ISGC 2022

N°247 / OC
TOPIC(s) : Industrial chemistry / Chemical engineering

Surface molecular imprinting over supported metal catalysts

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PURPOSE OF THE ABSTRACT

In chemical processes, one of the main challenges is insufficient selectivity to target products, which requires separation and recycling of by-products causing environmental problems and high technological costs. It slows down the technological transition from fossil to renewable resources. The insufficient selectivity is a result of the low specificity of the interaction between the active site and reagent leading to undesirable side reactions. The high selectivity of enzymes is explained by the confinement of active sites inside a protein matrix, which provides a correct orientation of the reagents and chemical environment before interaction with the active site.

This work is focused on the development of a new surface molecular imprinting (SMI) strategy for the control of the selectivity of heterogeneous catalysts. This SMI strategy involves adsorption of a template molecule over the catalyst surface, the deactivation of uncovered sites with specific poisoners with the creation of non-poisoned active islands with pre-determined shape and size (Figure 1). The strategy is different from selective deactivation, which has been used earlier to improve the selectivity of the catalysts [1] or molecularly imprinted polymers (MIPs) strategy with predetermined recognition sites in polymeric matrices [2]. Because of steric constraints, these active islands will exhibit extremely high selectivity in the chemical conversion of the molecules with the size, shape, and functional group orientation corresponding to the templates.

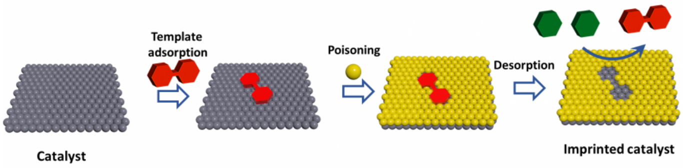
The concept of imprinting of heterogeneous catalysts has been proven by our recent work (Figure 2) [3]. The strategy is illustrated by selective hydrogenation occurring over supported Pd catalysts. Dimethylaminopropylamine (DMAPA) with high basicity and ability to coordinate with Pd nanoparticles via nitrogen was used as a poisoner. The carbon tails of DMAPA create steric hindrances on the poisoned surface and suppress the interaction of the molecules with the metal surface. After the first step of cleaning and reduction, the surface of the Pd catalyst is subjected to the adsorption of a template molecule (e.g. benzene). Further, the active sites of Pd, which remain still available after the template adsorption, are deactivated by interaction with dimethylaminopropylamine (DMAPA), which strongly coordinates on the Pd surface. During this step, the Pd sites covered by the template are protected and therefore are not expected to react with the poisoner. After deactivation, the adsorbed templates will be removed from the surface creating active islands, whereas the DMAPA poisoner remains on the surface. Finally, an imprinted Pd catalyst with created active islands has been produced.

These sites have been highlighted by the reduction of Pt over Pd surface by hydrogen, which is easily observed by TEM analysis (Figure 2). Pt salt forms a shell over Pd nanoparticles for the parent Pd/SiO2 catalyst. At the same time, Pt reduction over an imprinted catalyst (Print-Pd/SiO2) demonstrates the presence of small Pt islands over Pd surface, which confirms imprinting of the molecules over Pd surface.

The catalytic results confirm that these active islands are reactive for the transformation of molecules displaying similar structures with the template molecules. The imprinted Pd catalyst was then examined in an important practical application relevant to the selective hydrogenation of carcinogenic benzene in the mixture of aromatics.

The imprinted Pd catalysts with benzene as a template show a clear preference for the benzene hydrogenation compared with mesitylene (Figure 2). The molecular imprinting strategy that we describe not only provides a powerful way to design a selective catalytic surface but also offers an additional understanding of the phenomena occurring during adsorption and catalytic reactions on the metal surfaces.

FIGURES



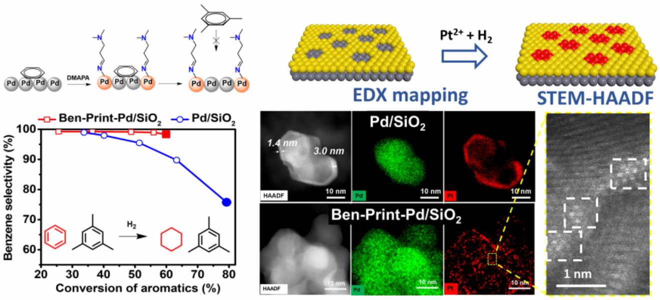


FIGURE 1

Surface Molecular Imprinting concept

FIGURE 2

Effect of imprinting of Pd/SiO2 catalyst for selective hydrogenation of benzene in benzene-mesitylene mixture and TEM analysis of the initial Pd/SiO2 and imprinted Pd/SiO2 catalysts after Pt deposition

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KEYWORDS

imprinting | Pd | hydrogenation | selectivity

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