From catalytic reaction mechanism to catalyst design: a valuable but complex pathway

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Abstract: Various strategies for designing new performing catalysts on the basis of reaction mechanisms are presented, to be applied to major industrial domains such as light alkanes and alcohols reforming, syngas chemistry, catalytic cracking of biomass derived pyrolytic oils or oxidative coupling of methane
Keywords: Catalyst design, Reaction mechanism, Strategies for new catalytic systems.

1. Introduction

In the wide field of heterogeneous catalysis and at variance with homogeneous or molecular catalysis, the proper mechanism of most reactions is intimately linked to the catalyst bulk and surface structure, interfacing the reaction medium and the catalyst itself. All the key structural parameters are mainly determined from the overall catalyst design, from synthesis to activation and possibly regeneration steps. Indeed the reaction mechanism which controls the elemental surface steps also combines with heat and mass transfer processes, being themselves closely related to the type of reactor selected for the considered reaction. The combination of all these processes control the observed performance of the tested systems. Such a long sequence of elemental events can be tackled via a number of quite distinct strategies, each of them displaying pros and cons, as it will be underlined in that presentation.

2. Combinatorial approach of new catalysts formulas

A first strategy deals with a combinatorial search of new catalyst formulas by using mechanistic and characterisation knowledge in a high throughput (HT) statistical approach. As an example, in order to develop new acid and bi-functional catalysts for refinery applications, a HT method was developed for the characterization of Brønsted acidity of bifunctional catalysts library by means of isomerization of 3,3-dimethylbutene testing [1]. It was shown to allow quantifying very accurately the acid strength leading to catalyst ranking and selection in conditions similar to practical applications. The pros and cons of the use of model reactions for HT quantitative characterization will be discussed.

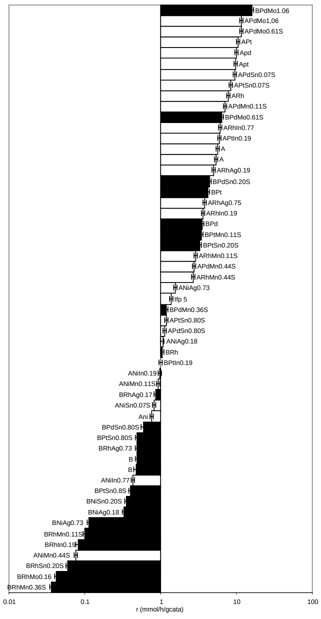
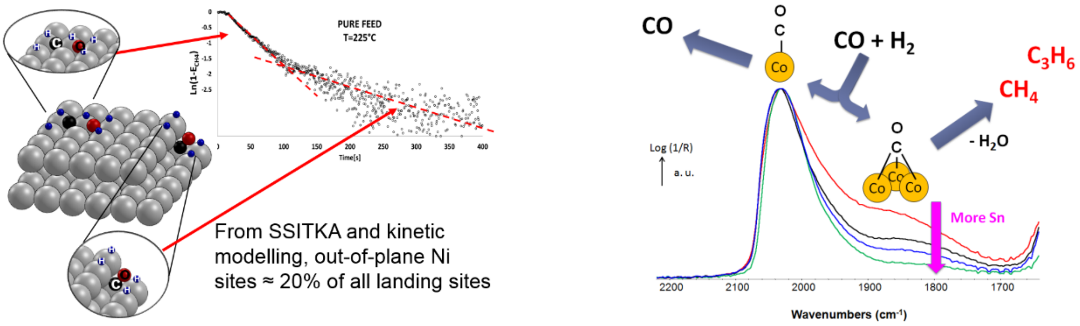


Figure 1: Example of classification histogram of a catalysts library tested for isomerization of 3,3-dimethylbutene. Black bars: αθ-alumina; white bars: δ-alumina [1]

3. Mechanistic and kinetic behaviour under realistic conditions for improving catalyst formulation

A second major strategy consists in analysing the mechanistic and kinetic behaviour of various catalysts under realistic conditions (e.g., using operando spectroscopies combined with transient kinetic investigation) and to derive from these observations adapted changes in catalyst formulation and/or structure to improve their efficiency, selectivity and resistance to deactivation. This strategy will be illustrated with deactivation processes during bio-syngas methanation and Fischer-Tropsch catalysts (Figure 2).



From SSITKA and kinetic modelling, out-of-plane Ni sites ≈ 20% of all landing sites

Figure 2: Links between SSITKA/DRIFT operando analysis and metal (Ni and Co) particles structure for a better understanding of the poisoning and ageing of methanation and FT catalysts [2, 3].

4. Mechanistic and kinetic behaviour under realistic conditions for improving catalyst formulation

Finally a third strategy is based on nanoscale engineering combining nano structures and size controlled metal particles for improved selectivities and resistance to ageing. An example of these new materials is given in Figure 3 where a yolk/core–shell material allows to protect nanoparticles against poisoning or sintering by a thin zeolite shell where chemical reactions can proceed as in nanoreactors.

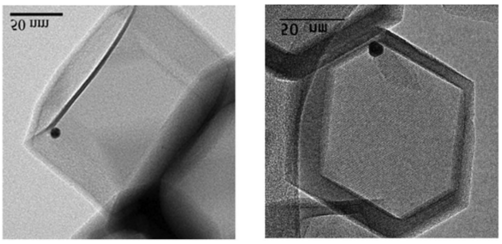


Figure 3: Representative images or Au@silicalite-1 (left) and Pt@silicalite-1 (right) hollow zeolites [3].

5. Conclusions

These various strategies can be applied to most industrially relevant cases such as light alkanes and alcohols reforming, syngas chemistry, catalytic cracking of biomass derived pyrolytic oils and oxidative coupling of methane.

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