupling mechanism of a model aryl radical via bond-level AFM imaging — ●QIGANG ZHONG¹, JANNIS JUNG², DANIEL KOHRS³, DANIEL EBELING¹, DOREEN MOLLENHAUER², HERMANN A. WEGNER³, and ANDRÉ SCHIRMEISEN¹ — ¹Institute of Applied Physics, Justus-Liebig University Giessen (JLU), Germany — ²Institute of Physical Chemistry, JLU, Germany — ³Institute of Organic Chemistry, JLU, Germany

Although on-surface dehalogenative and dehydrogenative C-C coupling has proved to be a versatile and prevailing approach to constructing atomically precise carbon-based nanostructures, understanding of the reaction mechanisms remains limited by the elusive intermediates. Here, we studied the intramolecular cyclodehydrobromination of 1-bromo-8-phenylnaphthalene on Cu(111) and Ag(111) using bond-level atomic force microscopy (BL-AFM). The reaction occurs at room temperature on both metal surfaces, while the reaction rate on Cu(111) is much higher than that on Ag(111) presumably due to the higher catalytic activity of copper. Surface-bound radicals, cyclized intermediates and dehydrogenated product were captured by BL-AFM imaging and verified by DFT calculations, suggesting a multi-step reaction process, i.e. debromination, radical cyclization and dehydrogenation. The large proportion (up to 65 percent) of cyclized intermediates on Cu(111) indicates that dehydrogenation is the rate-determining step, which is corroborated by DFT calculations of activation barriers. To achieve a reasonable activation barrier for dehydrogenation, multiple pathways were theoretically evaluated.

O 79.6 Fri 12:00 H4

Interplay between π -conjugation and exchange magnetism in one-dimensional porphyrinoid polymers — ●KALYAN BISWAS¹, MAXENCE URBANI¹, ANA SÁNCHEZ-GRANDE¹, DIEGO SOLER², KOEN LAUWAET¹, ADAM MATĚJ², PINGO MUTOMBO², JOSÉ M. GALLEGO¹, RODOLFO MIRANDA¹, DAVID ÉCJIA¹, PAVEL JELÍNEK², TOMÁS TORRES¹, and JOSÉ I. URGEL¹ — ¹IMDEA Nanoscience, Madrid, Spain — ²CATRIN, Olomouc, Czech Republic

The field of carbon magnetism has gained an increased attention in view of the recent progress made in the synthesis and characterization of open-shell polycyclic aromatic hydrocarbons following a bottom-up synthetic approach. In this work, we introduce an exemplary approach toward the bottom-up fabrication of unprecedented magnetic porphyrinoid-based polymers homocoupled via surface-catalyzed [3 +

3] cycloaromatization of isopropyl substituents studied on Au(111) under ultra-high vacuum conditions. The chemical structure of the polymer, formed by thermal-activated intra- and intermolecular oxidative ring closure reactions followed by controlled tip-induced hydrogen dissociation from the porphyrinoid units, have been clearly elucidated by scanning tunneling microscopy and non-contact atomic force microscopy. Scanning tunneling spectroscopy, complemented by computational investigations reveals the antiferromagnetic singlet ground state ($S=0$), which display singlet-triplet inelastic excitations observed between spins of adjacent porphyrinoid units only along a specific π -conjugation pathway. We envision that our approach can be a highly relevant in nanoscale spintronic devices.

O 79.7 Fri 12:15 H4

Photoactivation of Azide in SURMOFs — •JIMIN SONG, XIAOJUAN YU, MANUEL TSOTSALAS, ALEXANDER KNEBEL, ALEXEI NEFEDOV, STEFAN HESSLER, YUEMIN WANG, and CHRISTOF WÖLL — Institute of Functional Interfaces, Karlsruhe Institute of Technology, 76344, Eggenstein-Leopoldshafen, Germany

The ability to turn the surface activation of metal-organic frameworks (MOFs) is essential for developing advanced MOF applications. Here, we have successfully synthesized a surface-mounted MOF (SURMOF) model system with azide side groups in order to investigate the photoactivation of phenyl azide and its reaction pathways. In situ UHV infrared reflection absorption spectroscopy (IRRAS) was applied to precisely monitor the chemical changes taken place on the surface of highly oriented and crystalline SURMOFs under UV irradiation at different temperatures. Combining with in situ XRD, MS and XPS, a two-step mechanism is proposed including the activation and sub-

sequent reaction of azide with adjacent C=C bonds yielding pyrrole species.

O 79.8 Fri 12:30 H4

Differences in the Intermolecular Interaction of Electron-rich Phosphines on a Metal and a Salt Surface — •VLADIMIR LYKOV¹, FLORENZ BUSS², MILICA FELDT³, KARINA MORGENSTERN¹, and FABIAN DIELMANN⁴ — ¹Chair of Physical Chemistry I, Ruhr Universität Bochum, Germany — ²Institute for Inorganic and Analytical Chemistry, Westphalian Wilhelms University of Münster, Germany — ³Leibniz-Institut für Katalyse e.V. (LIKAT), Rostock, Germany — ⁴Department of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Austria

Electron-rich phosphines are attractive as capture molecules, for instance, for carbon dioxide (CO₂) and sulfur dioxide (SO₂) by forming zwitterionic Lewis base adducts with them [1]. The main focus of this project is understanding the interaction behind this capturing in real space. For this purpose, we use a low-temperature (7 K) scanning tunneling microscope (STM). To understand the influence of the metal surface on this capture process, we compare the molecules adsorbed on Ag(100) to those on NaBr(100). As a first step, the different interaction of phosphines with the salt multilayers and with the metal was investigated by step-wise heating from 43 K to 135 K. The difference in intermolecular interaction on these surfaces will be discussed in this presentation.

[1] Buß F., Röthel M.B., Werra J.A., Rotering P., Wilm L.F.B., Daniliuc C.G., Löwe P., Dielmann F., Chem. Eur. J. 10.1002/chem.202104021 (2021)