



Shaping the selectivity in heterogeneous hydrogenation by using molecular modification strategies: Experiment and theory



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ABSTRACT

Heterogeneous selective hydrogenation plays an important role in the manufacture of high value-added chemicals. Modification of noble metal catalysts, e.g. Pd, Pt and Au, by using inorganic or organic compounds has been emerging as one of the most effective strategies to enhance the substrate selectivity, chemoselectivity, and enantioselectivity as well. The purpose of this paper is to review recent experimental and theoretical advances on this topic. We will concentrate on the steric and/or electronic effects at the surface/interface induced by the surface molecular modifiers, and how these effects work alone or together to generate a high selectivity.

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1. Introduction

Heterogeneous catalysts are widely used in industrial processes owing to their stability and ease of separation from reactant mixtures [1]. The research in the heterogeneous catalysis in the past twentieth century has been focused on enhancing the activity of heterogeneous catalysts, and the enhancement of their catalytic selectivity has been less studied mainly due to complexity of heterogeneous catalysts. However, as stimulated by continuously growing cost of raw materials and emerging environmental challenges in the 21st century, the highly demanded are heterogeneous catalysts that allow the synthesis of targeting compounds with a 100% yield and 100% selectivity and thus avoid the production of waste [2–4].

Among all the reactions conducted via heterogeneous catalysis, hydrogenation is one of the most prominent types and widely used in almost every field of chemical industry, such as petrochemicals, fine-chemicals, and pharmaceuticals [5–7]. For the heterogeneous hydrogenation, the selectivity reflects the discrimination shown by the surfaces in competitive interaction with two or more substrates (substrate selectivity), or with enantiomers (enantioselectivity), or with two or more functional groups in the same substrate (chemoselectivity). For instance, selective hydrogenation of ethyne in the mixture of ethyne and ethylene has been widely used to purify

alkene streams [6–8]. The key for this reaction is to enhance the adsorption of C≡C triple bond while suppress the adsorption of C=C double bond, i.e. substrate selectivity. In addition, enantioselective hydrogenation on chirally modified noble metals has shown a great promise in the synthesis of enantiopure compounds [9–21]. Chiral modifiers were proposed to play an essential role in surface-mediated processes that leads to enantioselectivity. The classic example for chemoselectivity is the selective hydrogenation of α , β -unsaturated aldehydes into unsaturated alcohol [22]. In this case, preferential hydrogenation of C=O bond against the C=C bond is believed to be a big issue [23].

For the heterogeneous hydrogenation, Pd and Pt are commonly used due to their high catalytic activity. However, high activity catalysts usually lead to poor selectivity such that these metals could not be employed alone in most cases. To achieve high selectivity, the active centers should be dilute through alloying or isolated by inorganic species (such as CO, H and S) [24–30] and/or organic compounds (such as amines and thiol) [22,31–37]. The most famous catalyst developed for this purpose is Lindlar catalyst (Pd-Pb/CaCO₃), which is commercially used for the selective hydrogenation of alkynes to alkenes [38,39]. To prevent the deeper hydrogenation, quinoline or octanediol would be added to deactivate the activity of Pd sites, while CO would be mixed in the feed streams to further poison the catalysts [30]. Recently, the influence of surface/subsurface hydrogen on the selectivity has been emphasized, especially for Pd and Pt catalysts [24–29,40]. In these cases, H atoms could be better viewed as surface modifiers, which significantly change the electronic states as well as the accessibility

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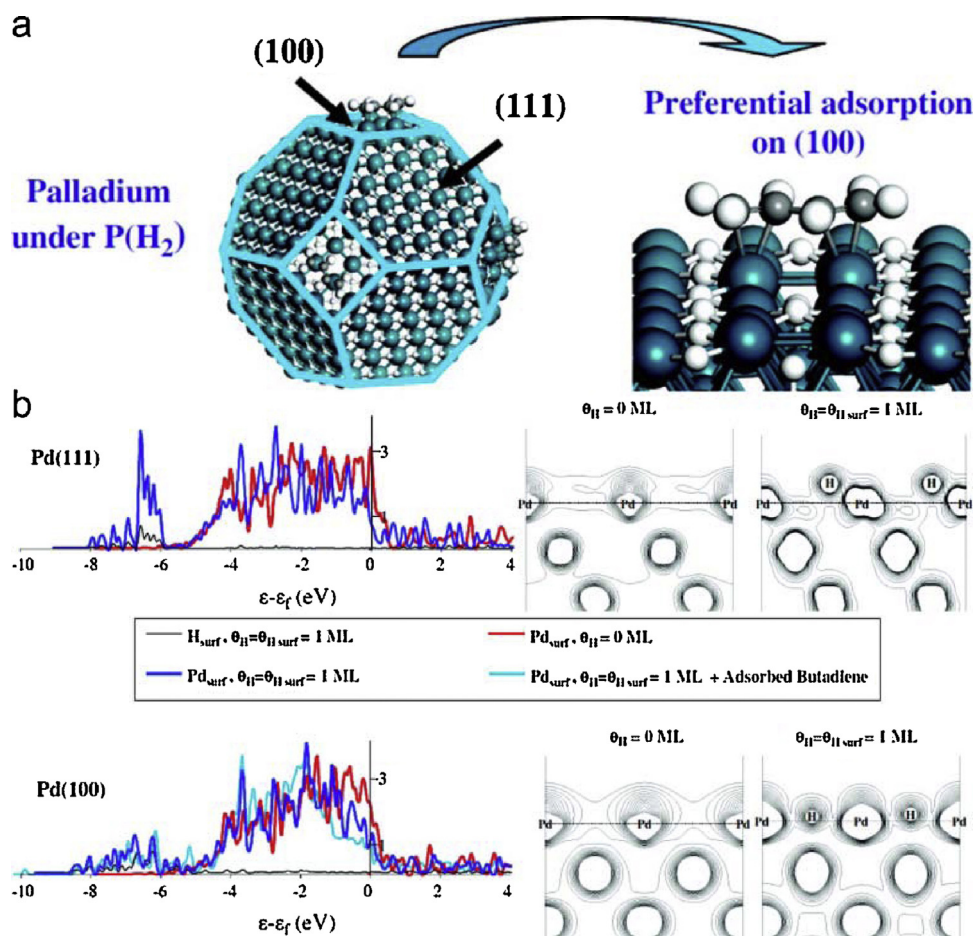


Fig. 1. (a) Under typical reaction conditions, the monolayer of hydrogen destabilizes butadiene on Pd(111) but not on Pd(100). (b) Density of states projected on surface atoms for $\theta_H = 0 ML$ and $1 ML$, for the Pd(111) and Pd(100) surfaces, respectively.

of the surfaces. In fact, the roles that the surface modifiers play are very similar to those of the ligands in homogeneous catalysis, which would induce significant steric and electronic effects on the central metal to determine the reactivity as well as selectivity. In this regard, modification of metal surfaces by using inorganic or organic compounds is an elegant way to bridge the gap between heterogeneous and homogeneous catalysis.

Herein, we discuss several of these approaches with an emphasis on the recent experimental and theoretical advances. We do not intend to review every aspect of selective hydrogenation because several excellent reviews have been published [5–7]. We will limit our scope on influence of surface adsorbed hydrogen, amine and thiol on the substrate selectivity, chemoselectivity and enantioselectivity. Plentiful experimental evidences will be provided to demonstrate that surface modification endows the resulting catalysts with unique selectivity that pristine metal catalysts could not easily access. Moreover, density functional theory (DFT) calculations were performed to understand the structure/selectivity relationship of modified systems.

2. H coverage effect on the selectivity

It is widely accepted that hydrogenation reactions on metal catalysts are structurally sensitive. Fundamentally, different exposed facets might have different atom arrangement and density, causing different adsorption and activation energies for various catalytic substrates, thus resulting in a big difference in the selectivity and activity. Many recent works indicated that the situation is more

complex than expected [41,42]. During hydrogenation, the high coverage H atoms on the Pt and Pd surface would strongly alter the adsorption behaviors of reactants and intermediates, or even change the hydrogenation mechanism.

By means of periodic DFT calculations and thermodynamic model, Chizallet et al. [24] explored the surface phase diagram of Pd(100) and Pd(111) in the presence of hydrogen, and proposed that both of the surfaces should be covered by at least one hydrogen monolayer (ML) under typical reaction conditions (Fig. 1a). Charge density analysis demonstrated that the surface states of metallic catalysts would be quenched to some extent upon hydrogen adsorption. Especially, at a high H coverage, the surface states of Pd atoms on (111) surface were nearly depleted, while Pd atoms on Pd(100) surface still has d_z^2 type surface states (Fig. 1b). DFT calculations showed that when keeping the hydrogen coverage at 1 ML, the adsorptions of both butadiene and butene were predicted to be endothermic on Pd(111) surfaces, while Pd(100) surfaces favored the adsorption of butadiene but still disfavored the adsorption of butene. These findings indicated that Pd(100) would be a good catalyst for selective hydrogenation of butadiene into butene.

Catalytic conversion of trans alkenes to their less thermodynamically cis counterparts is a very important reaction in the food industry. Experimentally, Lee et al. [25] found that in the presence of hydrogen, preferential trans-to-cis isomerization in C=C bond can be achieved on the Pt(111) surfaces. DFT calculations by Delbecq et al. [26,27] suggested that on the Pt(111) with a low H coverage, the di- δ adsorption mode is energetically more favorable than the π mode, and the adsorbed trans isomers via di- δ mode

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