

Bifunctional and concerted catalysis for hydrocarbon conversion

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Introduction

Bifunctional catalysis is defined by IUPAC as catalytic conversion by a bifunctional chemical species involving a mechanism in which both functions are implicated in the rate-controlling step, so that the corresponding catalytic coefficient is larger than that expected for catalysis by chemical species containing only one of these functional groups. In case the functions act in a sequential manner concerted catalysis is the correct term to be used.

Multifunctional and concerted catalysts are the keys to new generations of processes for clean and sustainable energy carriers. Concerted catalysts have been the critical elements in a variety of important processes in the refining industry with catalytic reforming being the largest process using this principle. In this example, the dehydrogenation and hydrogenation is needed to create sufficient concentrations of olefins to be converted on Brønsted sites.

However, the catalytic conversion of highly refractive molecules requires more complex catalysts acting with more than one site or function simultaneously (bi- and multifunctional catalysis) as well as in sequence (concerted catalysis) in order to achieve the required activity and selectivity. In this contribution, the potential of bi- and multifunctional catalysis will be systematized and highlighted using examples related to catalytic reactions for a sustainable production of clean energy carriers. These examples will include the bifunctional catalysis involving (i) the cooperation of Brønsted and Lewis acid sites, (ii) the cooperation of the spatial constraints and Brønsted acidity and (iii) the cooperation of a metal with the Lewis/Brønsted acid-base sites at the interface. The obvious existence of acid-base pairs will not be emphasized. Cooperative catalysis will be exemplified by the low temperature isomerization of alkanes and the hydrogenation of substituted phenols.

The effect of the **cooperation between Brønsted and Lewis acid-base sites** will be illustrated by comparing the dehydrogenation and cracking of alkanes by Brønsted acid sites (protolytic cracking) [1, 2] with the same reactions in the presence of a catalyst that contains strong Lewis and Brønsted acid sites [3]. It will be shown that the exceptionally strong polarization of C-H bond by Lewis acid sites allows low energy pathways to alkane conversion.

The **cooperation of spatial constraints with Brønsted acidity** allows for reactions that can exploit the gain in entropy in reactions like cracking for unusual increases in the reaction rate in comparison with unconstrained environments for catalytic sites. Protolytic cracking of n-alkanes on constrained sites will be compared with less constrained sites. Using olefin cracking it will be shown that this cooperative effect requires late transition states to manifest.

Finally, the **cooperation of a metal with Brønsted acid and base sites** will be outlined by the hydrogenation of benzene [4] and the reforming of methane with carbon

dioxide. In both cases the catalytic conversion depends on the specificity of the interface between the acid component and the metal.

The combination of the oxidative dehydrogenation of an alkane together with the subsequent Brønsted acid catalyzed isomerization and the combination of hydrogenation of aromatic rings with the acid catalyzed dehydration of cyclic alcohols will illustrate how important the balance between the concentration of sites and their activity is for **cooperative catalysis**. Especially the combination of oxidation and acid catalysis requires a subtle balance between the functions in order to be able to achieve stable catalytic activity.

Finally, the challenges for catalysis with increasingly difficult and diverse feedstocks will be compared to the potential arising from the better understanding of catalysts acting with multifunctional sites and through cooperation of sites. Such novel complex nanostructured catalysts will be able to emulate the functions of biocatalysts, while aiming to maintain the robustness of heterogeneous catalysts.

References

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