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Predictive Heterogeneous Catalysis by Design: Well-Defined Single-Site Catalysts

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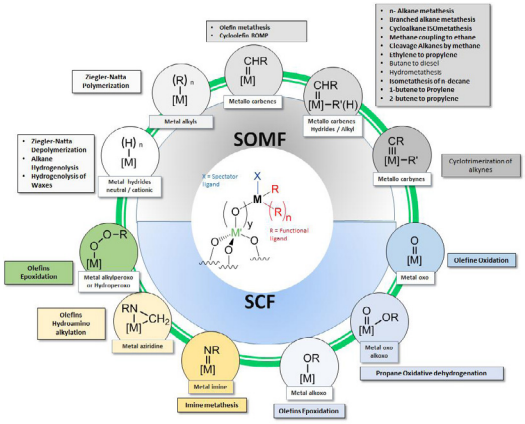
"Predictive catalysis" or "catalysis by design" in heterogeneous catalysis has recently benefited from using "surface organometallic fragments" (SOMF) or Surface Coordination fragments (SCF) to enter any presumed catalytic cycle. These conceptual tools in which one or several fragments of the molecule are linked to metal grafted on the surface (M-H, M-R, M=CR2, M≡CR, M=O, M=NR) became the logical continuation of the abundant work published in the field of Surface Organometallic Chemistry (SOMC). To note, SOMC has produced new catalytic reactions (e.g. Ziegler Natta depolymerisation, alkane metathesis, non-oxidative methane coupling etc…) and had improved the activity or selectivity or life time of known ones. The catalytic mechanisms employs the concepts of molecular chemistry (organic, organometallic, coordination chemistry) to explain how bonds can be broken and reformed. In this context, the reactivity of "surface organometallic fragments" (SOMF) or Surface Coordination fragments (SCF) is pivotal to the outcome of the catalysis.

Both types of fragments were identified within SOMC as it allows the isolation of single-site well-defined heterogeneous catalyst. SOMC can generate catalytic sites that are in principle identical (single-site or single atom) by grafting transition metal atoms onto highly dehydroxylated metal oxide support handled under controlled atmosphere. This strategy presents considerable advantages over traditional heterogeneous catalysts in which various populations of metallic potentially active sites coexist.

In this framework, all the steps of the preparation are carefully controlled with the concepts and tools of organometallic and/or coordination chemistry. Hence, the coordination sphere of the grafted metal can be determined with a high degree of accuracy (well-defined catalytic site) by the modern solid characterization tools (Surface Microanalysis, in situ IR, in situ UV, in situ solid state NMR, EXAFS and in operando EXAFS, etc…). It means that all atoms coordinated to the metal or in its close vicinity are identified. Another benefits came from the surface to be considered as a rigid ligand, preventing in most cases undesired interferences between the catalytic sites (e.g. by bimolecular deactivation in homogeneous catalysis).

Within this framework, the relationship between structure and activity become possible; with the addition of the SOMF tools, it becomes predictable. It is now possible to follow the various steps of the catalytic cycle, understand deactivation, increase activity and/or selectivity by changing the support or ligand environment of the active site. The existing gap which was existing between heterogeneous catalysis and homogeneous catalysis has completely disappeared and a new domain is emerging. We shall review here some of the recent catalytic results obtained on oxides.



Biography:

Jean-Marie Basset is the Distinguished Professor for Chemical Science in the Physical Science and Engineering Division at King Abdullah University of Science & Technology.

Prof. Basset, who has authored more than 500 scientific papers 50 patents, pioneered the field of "Surface Organometallic Chemistry", which focuses on possible relationships between homogeneous and heterogeneous catalysis. Professor Basset received his PhD in 1969 from the University of Lyon, France. After a postdoctoral position in Toronto he moved to the Institute of Catalysis in Lyon where he became vice-director. In 1987, he founded the Laboratory of Surface Organometallic Chemistry that became later the laboratory of Chemistry, Catalysis, Polymer, Process (C2P2). Professor Basset's Lyon lab was home to 100 scientists, including Nobel Laureate Yves Chauvin who got his Nobel in 2005. In 2009 he moved to the King Abdulla University of Science and Technology in Saudi Arabia as director of the KAUST Catalysis Center.