O 90: Poster Session VII: Surface reactions I

Time: Thursday 10:30–12:30 Location: P

O 90.1 Thu 10:30 P

Hierarchically Structured Janus Membrane Surfaces for Enhanced Membrane Distillation Performance — •Nick Chew[1,2], Yujun Zhang[2], Kunli Goh[2], Jia Shin Ho[2], Rong Xu[2], and Rong Wang[2] — [1]University of North Carolina at Chapel Hill, Chapel Hill, USA — [2]Nanyang Technological University, Singapore, Singapore

Commercial hydrophobic poly(vinylidene fluoride) (PVDF) membranes are vulnerable to membrane fouling and pore wetting, hampering the use of membrane distillation (MD) for the treatment of surfactant- and oil-containing feed streams. To address these challenges, we designed novel Janus membranes with multilevel roughness. Specifically, fouling- and wetting-resistant Janus MD membranes with hierarchically structured surfaces were tailored via oxidant-induced dopamine polymerization followed by in-situ immobilization of silver nanoparticles (AgNPs) on commercial PVDF hollow fiber substrates. These membranes demonstrated outstanding anti-fouling properties and salt-rejection performances in comparison to membranes with single-level structures. We ascribed their excellent performance to the coupled effects of improved surface hydrophilicity and self-healing mechanism brought about by AgNPs. Furthermore, the newly engineered membranes exhibited antibacterial properties in Bacillus acidicola solutions as evidenced by clear inhibition zones observed on a confocal laser scanning microscope. The development of hierarchically structured Janus MD membranes with multilevel roughness paves a way to mitigating membrane fouling and pore wetting caused by low-surface-tension feed streams in the MD process.

O 90.2 Thu 10:30 P

Dehydrogenation Reactions of O-Heterocyclic LOHC Molecules — •Felix Hemauer, Philipp Bachmann, Fabian Düll, Johann Steinhauer, Hans-Peter Steinrück, and Christian Papp — Friedrich-Alexander-Universität, Erlangen, Germany

With the dwindling of fossil fuels and the alarming progression of global warming, the ecological and social demand for cleaner and more sustainable energy sources has never been as high. As renewable sources, such as wind and solar power, give no continuous and constant power output, hydrogen is a promising candidate for the chemical storage of energy. The concept of Liquid Organic Hydrogen Carriers (LOHCs) avoids unfavorable handling of elemental hydrogen.

Heterocyclic LOHC molecules display advantageous thermodynamic properties regarding their heat of dehydrogenation. Consequently, several N-heterocycles have been successfully investigated, e.g. the indole-based systems and their derivatives.

In order to investigate the feasibility of O-heterocyclic compounds as possible LOHCs, synchrotron radiation-based high resolution X-ray photoelectron spectroscopy and temperature-programmed desorption measurements of furan and benzofuran were performed on Pt(111) under UHV conditions. By applying heating ramps after the adsorption experiment, the respective dehydrogenation and decomposition reactions are monitored via evaluation of the characteristic spectra. This allows for fundamental insights into the reactivity and stability and helps assessing the viability of the compound class as LOHC.

O 90.3 Thu 10:30 P

Intramolecular Coupling of Terminal Alkynes by Atom Manipulation — •Florian Albrecht[1], Dulce Rey[2], Shadi Fatayer[1], Fabian Schulz[1], Dolorez Perez[2], Diego Pena[2], and Leo Gross[1] — [1]IBM Research - Zurich, Switzerland — [2]CiQUS and Departamento de Quimica Organica Universidade de Santiago de Compostela, Spain

Performing chemical reactions in a scanning probe microscope offers ultimate control over the reaction. The characterization of both, reactant and product, can be performed. Functionalizing the tip of an AFM enables elucidation of molecular geometries down to the atomic level [1] and performing the reaction on ultra-thin insulating films decouples the molecules sufficiently to characterize their electronic structure [2].

Here, we show a Glaser-like coupling reaction of terminal alkynes within individual molecules. Voltage pulses from the tip initiate the reaction and geometric as well as electronic structure of reactant and product are characterized on bilayer NaCl on Cu(111). The observation of partially dehydrogenated reaction intermediates provides insight into the reaction pathway [3].

References: [1] L. Gross, et al. Science 325, 1110 (2009) [2] J. Repp, et al. Phys. Rev. Lett. 94, 026803 (2005) [3] F. Albrecht, et al. Angew. Chem. Int. Ed. 59, 22989 (2020)

O 90.4 Thu 10:30 P

Temperature-dependent decomposition reactions of oxygen-containing LOHC contaminants on Pt(111) — •Valentin Schwaab, Johann Steinhauer, Felix Hemauer, Eva Marie Freiberger, Natalie Waleska, Christian Papp, and Hans-Peter Steinrück — Friedrich-Alexander-Universität, Erlangen, Germany

Liquid organic hydrogen carriers (LOHCs) represent an attractive way for energy storage and transportation utilizing reversible hydrogenation of an organic compound. The system of dibenzyltoluene (H0-DBT) and perhydro dibenzyltoluene (H18-DBT) has been reported as promising candidate featuring suitable physicochemical properties and a favorable toxicology. Technical H0-DBT, however, contains up to 1% of oxygenate impurities, which might negatively affect the quality of the released H_2 gas from the hydrogenated molecule.

To gain insight in the surface reaction of these oxygenates, we investigated several model compounds on Pt(111) using high-resolution temperature-programmed X-ray photoelectron spectroscopy (HR-TPXPS). Diphenylmethanol, benzophenone and dicyclohexylmethanol are found to undergo C-O bond cleavage at the methylene bridge around 350 K, leading to an oxygen-free carbon fragment and adsorbed atomic oxygen. By contrast, dicyclohexylketone shows C-C bond cleavage and the formation of carbon monoxide above 220 K.

CO represents a catalyst poison and is problematic for further applications of the released H_2 gas. A possible solution might be prepurification of industrially produced H0-DBT.

O 90.5 Thu 10:30 P

On-surface synthesis of graphene nanoribbons on the superconducting Ag/Nb(110) substrate — •Jung-Ching Liu[1], Philipp D'astolfo[1], Carl Drechsel[1], Xunshan Liu[2], Silvio Decurtins[2], Shi-Xia Liu[2], Rémy Pawlak[1], and Ernst Meyer[1] — [1]Department of Physics, University of Basel, Klingelbergstrasse 82, Basel, CH 4056 — [2]Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, Bern, CH 3012

Previously, Majorana bound states (MBS) realized in condensed matter systems were based on the interaction between 1D magnetism and s-wave superconductivity[1-3]. To improve the structural diversity for studying MBS braiding, we propose realizing MBSs in graphene sheets or nanoribbons (GNR) through on-surface synthesis[4,5] on a superconducting substrate. Using DBBA as monomers[4], GNR on-surface synthesis is completed via Ullmann polymerization in ultra-high vacuum environment. As the surface reaction is limited on noble metal surfaces, we grow Ag films on the superconducting Nb(110), and introduce superconductivity to Ag by proximity[6]. Measuring with STM and AFM at 4.7K, we confirm proximity-induced superconductivity on Ag with thicknesses up to 5 ML, as well as successful GNR synthesis on the Ag/Nb substrate. We believe our work paves the way to a new research field in graphene topology. References: [1]S. Nadj-Perge et al. Science 2014, 346, 602-607 [2]M. Ruby et al. Nano Lett. 2017, 17, 4473-4477 [3]R. Pawlak et al. Npj Quantum Inf. 2016, 2, 16035 [4]J. Cai et al. Nature 2010, 466, 470-473 [5]K. A. Simonov et al. Nature 2018, 8, 3506 [6]T. Tomanic et al. Phys. Rev. B 2016, 94, 20503

O 90.6 Thu 10:30 P

Impact of atomic hydrogen on decomposition reactions of SiO_2 layers on Si(100): a LEEM study — •Jonas Darius Fortmann[1,2], Gerhard Lilienkamp[1], and Winfried Daum[1] — [1]Institute of Energy Research and Physical Technologies, TU Clausthal, Leibnizstraße 4, 38678 Clausthal-Zellerfeld, Germany — [2]Department for Physics, Experimental Physics, Universität Duisburg-Essen, Lotharstr. 1-21, 47057 Duisburg, Germany

Clean and well-ordered Si surfaces can be obtained by annealing Si wafers covered with a thin, protective layer of SiO_2 in UHV. Tromp et al. first showed that the decomposition of thermally grown SiO_2 layers on Si(100) upon annealing occurs in form of square-like voids appearing spontaneously or at defects [1]. Accordingly, diffusion of Si monomers from the voids to the reaction fronts and their reaction with SiO_2 at the interface are crucial elements of the decomposition process. In this study, we used LEEM to investigate the impact of atomic hydrogen on decomposition reactions of thermally grown and native surface films of SiO_2 on Si(100). For 10 nm thermal oxide, the presence of atomic hydrogen leads to voids of highly irregular shape with crack-like extensions of the reaction fronts into the surface oxide. Moreover, the growth rates of these voids at 900°C are much higher than those found in comparative experiments without hydrogen. In contrast, atomic hydrogen reduces the growth rates of more circular voids in 2 nm native SiO_2 layers on Si(100) at 790°C. The different impact of atomic hydrogen for native and thermal surface oxides will be discussed. [1] R. Tromp et al., Phys. Rev. Lett. **55**, 2332 (1985).

O 90.7 Thu 10:30 P

Surface-controlled intramolecular radical addition versus C-H insertion toward cyclodehydrogenation under mild conditions — •Qigang Zhong[1], Daniel Kohrs[2], Jannis Jung[3], Daniel Ebeling[1], Doreen Mollenhauer[3], Hermann A. Wegner[2], and Andre Schirmeisen[1] — [1]Institute of Applied Physics, Justus-Liebig University Giessen, Germany — [2]Institute of Organic Chemistry, Justus-Liebig University Giessen, Germany — [3]Institute of Physical Chemistry, Justus-Liebig University Giessen, Germany

Despite the ubiquitous existence of aryl radicals in surface reactions, the reactivity of surface-stabilized aryl radicals and its influence on the reaction pathways to C-C coupling remain elusive. Here, we studied the debromination and cyclodehydrogenation of 1-bromo-8-phenylnaphthalene (BPN) on Cu(111) and Ag(111) using bond-resolved scanning probe microscopy. Debromination of BPN at room temperature generated a radical at the naphthyl group which enabled the subsequent cyclodehydrogenation to proceed at mild temperatures (about 350 K on Cu and 420 K on Ag). The reaction temperature is lower on Cu than Ag due to the higher activity of Cu. High-resolution imaging of the cyclized intermediates revealed that radical addition to the phenyl ring transformed the connected C(sp2)-H bond into an out-of-plane C(sp3)-H bond on Cu(111), while the protruding hydrogen atom was shifted to the naphthyl group on Ag(111), reminiscent of C-H insertion in solution. In combination with DFT calculations, we rationalized the different routes to radical C-H activation by the varied reactivity of the aryl radicals depending on the substrate materials.

O 90.8 Thu 10:30 P

On-surface synthesis of diradical organic one-dimensional polymers — •Ana Sánchez-Grande[1], José I. Urgel[1], Ales Cahlík[2], José Santos[1,3], Shayan Edalatmanesh[2], Koen Lauwaet[1], Pingo Mutombo[2], Bruno de la Torre[2], Rodolfo Miranda[1,4], Oliver Gröning[5], Nazario Martín[1,3], Pavel Jelínek[2], and David Écija[1] — [1]C/ Faraday 9, Campus de Cantoblanco. 28049 Madrid (Spain) — [2]Institute of Physics of the Czech Academy of Science, 6253 Praha (Czech Republic) — [3]ltad de Ciencias Químicas, Universidad Complutense de Madrid. 28040 Madrid (Spain) — [4]Departamento de Física de la Materia Condensada, UniversidadAutónoma de Madrid, 28049 Madrid (Spain) — [5]Empa, Swiss Federal Laboratories for Materials Science and Technology 8600 Dübendorf (Switzerland)

In this work, we present the on-surface synthesis of one-dimensional polymers based on cumulene-bridged peripentacene units on a bare Au(111) surface under ultra-high-vacuum (UHV) conditions. The structural characterization of the polymers has been realized via scanning tunneling microscopy (STM) and confirmed by non-contact atomic force microscopy (nc-AFM). The electronic characterization of polymers has been performed via scanning tunneling spectroscopy (STS) which, complemented by theoretical calculations, reveals that the polymers present an experimental band gap of 0.8 eV and pure diradical character, exhibiting one unpaired spin at each end. We observe a transition from an antiferromagnetic ground state for peripentacene dimers to a paramagnetic ground state for trimers or longer polymers.