

## CHEMISTRY

## Special Topic: Single-Atom Catalysts

## Predictive approach of heterogeneous catalysis

Jean-Marie Basset\* and Jérémie D.A. Pelletier

'Predictive catalysis' or 'catalysis by design' has recently advanced heterogeneous catalysis by using the conceptual tool of surface fragments [1] such as 'surface organometallic fragments' (SOMF) or 'surface coordination fragments' (SCF) to achieve and understand a presumed catalytic cycle (see Fig. 1). One or several fragments of the molecule are linked to one metal atom linked to the surface ( $[M]-H$ ,  $[M]-R$ ,  $[M]=CR_2$ ,  $[M]\equiv CR$ ,  $[M]=O$ ,  $[M]=NR$ ,  $[M]-O-OH$  in which  $[M]$  is a surface metal atom linked to an oxide by one, two or several sigma or pi bonds). Surface fragments are the logical continuation of the abundant work published in the field of Surface Organometallic Chemistry (SOMC). In this paradigm based on molecular understanding of surface catalytic sites, one 'single' metal atom is surrounded by ligands and linked to the surface of an oxide via covalent or ionic bonds [2]. It is a continuation of classical heterogeneous catalysis in the direction of single-atom catalysis (SAC). In SAC, single metal atoms are also linked to an oxide by coordination, covalent or ionic bonds but are at the other extreme of catalysis by metal nanoparticles because SAC is the result of a conceptual evolution from metal nanoparticles to a single atom by size reduction of the nanoparticle. It is a continuation of homogeneous catalysis but with a rigid surface as a ligand.

SOMC has allowed the discovery of new catalytic reactions (e.g. Ziegler-Natta depolymerization [3], alkane metathesis [1], non-oxidative methane coupling [1], cyclo-alkane metathesis [4], etc.) and has improved the activity, the selectivity or the lifetime of known ones. The concepts of molecular chemistry (organic, organometallic, coordination chemistry) are the keys to explaining how bonds can be broken and formed [2]. In this context, the reactivity

of SOMF or SCF and their sequence in the cycle are pivotal to the overall outcome of catalysis.

SOMC can generate catalytic sites that are *in principle* identical (single-site or close to single atom) by grafting transition metal atoms onto highly dehydroxylated metal oxide support handled under a controlled atmosphere. This strategy, limited to metal-oxides or metallic surfaces, presents considerable advantages over traditional heterogeneous catalysts in which various populations of potentially active metallic sites coexist. All the steps of the preparation are carefully controlled using the methods of organometallic and coordination chemistry. Hence, the coordination sphere of the grafted metal can be accurately determined (well-defined catalytic site) by modern solid/surface characterization techniques (elemental analysis, *in situ* IR, *in situ* UV, Solid State Nuclear Magnetic Resonance spectroscopy (SS NMR), Extended X-ray absorption fine structure (EXAFS) and *in operando* EXAFS, etc.) [2]. The surface should be considered as a bulky rigid ligand preventing most undesired interferences between catalytic sites (e.g. leading to bimolecular deactivation). The relationship between structure and activity become possible to establish; with the addition of the SOMF tools, it is now a predictable discipline.

The various steps of the catalytic cycle are monitored to understand deactivation, to increase activity and/or selectivity by changing the support or ligand environment of the 'active site' (Fig. 2). The existing gap between heterogeneous catalysis and homogeneous catalysis has almost completely disappeared, because the elementary steps of molecular chemistry are applicable to 'single-atom catalysis'. We shall review here some of

the recent catalytic results obtained on oxides.

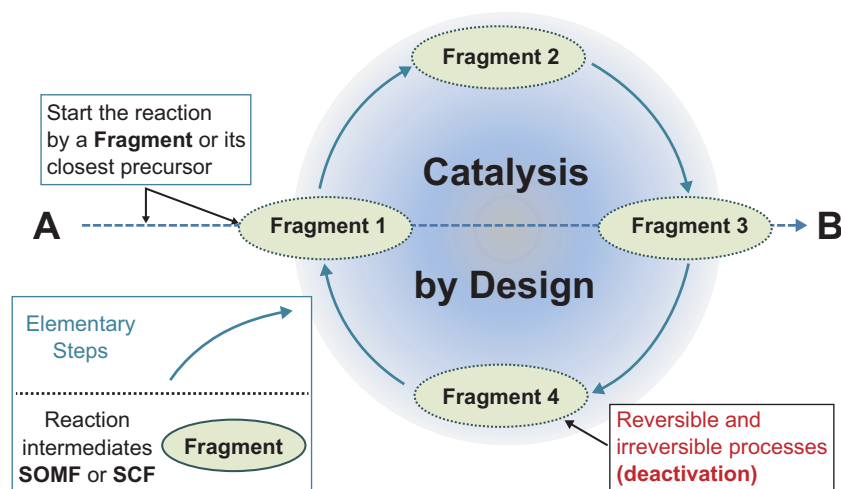
Metal hydrides are the simplest and most frequent surface fragments, yet do not belong to 'organometallic' classification *stricto sensu*. ( $[M]-H$ ) are mostly generated by hydrogenolysis of metal-alkyl ( $[M]-R$ ) and generally promote low-temperature C-H bond activation of alkanes (i.e. methane activation) [5]. ( $[M]-H$ ) and ( $[M]-R$ ) can convert into each other by  $\beta$ -hydride elimination of the metal-alkyl and CH insertion. This has been evidenced in alkane depolymerization [3] (polyethylene is transformed into diesel-range gasoline by group 4 metal-based catalysts under hydrogen).

( $[M]-R$ ) SOMF have numerous examples as polymerization catalysts [6,7]. Another case is the bis-alkyl SOMF with dual ( $[M]-R$ ) SOMF for propane homologation to higher alkanes [8].

Surface carbenes were first evidenced with Nb [9] ( $[(\equiv Si-O)_2 Nb(=CH)]$ ), Mo Mo ( $[(\equiv Si-O) Mo(=CHCMe_3)(=NH)Np]$ ) [10] and Re ( $[(\equiv Si-O) Re(Np)(\equiv C-CMe_3)(=CHCMe_3)]$ ) [10]. They were eventually successfully employed as catalysts for olefin metathesis. This reactivity is specific to the ( $[M]=CR_2$ ) SOMF, consistently with the metallacyclobutane intermediate proposed by Chauvin [11]. Variation of activity and selectivity had been linked to both the nature of the metal employed and that of the spectator ligands (i.e. oxo, imido, amido, alkyl, etc.) [12,13].

The first multifunctional SOMF fragments  $[M](H)(=CR_2)$  were identified following the discovery of alkane metathesis using tantalum, tungsten and then molybdenum hydride [14] catalysts supported on alumina or silica in 1997 [15]. In this reaction, saturated hydrocarbons, linear and branched, were re-arranged to longer or shorter paraffins. For example, n-propane can be converted





**Figure 2.** Typical schematic to build 'catalysis by design' mechanism. Version from the figure published by Pelletier and Basset, in *Acc Chem Res* 2016; **49**: 664–77.

catalysts for 1-octene epoxidation by *tert*-butylhydroperoxide.

Although [M]-Cl are not *stricto sensu* reaction intermediates in CO<sub>2</sub> reaction with epoxides to give cyclic carbonates, the work below is a rare example of cooperating surface bimetallic catalysis. CO<sub>2</sub> and epoxide are each activated by two separate Lewis acid centers ( $\equiv\text{Si-O-NbCl}_4\cdot\text{OEt}_2$ ) maintained in very close proximity by silica [19].

SOMC, alongside surface fragments, allow the prediction of catalysis by determination of the sequence of intermediates and to control the coordination sphere of the metal to achieve targeted reactions. In SAC, the atom grafted onto the surface depends on the reagents/substrates to adopt the right coordination sphere. The SOMC strategy may be seen as the result of a molecular understanding of the elementary steps necessary to achieve a given reaction. One of the questions raised could be the advantage of using SOMC rather than classical heterogeneous catalysis. It is true that 'classical catalysis', mostly

based on a 'trial and error approach', could be considered as easier in terms of practical advantages, but the SOMC approach offers several competitive advantages: prediction of new catalytic reactions, never observed in classical heterogeneous catalysis; a reliable structure activity relationship because we are dealing with well-defined structures where the physicochemical tools are used with maximum efficiency; and the possibility to control the activity and selectivity with a careful choice of 'ligands', 'spectators ligands' and supports. This strategy progressively removes the existing gap between heterogeneous and homogeneous catalysis mainly because the concepts of molecular chemistry (in particular the elementary steps) are easily applied to heterogeneous catalysis.

Jean-Marie Basset\* and Jérémie D.A. Pelletier  
King Abdullah University of Science and  
Technology, Saudi Arabia

\*Corresponding author.

E-mail: [jeanmarie.basset@kaust.edu.sa](mailto:jeanmarie.basset@kaust.edu.sa)

## REFERENCES

- Pelletier JDA and Basset JM. *Acc Chem Res* 2016; **49**: 664–77.
- Basset JM, Psaro R and Roberto D *et al.* *Modern Surface Organometallic Chemistry* 2009, 23–135.
- Dufaud VR and Basset JM. *Angew Chem Int Ed* 1998; **37**: 806–10.
- Riache N, Dery A and Callens E *et al.* *Organometallics* 2015; **34**: 690–5.
- Corker J, Lefebvre F and Lecuyer C *et al.* *Science* 1996; **271**: 966–9.
- Millot N, Soignier S and Santini CC *et al.* *J Am Chem Soc* 2006; **128**: 9361–70.
- Williams LA, Guo N and Motta A *et al.* *Proc Natl Acad Sci USA* 2013; **110**: 413–8.
- Thieuleux C, Maraval A and Veyre L *et al.* *Angew Chem Int Ed* 2007; **46**: 2288–90.
- Asakura K, Nishimura M and Iwasawa Y. *J Mol Catal* 1989; **55**: 159–69.
- Lesage A, Emsley L and Chabanas M *et al.* *Angew Chem Int Ed* 2002; **41**: 4535–8.
- Herisson JL and Chauvin Y. *Makromol Chem* 1971; **141**: 161–76.
- Mazoyer E, Merle N and de Mallmann A *et al.* *Chem Commun* 2010; **46**: 8944–6.
- Basset JM, Coperet C and Soulvong D *et al.* *Acc Chem Res* 2010; **43**: 323–34.
- Blanc F, Coperet C and Thivolle-Cazat J *et al.* *Angew Chem Int Ed* 2006; **45**: 6201–3.
- Vidal V, Theolier A and ThivolleCazat J *et al.* *Science* 1997; **276**: 99–102.
- Hamzaoui B, El Eter M and Abou-Hamad E *et al.* *Chem Eur J* 2015; **21**: 4294–9.
- Hamzaoui B, Pelletier JDA and El Eter M *et al.* *Adv Synth Catal* 2015; **357**: 3148–54.
- Hamzaoui B, Pelletier JDA and Abou-Hamad E *et al.* *Chem Commun* 2016; **52**: 4617–20.
- D'Elia V, Dong HL and Rossini AJ *et al.* *J Am Chem Soc* 2015; **137**: 7728–39.

National Science Review

5: 633–635, 2018

doi: 10.1093/nsr/nwy069

Advance access publication 12 July 2018