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# A Few Notes to Heterogeneous Catalysts for Hydrogenation

Jiri Krupka

Department of Organic Technology, Faculty of Chemical Technology, University of Chemistry and Technology, Prague, Czech Republic, European Union

### Email address

Jiri.Krupka@vscht.cz

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### Abstract

Hydrogenations are accelerated by catalysts based on some transition metals. In industrial-scale use, the heterogeneous catalysts are preferred. Although hydrogenation is affected by a number of factors, the fundamental way how to influence the course of the catalytic hydrogenation still consists in selecting a suitable active metal. Pd, Pt, Ni, Cu, Ru, Co and Rh are the most used for hydrogenation of organic substrates. In this brief review, differences in the specific catalytic properties of the above-mentioned metals are summarized and possible causes of these differences are discussed.

## 1. Introduction

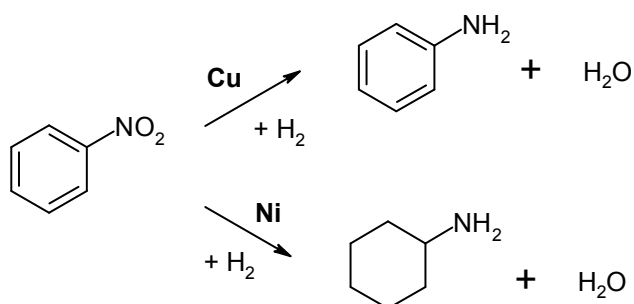
Catalytic hydrogenations belong to fundamental processes of the modern chemical industry. They find their use in liquid and gaseous fuel production, in syntheses of monomers of plastics and synthetic rubbers, in the food industry for the fat hardening, in the large-scale production of important alcohols and amines, as well as in the production of specialty chemicals, such as pharmaceuticals, fragrant substances, auxiliary chemicals for polymers, pesticides etc. On average, approximately 10% of all chemical steps in the production of such chemicals are catalytic hydrogenations. They can be classified as the so called zero-waste or minimum-waste processes and therefore, from the environmental point of view, are far more acceptable than, e.g., reductions or oxidations by chemical agents which not always lead to usable reaction products of the agents used. [1, 2]

Hydrogenations are accelerated by catalysts based on some transition metals. In particular, Pt, Pd, Ru, Rh, Co, Ni, Cu and Fe are used. In the technological practices, the hydrogenation catalysts are applied mainly as solids. In spite of the fact that, basically, also oxides (or even sulfides) of the above mentioned metals can catalyze the hydrogenation/dehydrogenation processes, virtually only catalysts having their active component in a metallic form find their use in hydrogenations procedures because oxides are active at higher temperatures only, when the thermodynamic equilibrium is unfavorable for hydrogenations. In most cases, the active metals are applied on a suitable support with a large specific surface (alumina, activated charcoal, silica, zeolites etc.), or, pertinently, they are used in the form of the so called Raney catalyst (in case of Ni, Co, Fe, Cu), prepared by a reaction of the corresponding metal/aluminum alloy with the sodium hydroxide solution. The Raney Ni catalyst is one of the few unsupported catalysts which has been widely utilized industrially. [1-3]

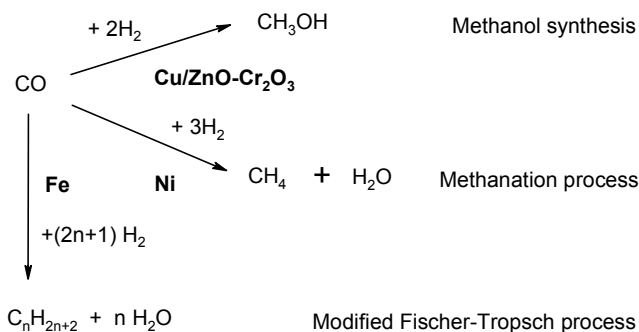
## 2. Specific Catalytic Properties of Individual Metals

Specific properties of individual metals [2, 4] predestine them for a particular use. The

platinum catalyst is a universal hydrogenation catalyst suitable for hydrogenations of broad range types of bonds. Palladium is a catalyst highly selective to the conversion of triple bonds to double bonds but very little active for the carbonyl group hydrogenation. In comparison to platinum it is also much less active for the aromatic ring hydrogenations. For these hydrogenations, catalysts based on rhodium and ruthenium are very active. Iridium and rhenium are most frequently utilized in platinum-based bimetallic and trimetallic catalysts as promoters (Ir especially in a form of an alloy with platinum), while osmium catalysts are virtually not applied for hydrogenations. Catalysts based on nickel and cobalt are used vastly. They have similar catalytic properties as the platinum-group metals, but they are less active. The platinum-group metals enable one to perform hydrogenations even at room temperature, whereas the nickel and cobalt catalysts need to operate at around 100 °C to achieve a sufficient reaction rates. The nickel catalysts are utilized for various technical hydrogenations such as oil hardening, hydrogenation of carbonyl compounds, benzene, phenol etc. They possess a strong hydrogenolytic ability which limits the working temperature. The application of the cobalt catalysts is similar: they are applied most frequently for the hydrogenation of the rings of the aromatic amines, and also for the nitrile hydrogenation to give amines. The sorption of amines onto cobalt is weaker than onto nickel, so that the reaction is not hampered by the products [5, 6]. The cobalt catalysts yield primary amines with a high selectivity. On the contrary, palladium and platinum, when used for the nitrile hydrogenations, give secondary and tertiary amines. Also copper shows specific catalytic properties. It is active for carbonyl compounds hydrogenations and, at the same time, does not catalyze hydrogenations of the benzene or furan rings. Its activity for the C=C bond hydrogenation is not high. The use of copper catalysts for the hydrogenation of nitrobenzene to aniline is widespread (Scheme 1). Cu catalysts in the form of CuO - Cr<sub>2</sub>O<sub>3</sub> (Adkins catalysts) are used for the hydrogenolysis of esters to alcohols. Iron catalysts have found only limited use in usual hydrogenations, but they play industrially important roles in the ammonia synthesis and Fischer-Tropsch process (Scheme 2). [2, 4]



**Scheme 1.** Illustrative chemoselectivity of Cu and Ni in nitrobenzene hydrogenation.



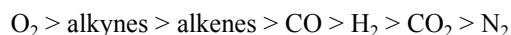
**Scheme 2.** Example of specific catalytic properties of individual metals.

### 3. What Causes the Differences in Catalytic Properties of Metals in Hydrogenations

Undoubtedly, the differences in the specific catalytic properties of individual metals (i.e. discriminations and preferences in hydrogenations of particular unsaturated functional groups in organic compounds) are given by their electronic structure, more specifically by electronic properties of their *d*-bands. Characteristic electron-acceptor sites of these metals predestine the electronic and thus also catalytic properties [7-10]. However, till now, no comprehensive theory exists which would explain so much differing properties of metals in heterogeneously catalyzed hydrogenations of common organic substrates, as illustrated above. On the other hand, in case of reactions of simple molecules on the transition metals (e.g., the methanation or the low-temperature water-shift-gas reaction), such a coherent theory does exist, is described in works [11] by J. K. Norskov et al. and represents an important advance in the field of heterogeneous catalysis. In this theory, the analysis of the catalytic processes on metallic surfaces consists, on the one hand, in theoretical methods (DFT calculation [12-14]) and, on the other, in a large amount of high-quality experimental data on an adsorption of simple molecules (such as, e.g., CO) onto the surfaces of transition metals. The experimental data concerned the geometric structure, vibrational properties, electronic structure, kinetics and thermochemistry [15-17]. The theory [11] shows, how the surface bonding and catalytic activity are closely interconnected. One of the principle conclusions of the theory is that the adsorption energy of the main intermediates of the surface-catalyzed reaction is often a very good descriptor of the catalytic activity. For many surface reactions, a correlation (Bronsted-Evans-Polanyi relations) was found between the activation barriers and the reaction energies. Combining with simple kinetic models, such correlations lead to volcano-shaped relations between the catalytic activity and adsorption energies [11]. Obviously, to get to understand the trends in complex reactions with more reaction steps (and most hydrogenation reactions are of such nature), it will be inevitable to develop new, more complicated models.

The necessary condition that a heterogeneous catalyst shows a hydrogenation activity is its ability to chemisorb hydrogen molecules in a dissociated form and, according to the Sabatier's principle of "volcano curves" [18-20], also with certain "optimum" bond energy (adsorption heat). The chemisorption of hydrogen onto the transition metal surface influences the lowering of the activation energy of hydrogenation.

Generally it holds that, for the transition metals (with the exception of gold), the gaseous reagents can be arranged according to their chemisorption strength in the following array:



The chemisorption strength changes also in dependence on the metal used. Generally, the chemisorption strength is highest for the transition metals in the left hand part of the periodical table and drops in the period of transition metals with increasing atomic number. The chemisorption on Sc, Ti, V and Cr is too strong so that these elements are rarely used as hydrogenation catalysts [21, 22]. Hydrogen is selectively chemisorbed by W, Mo, Zr, Fe, Ni, Co, Pt, Rh and Pd [23]. Suitable chemisorption strength is shown by Co, Rh, Ir, Ni, Pt and Pd which are thus predestined for the application in hydrogenation reactions [21, 22].

Heterogeneously catalyzed hydrogenation is affected by a number of factors (catalyst, reaction conditions, thermodynamic factors, specific factors). As for the catalyst, there are several basic factors that may affect the catalytic properties [7, 24, 25]:

(1) the type of the metal, (2) the structure and morphology of the metal particles, (3) the surface association of two or more metals or other components, (4) the presence of surface ligands, (5) the role of a support and (6) the effect of the metal distribution in a porous matrix of a support.

The principle way how to affect the course of a catalyzed hydrogenation relies in a selection of a suitable active metal. The effects of other factors are usually less pronounced.

The hydrogenation of organic substrates is influenced not only by the properties of the catalyst (by the structure of the active site) and the chemisorption of hydrogen, as mentioned above, but also by the electronic structure of the other reacting molecule, i.e., the organic substrate, since it is generally supposed that the surface hydrogenation proceeds between two adsorbed particles (Langmuir-Hinshelwood mechanisms) [26, 27]. A substantial attention has been devoted to the effect of the structure of the substance being hydrogenated on the course of the heterogeneously catalyzed hydrogenation in the liquid phase. These studies are often focused on a quantitative assessment of the effect of a substituent present in the molecule being hydrogenated on the course of the reaction. A number of empirical correlations were found and successfully applied to many heterogeneously catalyzed reactions; thus, a more general theory of structural effects in heterogeneous catalysis has gradually been built on the basis of these studies. For example, the structural effects in hydrogenation reactions on platinum metals were extensively studied by Cerveny et al.

[28-30 and refs. therein] and Kacer and Cerveny [7 and refs. therein]. In their papers a well-known experimental method of competitive hydrogenation [31] was chosen to assess the effect of structural changes within a series of properly selected substrates. This kinetic method allows one to obtain data, reflecting quantitatively relative differences in adsorptivities and reactivities of the substrates under study. Therefore it enables one to discuss separately the effect of molecular structure on the rate of the surface reaction on the one hand, and on the stability of the adsorbed complex on the other. Experimental results thus obtained were then interpreted with the help of methods of molecular modeling, assuming that the increase of electronic density in the reaction center leads to an increase of the stability of the complex being formed, whereas the decrease of this density destabilizes the process of adsorption [7]. Such a simplified approach, assuming that the properties of the catalyst are a constant that does not change, cannot affect the differences in the behavior of the individual catalysts. This can be solved only by molecular modeling in which the model of the studied system will also include active sites on the catalytic surface – in the form of (i) clusters, (ii) embedded clusters or (iii) slabs that are the closest approximation of the real state [31-35]. Hydrogenation of organic substrates located on the surface of a metal catalyst is, by its very nature, a very complex set of partial processes (in addition, running on the phase interface) and its modeling is therefore exacting. Nevertheless, we can expect there will be just molecular modelling that will provide a major contribution to creating a comprehensive theory explaining the different performances of metals in the hydrogenation of individual organic compounds in the future.

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