# Catalysis and electrocatalysis by sub-nanometer clusters

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Supported subnanometer clusters can be considered as models of the catalytic active site, and changes in their size and composition by a single atom or altering the support can lead to a significant change in their activity and selectivity.[1-2] Thanks their uniform size and composition, subnanometer clusters provide ways to optimize catalytic performance in an atom-by-atom fashion, while also offer an efficient use of the catalytic material. Another advantage of such well-defined systems is that they can be treated with high level DFT calculations to bring detailed insights into the reaction mechanisms. At last but not least, size and composition selected clusters can serve at the validation of new catalysts predicted by theory.

The presentation will focus on the study of in their size and composition uniform subnanometer clusters and their assemblies in heterogeneous catalysis and electrocatalysis. The ligand-free clusters are synthesized in the gas phase and, after mass selection with atomic precision, deposited on oxide and carbon based supports. The first part of the lecture will focus on model catalysts interrogated under realistic reaction conditions of pressure and temperature using in situ X-ray scattering and X-ray absorption spectroscopy combined with the monitoring of the reaction products. In the second part of the presentation, the performance of clusters in Li-Air batteries will be discussed.

*Epoxidation of propylene on subnanometer $Ag_3$ clusters and their assemblies.* Results of joint experimental and theoretical studies will be presented on the efficient and highly selective epoxidation of propylene with molecular oxygen on alumina supported silver trimer and its nanoassemblies[3] and compared with the performance of nanosized silver particles.[4]

*Low-temperature oxidative dehydrogenation of cyclohexane on subnanometer Cu, Pd and CuPd clusters.* The effect of support and size of monometallic Cu and Pd clusters on their activity and selectivity towards the production of benzene, cyclohexadiene, cyclohexene and undesired $CO_2$ will be discussed. Next, in the best performing monometallic $Cu_n$ and $Pd_n$ clusters the atoms of one metal are exchanged with one or more atoms of the other metal, creating copper or palladium rich n-atom bimetallic $Cu_xPd_{n-x}$ clusters, to fine-tune catalyst performance.[5]

*Subnanometer clusters in Li-Air batteries.* The strong size effect of subnanometer Ag and Ir clusters and their assemblies on the performance of Li-Air batteries will be discussed as results from a joint theoretical and experimental effort.[6,7]

## References

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