doi:10.2533/chimia.2021.979 Chimia 75 (2021) 979

Swiss Science Concentrates

A CHIMIA Column

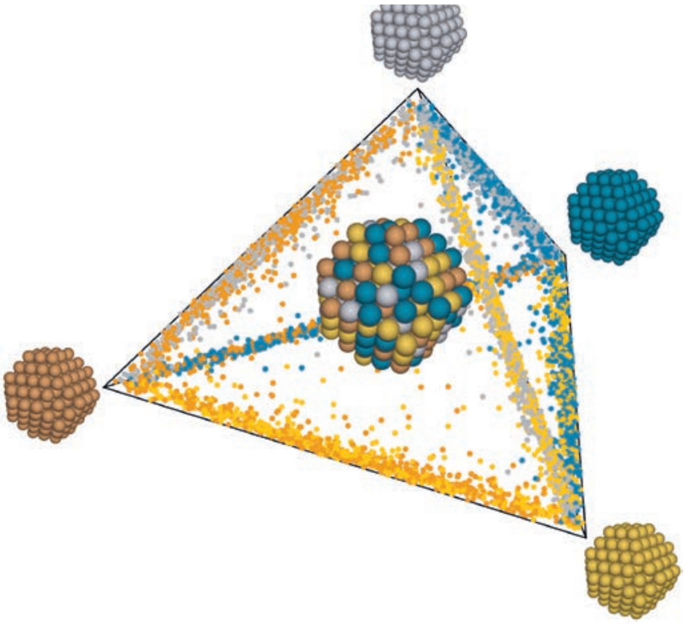
Short Abstracts of Interesting Recent Publications of Swiss Origin

Bayesian Optimization of High-Entropy Alloy Compositions for Electrocatalytic Oxygen Reduction

J. K. Pedersen, C. M. Clausen, O. A. Krysiak, B. Xiao, T. A. A. Batchelor, T. Löffler, V. A. Mints, L. Banko, M. Arenz, A. Savan, W. Schuhmann, A. Ludwig, J. Rossmeisl, *Angew. Chem. Int. Ed.* **2021**, Just Accepted. https://doi.org/10.1002/anie.202108116
University of Copenhagen / Center for High Entropy Alloy Catalysis, University of Bern, Ruhr University Bochum

Active, selective, and stable catalysts are imperative for sustainable energy conversion, and methods to access such materials is highly desired. However, efforts are hampered by the magnitude of the tuneable compositional space. In this paper, the authors elegantly combined a kinetic model with Bayesian optimization to predict compositions of highest current density for the electrochemical oxygen reduction reaction (ORR), starting from quinary high-entropy alloys (HEAs), Ag-Ir-Pd-Pt-Ru and Ir-Pd-Pt-Rh-Ru. The models were then successfully confirmed with experimentation, demonstrating that the number of experiments needed for optimizing the vast compositional space of multimetallic alloys is in the order of 50 for ORR on these HEAs.

Authors' comments:
"Now we have an idea of how many experiments are needed to find the optimal catalyst of a multi-metallic alloy. One need not do a thousand experiments, 50 is sufficient."

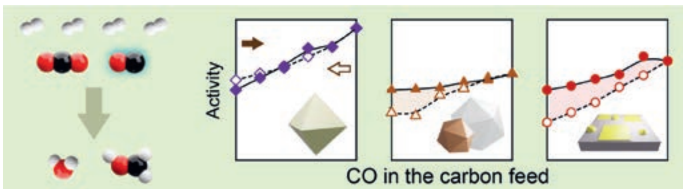


Methanol Synthesis *via* Hydrogenation of Hybrid CO_2-CO Feeds

T. Pinheiro Araújo, A. H Hergesell, D. Faust-Akl, S. Büchele, J. A Stewart, C. Mondelli, J. Pérez-Ramírez, *ChemSusChem* **2021**, *14,* 2914–2923. https://doi.org/10.1002/cssc.202100859
ETH Zurich, Department of Chemistry and Applied Biosciences. Institute for Chemical and Bioengineering

To investigate the impact of carbon monoxide on CO_2-to-methanol catalysts, in this study, copper-based systems and $ZnO-ZrO_2$ are assessed in cycling experiments with hybrid CO_2-CO feeds and their CO sensitivity is compared to In_2O_3-based materials. The results are a revised categorization of the most relevant catalyst systems for one of the most attractive and developed routes to utilize CO_2 as a chemical feedstock from an application–oriented perspective, uncovering the unique robustness of $ZnO-ZrO_2$ against feed composition fluctuations. While mild-to-moderate deactivation occurs for copper- and indium oxide-based catalysts upon re-exposure to CO_2-rich streams owing to water-induced sintering, $ZnO-ZrO_2$ shows a fully reversible behaviour, likely owing to its more hydrophobic nature and the atomic mixing of its metal components. The authors suggest that catalyst and, especially, process design should take center stage to minimize the impact of water on the multiphase systems, which operate at lower temperature, to achieve an industrially viable catalytic technology.

Authors' comments:
"At a process level, CO will inevitably be present as feed component or recycled byproduct in CO_2-based methanol synthesis. Hence, performance evaluation of catalytic systems using hybrid CO_2-CO feeds is a crucial step towards the establishment of a green methanol technology."



Prepared by David Lim, Pablo Diaz Kruik, Lucia Robustini, Stefania Gianolio, and Francesca Paradisi*
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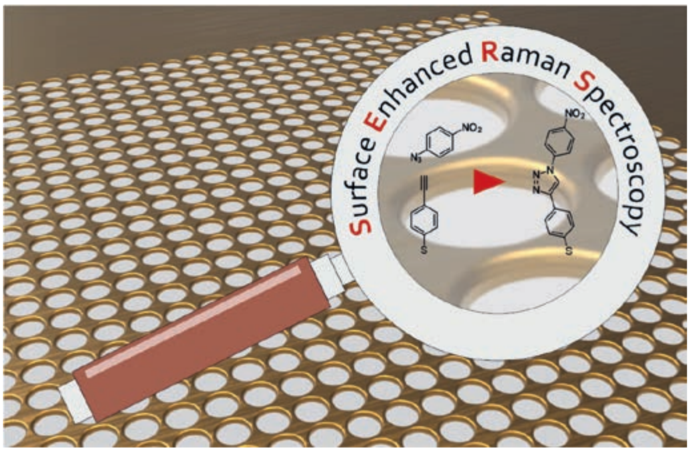
Monitoring Solid-Phase Reactions in Self-Assembled Monolayers by Surface-Enhanced Raman Spectroscopy

D. Scherrer, D. Vogel, U. Drechsler, A. Olziersky, C. Sparr, M. Mayor, E. Lörtscher, *Angew. Chem. Int. Ed.* **2021**, *60*, 17981-17988. https://doi.org/10.1002/anie.202102319
Department of Chemistry University of Basel, Switzerland
Science and Technology department, IBM Research Europe - Zurich, Switzerland

Nanopatterned surfaces enhance incident electromagnetic radiation, for example in surface-enhanced Raman spectroscopy (SERS) for the detection and characterization of self-assembled monolayers (SAMs). In this article the authors have developed and characterized Au nanohole arrays as SERS substrates for monitoring a solid-phase deprotection-immobilization reaction sequence.
They demonstrated that the deprotection and the subsequent 'click' reaction can be monitored by characteristic vibrations present in the SERS spectra. Such plasmonic surfaces can for instance be integrated as analytical tags in microfluidic lab-on-a-chip systems to enable the local analysis of biological assays, chemical solutions, surface coatings with receptors, catalysts, *etc.*

Authors' comments:
"Nanotechnology-enabled chemical analysis systems open many doors for studying miniaturized chemical reaction systems down to the realm of molecular monolayers or single molecules."



Heterogeneously-catalyzed Aerobic Oxidation of Methane to a Methyl Derivative

A. N. Blankenship, M. Ravi, M. A. Newton, J. A. Van Bokhoven, *Angew. Chem. Int. Ed.* **2021**, *60*, 18138–18143. https://doi.org/10.1002/anie.202104153

ETH Zurich, Department of Chemistry and Applied Biosciences. Institute for Chemical and Bioengineering
To address the pressing limitations of direct methane conversion, the authors propose an alternative approach that combines the heterogeneously-catalyzed partial oxidation of methane to methanol with esterification of the product to methyl trifluoroacetate using air as the oxidant source at a moderate temperature and pressure. By diluting the trifluoroacetic acid reaction medium below 25 wt% with inert perfluoroalkane co-solvent, the authors managed to strongly reduce the corrosivity of the reaction medium and enhance the recovery of the methyl ester and perfluoroalkane via a simple liquid-liquid extraction with a non-fluorous polar solvent. This cobalt-catalyzed process provides higher methane conversion and product yields compared to other heterogeneous transition metal-based high-temperature catalytic processes that use molecular oxygen as the oxidant.

Authors' comments:
"Product protection is the key to high-yield methane valorization and still relatively underexplored. We aim to reinvigorate the field through innovative application of concepts from across the chemistry community."