ISSN 2070-0504, Catalysis in Industry, 2022, Vol. 14, No. 1, pp. 131–144. © Pleiades Publishing, Ltd., 2022.
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An Essay on the History of Catalytic Hydrogenation of Organic Compounds. From P. Sabatier and V. N. Ipatieff to the Present Days

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Received May 19, 2021; revised June 2, 2021; accepted June 4, 2021

Abstract—The essay considers historical aspects of the appearance and development of methods for catalytic hydrogenation of organic compounds, starting from the works by P. Sabatier and V.N. Ipatieff. Particular attention is paid to the results of synthesis and investigation of hydrogenation metal catalysts based on Ni, Pd and Pt since they are significant for practical application. Modern trends and promising lines of investigation in the field of hydrogenation processes and catalysts are revealed.

Keywords: history of catalysis, catalytic hydrogenation, organic synthesis, nickel catalysts, palladium catalysts, platinum catalysts

DOI: 10.1134/S2070050422010056

> *"A retrospect of the past, especially in the exact sciences, alone affords a proper comprehension of what is accepted to-day. [...] Even when new modes of explanation are proposed, traces of former opinions may still be recognised in the direction which these take."*
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> *A. Ladenburg*

INTRODUCTION

Hydrogenation reactions of organic compounds with the use of molecular hydrogen under the action of metal catalysts are among the most widely used both in the practice of laboratory research and in the industrial organic synthesis of pharmaceuticals, dyes, fragrances, agrochemicals, and in the large-scale production of polymeric materials and synthetic fibers [1–3].

In 90% of cases, the production of any chemical requires the use at least one catalytic stage which is often based on hydrogenation (about 25% of all catalytic reactions), and the market for hydrogenation catalysts is estimated at about $3 billion [1, 4]. The high practical significance of hydrogenation processes can explain the fact that for more than 150 years after the first observations of catalytic hydrogenation, intensive studies of the nature of the action of hydrogenation catalysts, the chemistry of the reductive transformations of organic substrates occurring on a catalytically active surface, as well as the development of new and improvement of already known catalytic systems are still ongoing. In addition, great attention paid to hydrogenation reactions may be due to the fact that these reactions are relatively simpler than others and therefore more accessible and convenient for study. At the first stages of the development of organic catalysis, this circumstance was especially important in establishing the kinetics of catalytic reactions and their mechanism and also in connection with the development of various theories of catalysis [5, 6].

The first experimental studies on the catalytic hydrogenation of organic compounds were performed in the second half of the 19th century. In 1863, the German chemist H. Debus obtained methylamine by passing the vapor of hydrogen cyanide mixed with hydrogen through a tube with platinum black heated to 100°C. In an experiment with ethyl nitrite under the same conditions he observed the formation of ethyl alcohol and ammonia [7]. In 1866 and 1874, the Belgian chemist P. de Wilde showed that, in the presence of platinum black, acetylene reacts with hydrogen to form ethylene, which is then hydrogenated to ethane [8, 9]. In 1871, the Russian chemist M.M. Zaitsev, working in the laboratory of H. Kolbe, carried out experiments on the gas-phase hydrogenation of organic compounds (benzoyl chloride to benzaldehyde, nitrobenzene to aniline) in the presence of palladium black [10, 11]. Moreover, M.M. Zaitsev was the first to perform liquid-phase hydrogenation of organic compounds, thus obtaining aminophenol from nitrophenol and methylamine from nitromethane [11].

These isolated experiments, however, had no significant effect on the development of catalytic hydro-

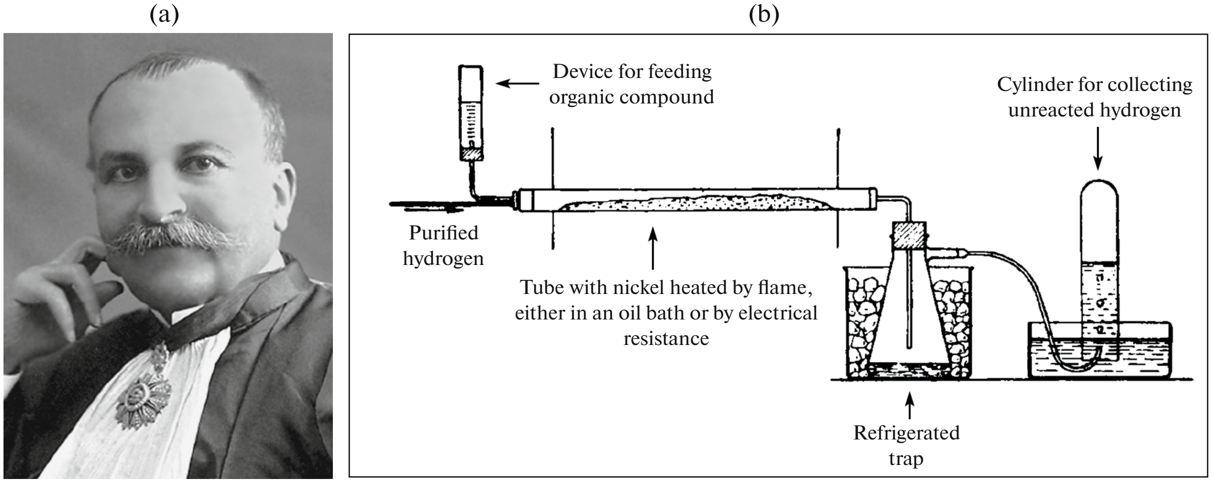

Fig. 1. (a) P. Sabatier and (b) the schematic representation of the setup used by him and his co-workers for the catalytic hydrogenation of organic compounds [18].

genation, and further progress in this area is associated with systematic studies performed in the first quarter of the 20th century, primarily by P. Sabatier and V.N. Ipatieff. Note that the appearance and success of new research work in the field of organic catalysis would have been impossible without the achievements, on the one hand, of organic chemistry, which has developed rapidly since the middle of the 19th century, and on the other, physical chemistry, a new field that was formed in the 1890s [12]. Investigations of the catalysis of organic reactions, primarily hydrogenation reactions, at the beginning of the 20th century made it possible to solve many problems of synthetic chemistry that existed at that time and laid the foundation for modern industrial organic synthesis.

Turning to the past, you can always better understand the present day and even look into the future. Believing in this and relying on the facts of history, within the framework of this small work, we tried to evaluate when the modern appearance of hydrogenation processes and catalysts arose and formed, and also to answer the question about the limit of their possible improvement.

To obtain more detailed information on the issues considered here, one can recommend special monographs devoted to the history of catalysis and the evolution of catalytic organic synthesis [5, 6, 13–16].

DEVELOPMENT OF METHODS FOR CATALYTIC HYDROGENATION

A start of systematic studies of the catalytic hydrogenation of organic compounds has been made by the eminent French chemist P. Sabatier (Fig. 1a). In 1897, P. Sabatier and his collaborator J.-B. Senderens began investigating the hydrogenation reactions of unsaturated compounds in the presence of metallic nickel [17]. The experimental technique was quite simple and consisted of passing a mixture of hydrogen and an organic compound through a heated tube with a nickel catalyst (see Fig. 1b) which was obtained immediately before the reaction by reducing nickel oxide with hydrogen. Subsequently, finely dispersed cobalt, copper, iron, and platinum were also used as catalysts. Ethylene was quantitatively converted to ethane during hydrogenation over nickel at temperatures up to 150°C. Similarly, other olefins in the presence of nickel reacted with hydrogen at temperatures up to 200°C to form the corresponding saturated hydrocarbons.

In 1901, P. Sabatier applied the developed method to the hydrogenation of benzene and its homologs [19]. This work was of great importance for the development of organic synthesis, since the previous methods of obtaining hydrocarbons of the cyclohexane series were technically difficult (e.g., the cyclization of dicarboxylic acids with subsequent reduction of the resulting cyclohexanones) and did not allow achieving high yields. P. Sabatier showed that cyclohexane and its alkyl-substituted derivatives can be easily obtained in quantitative yield by hydrogenation of the corresponding aromatic hydrocarbons over nickel at temperatures of 150–180°C.[1]

Later, P. Sabatier, using the method he developed, studied the hydrogenation of a wide range of organic heteroatomic compounds: aldehydes and ketones to the corresponding alcohols, phenols to cyclohexanols, nitro compounds, oximes, amides, nitriles to the corresponding amines [21, 22]. In total, P. Sabatier together with his co-workers (J.-B. Senderens, A. Mailhe, M. Murat) studied more than 200 hydrogenation

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[1] Without diminishing the importance of this study by P. Sabatier, we note, however, that almost at the same time G. Lunge and J. Akunoff obtained cyclohexane by passing benzene vapor in a mixture with hydrogen over platinum or palladium black [20].

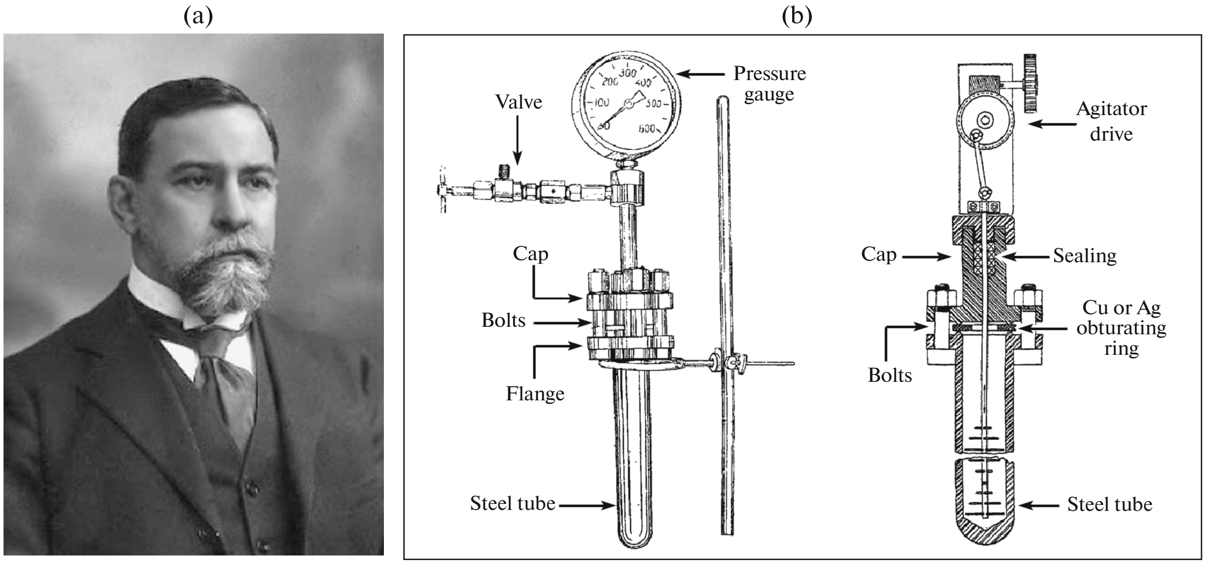

Fig. 2. (a) V.N. Ipatieff and (b) the design of the "bombs" he used to study catalytic reactions at high temperatures and pressures [26].

reactions, and the results of these studies were summarized in the monograph [23]. We emphasize that the merit of P. Sabatier consisted primarily in the fact that he was the first to demonstrate the inexhaustible possibilities of heterogeneous catalysis for organic chemistry, proposing a simple catalytic method for the synthesis of organic compounds that were previously either unknown or difficult to obtain using classical synthetic approaches. The works of P. Sabatier were highly appreciated by his contemporaries, and in 1912, he was awarded the Nobel Prize in Chemistry "for his method of hydrogenating organic compounds in the presence of finely disintegrated metals whereby the progress of organic chemistry has been greatly advanced in recent years" [24].

The method of catalytic hydrogenation under conditions of elevated pressures and temperatures was introduced into the practice of organic synthesis by the outstanding Russian chemist V.N. Ipatieff (Fig. 2a). Before his works, attempts at preparative synthesis of organic compounds at temperatures above 300–400°C, i.e. significantly higher than in the Sabatier method, did not lead to practically valuable results, and therefore in classical synthetic chemistry of the 19th century typical was the use of mild temperature conditions that would exclude unwanted "pyrogenic decomposition". So, A. M. Butlerov noted that conclusions about the chemical structure of compounds are best based "on those syntheses that are performed at a slightly elevated temperature and, in general, under such conditions when it is possible to control the progress of the gradual complication of a chemical particle" [25]. Likewise, elevated pressures in classical organic synthesis were almost never used [6]. From this point of view, the works by V.N. Ipatieff and his co-workers [26], which were performed in the period 1901–1933 and devoted to the study of the catalytic conversions of organic compounds under the influence of high temperatures and pressures (not only hydrogenation, but also dehydrogenation, dehydration, isomerization, alkylation), marked an even more significant departure from the classical methods of synthesis in comparison with the Sabatier method, introduced essential elements of novelty in chemistry, and ultimately laid the foundations of modern industrial catalysis of organic reactions.

To study catalytic reactions at high temperatures and pressures, V.N. Ipatieff developed a special apparatus ("Ipatieff bomb", see Fig. 2b), which became the prototype of modern batch reactors (autoclaves) widely used in chemical practice. The apparatus consisted of a steel tube with a capacity of 0.25 to 3 L, a cap with a valve through which gas (hydrogen in the case of hydrogenation) was pumped into the tube, and a copper or silver obturator (sealing ring) clamped between the tube flange and the cap using bolts. When assembled, the "Ipatieff bomb" made it possible to perform reactions at pressures up to 40 MPa and operating temperatures up to 600°C [26]. The temperature rise in the "bomb" was carried out either by electrical heating or by immersing it in a bath of molten lead or tin. To measure the pressure inside the tube, the apparatus was equipped with a pressure gauge. The pressure decreased as the hydrogenation proceeded, and the recording of the pressure gauge data made it possible to reveal the kinetics of the process and to judge the catalyst activity. The first experiments were carried out without stirring the reaction mixture, but soon V.N. Ipatieff designed an apparatus with a stirring device.

V.N. Ipatieff began to study hydrogenations of organic compounds in 1904. He established the reversibility of hydrogenation-dehydrogenation reactions when investigating the hydrogenation of aldehydes and ketones to the corresponding alcohols in the presence of iron or nickel at temperatures of 300–400°C and pressures of 6–10 MPa [27]. In 1905–1912, V.N. Ipatieff studied the hydrogenation of a wide range of organic substrates (aromatic hydrocarbons, unsaturated aldehydes, ketones and carboxylic acids, phenols, amines, terpenes, heterocyclic compounds) in the presence of Pd, Ni, Fe, NiO, CuO catalysts at elevated temperatures and pressures [26]. In many cases, he succeeded in obtaining the target hydrogenation products in yields close to theoretical. Moreover, V. N. Ipatieff showed that the method developed by him could be successfully applied in cases where the Sabatier method, which requires contact of the catalyst with the vapor of the hydrogenated compound, turned out to be of little use, for example, in the hydrogenation of high molecular weight organic compounds such as carbohydrates [28] and polycyclic aromatic hydrocarbons [29].

Almost simultaneously with the studies by P. Sabatier and V.N. Ipatieff, other chemists started works in the field of catalytic hydrogenation of organic compounds. While continuing to use traditional approaches of organic synthesis, they were looking for new catalytic systems. One of the research directions was associated with the use of colloidal metals, mainly palladium and platinum, as catalysts for hydrogenation. To obtain them, the German chemist G. Bredig in 1899 developed a method that consisted of spraying metals in water using an electric arc [30]. Later, colloidal metal catalysts began to be prepared by chemical reduction of metals from aqueous solutions of their compounds. The metal hydrosols obtained in this way have shown themselves to be highly active catalysts for inorganic reactions; however, these hydrosols lost their stability upon contact with many organic compounds. To stabilize them, it was proposed to use natural high-molecular substances (protective colloids), which covered the surface of metal particles and thereby prevented their coagulation. For example, the German chemist C. Paal used lysalbinic and protalbinic acids, which are obtained by alkaline hydrolysis of egg albumin, as protective colloids for the preparation of colloidal platinum and palladium catalysts [31]. Later, A. Skita suggested using gum arabic for this purpose [32]. It was shown that the Pd and Pt hydrosols stabilized in this way are rather active and selective catalysts for the liquid-phase hydrogenation of various organic compounds (for example, unsaturated aldehydes, ketones, nitro compounds) under mild conditions, i.e., at low temperatures and atmospheric pressure [33–35]. However, this hydrogenation method, which later became known as the Paal–Skita method, was employed relatively rarely. First, it was limited to the use of exclusively metal hydrosols and therefore could only be used for hydrogenation of a narrow range of organic compounds that are soluble in water. Second, the activity of colloidal catalysts strongly depended on the method of their preparation and, in particular, on the nature of the protective colloid. Finally, the separation of colloidal metal from the reaction products caused difficulties.

The method, the main feature of which was the use of fine powders of various metals (mainly platinum and palladium blacks) as catalysts, was devoid of these disadvantages. This direction in the field of liquid-phase hydrogenation of organic compounds arose in the works of the Russian chemist S.A. Fokin, who performed in 1906–1908 the hydrogenation of unsaturated fatty acids and some common vegetable oils in the presence of platinum and palladium blacks [36–38]. In his experiments, S.A. Fokin suspended powdered catalysts in ethereal or alcoholic solutions of substrates and then passed a continuous stream of hydrogen through the resulting suspensions under constant stirring (e.g., by shaking). The reaction was monitored by registering the volume of consumed hydrogen, which made it possible to estimate the rate of hydrogenation and to judge the catalyst activity. The advantage of the hydrogenation method proposed by S.A. Fokin consisted first of all in the fact that this method allowed the selective reduction of high-boiling organic substrates, which could undergo decomposition under high-temperature reaction conditions according to the Sabatier and Ipatieff methods. Employing the Fokin method, hydrogenation was carried out at atmospheric pressure and at room or slightly elevated temperature. Therefore, no specific apparatus was required for the experiments, and the equipment used was available to organic chemists. Thanks to the subsequent work of the German chemist R. Willstätter, who together with collaborators studied numerous hydrogenations of unsaturated oxygen-containing substrates (alcohols, terpenes, cholesterol) and aromatic compounds [39–42], this hydrogenation method, which was later called as the Fokin–Willstätter method, firmly entered the practice of synthetic organic chemistry.

An important feature of the Fokin–Willstätter method was the possibility to study the reaction kinetics by registering the rate of hydrogen consumption during hydrogenation. The first kinetic measurements were made as early as in the studies of S.A. Fokin [38], and much attention was paid later on to elucidating the mechanism of hydrogenation based on the results of the kinetic description of the process. In this regard, we have to note the pioneering work of the French chemist G. Vavon, which was devoted to the selectivity of catalytic hydrogenation processes and to the study of the relations between the hydrogenation rate and the structure of unsaturated compound [43, 44]. In particular, using the Fokin–Willstätter method for the hydrogenation of olefins over platinum black, G. Vavon established that the reaction of hydrogen addition to the C=C bond is influenced by the degree of branching of the carbon chain in substrate molecules: unbranched compounds are hydrogenated faster than branched ones. G. Vavon explained the slower hydrogenation of iso-compounds by steric hindrances. Subsequently, the role of structural factors in hydrogenation processes was studied in detail by S.V. Lebedev, B.A. Kazansky, Yu.S. Zalkind and others.

Thus, within fifteen years after the first experiments of P. Sabatier, at least 4 methods of catalytic hydrogenation were developed, allowing the reduction of organic substrates both in liquid media and in the gas phase, as well as in a wide range of temperatures and pressures. These methods complemented each other and became the foundation for subsequent work in the field of heterogeneous catalysis of organic reactions. Further improvement of experimental techniques contributed to the rapid development of hydrogenation methods and their widespread use in organic synthesis. The features of the methods considered above, their application for hydrogenation of various organic substrates, as well as their subsequent evolution are discussed in detail in a number of reviews [21, 22, 44–46] and special monographs [23, 26, 33, 47–51]. Subsequently, a kind of hybridization of these methods took place with the appearance of a large number of combinations in which catalysts of different nature were used. Since the 1920s, in close connection with the development of catalytic hydrogenation methods, considerable attention has been paid to studying the effect of catalyst preparation conditions on the catalyst structure and activity, as well as to the development of fundamentally new catalytic systems [51, 52].

DEVELOPMENT AND STUDY OF HYDROGENATION CATALYSTS

In the first systematic studies, mainly bulk metal catalysts were used for the catalytic hydrogenation of organic compounds. Supported catalysts became widespread in hydrogenation processes only in the 1920s, although the main approaches to their preparation were developed in the middle of the 19th century [16, 53], and some supported systems have been successfully applied in oxidation processes even on an industrial scale, for instance, in the contact production of sulfuric acid by the oxidation of SO_2 over platinized asbestos, as suggested by C. Winkler [54]. Currently, a large number of both bulk and supported catalysts having a unique combination of physicochemical and catalytic properties are known and indispensable in many catalytic hydrogenation processes. Table 1 lists the composition, preparation methods, and applications of some of the well-known catalysts named after the researchers who proposed their use or made a significant contribution to their study. This section discusses the historical aspects of the development of some of the best-known hydrogenation catalysts. Taking into account the uniqueness of any catalyst in terms of structure, set of properties, and areas of application, we considered each of them separately. We note right away that the history of the creation and study of all the heterogeneous catalysts presented below is inextricably linked with the development of a number of physical methods, which over the past 70 years have been increasingly involved in studies of the structure of solids, including in revealing the nature of their catalytic action. Theoretical concepts in heterogeneous catalysis developed in the 1920–1940s (Taylor's concept of active sites, Balandin's multiplet theory, Kobozev's theory of active ensembles, etc.) needed experimental verification and thus also stimulated detailed studies of the structure of hydrogenation catalysts.

Nickel Catalysts

The work of P. Sabatier on hydrogenation over nickel, as well as the organization of the first industrial hydrogenation processes in the presence of nickel, became the impetus for intensive research of nickel-based catalysts. Finely dispersed metallic nickel used by P. Sabatier and then by other researchers was prepared immediately before the reaction by the reduction of nickel oxide with hydrogen (see Fig. 1b and Table 1). It was shown that the catalytic activity of nickel obtained by this method depends on the reduction temperature, and the catalysts reduced at 700°C exhibit maximum activity in hydrogenations. In addition, it was found that during hydrogenation, a nickel catalyst can completely lose activity, firstly, if the hydrogen or the hydrogenated compound contains even traces of chlorine, bromine, iodine, sulfur, phosphorus, which are catalytic poisons, and secondly, due to the formation of carbonaceous deposits on the catalyst surface during side reactions of the destruction of organic compounds [23].

Despite its versatility, Sabatier nickel, as this catalyst began to be called, was not widely used in industrial organic synthesis, not only because of its ability to quickly deactivate during hydrogenation, but also because of its pyrophoricity, which caused great difficulties in large-scale production [51]. Further progress in the development of nickel catalysts for hydrogenation processes was associated with the development and study of supported nickel-containing systems, especially on the basis of such supports as diatomite (i.e., natural silica consisting of diatom residues) and aluminum oxide.

Apparently, the supported Ni/diatomite catalyst was initially proposed in 1910 for the industrial hydrogenation of unsaturated fats and oils [63]. The catalytic properties of the first Ni/diatomite catalysts in this process significantly depended on the conditions of their preparation and were poorly reproduced. In the 1930s, the American chemist H. Adkins studied the Ni/diatomite catalysts and tried to optimize the procedure for their preparation [64]. This procedure,

Table 1. Some “named” catalysts for hydrogenation of organic compounds

Year	Catalyst name	Composition	Preparation method	Application in hydrogenations	Reference
1897	Sabatier nickel	Ni	High-temperature reduction of NiO in a stream of H_2	Multipurpose	[17]
1922	Adams catalyst	PtO_2	Fusion of H_2PtCl_6 with $NaNO_3$	Multipurpose	[55]
1924	Zelinsky catalyst	Ni/Al_2O_3	Coprecipitation of $Ni(OH)_2$ and $Al(OH)_3$ from solutions of Ni and Al nitrates followed by reduction in a stream of H_2	Hydrogenation of aromatic compounds to the corresponding alicyclic compounds	[56]
1927	Raney nickel (Ra–Ni)	Ni	Leaching of aluminum from Ni–Al alloy ($Ni : Al \approx 1$) with NaOH solution	Multipurpose	[57]
1929	Bag’s catalyst	Ni-Al	Partial leaching of aluminum from Ni–Al alloy ($Ni : Al \approx 0.4$) with NaOH solution	Multipurpose	[58]
1931	Adkins catalyst	$CuCr_2O_4$	Calcination of basic copper ammonium chromate obtained by coprecipitation from $(NH_4)_2CrO_4$ and $Cu(NO_3)_2$ solutions	Hydrogenation of aldehydes, ketones, carboxylic acids, and esters to the corresponding alcohols	[59]
1949	Lindlar catalyst	5% $Pd/CaCO_3 + Pb(OAc)_2$	Impregnation of $CaCO_3$ with a solution of H_2PdCl_4 followed by reduction with sodium formate; then, impregnation of $Pd/CaCO_3$ with a solution of lead acetate	Selective hydrogenation of alkynes to *cis*-alkenes	[60]
1951	Urushibara nickel (U–Ni)	Ni	Precipitation of nickel from a $NiCl_2$ solution with zinc or aluminum dust, followed by treatment with an alkali or acid solution	Multipurpose (it is similar in catalytic properties to some varieties of Ra-Ni under the same reaction conditions)	[61]
1960	Nishimura catalyst	$Rh_2O_3–PtO_2$	Fusion of H_2PtCl_6 and $RhCl_3$ with $NaNO_3$	Hydrogenation of aromatic compounds to the corresponding alicyclic compounds under mild conditions	[62]

which is still used today, consists in the deposition of basic nickel carbonate on the surface of diatomite from a nickel salt solution, followed by heat treatment and reduction with hydrogen at temperatures of 300–400°C. Detailed studies of the formation and structure of the Ni/diatomite system were carried out in the 1940–1950s and showed that during the deposition of nickel compounds on diatomite in an alkaline medium, various interactions occur on the support surface with the formation of a complex mixture of nickel hydroxide and hydroxysilicates [65, 66]. The study of high-temperature hydrogen reduction of these nickel compounds supported on diatomite made it possible to optimize the conditions for the formation of highly dispersed crystallites of metallic nickel. The results of these studies became the foundation of modern technology for the production of industrial Ni/diatomite catalysts, and were later used to create other similar systems, for example, the well-known EuroNi-1 catalyst (25% Ni/SiO_2) developed in the 1980s by a large group of researchers under the leadership of J.W.E. Coenen [67].

At present, one of the most important areas of industrial application of diatomite-supported nickel catalysts is the hydrogenation of vegetable oils, the so-called fat hardening [16, 68–70]. Note that this catalytic process was the first commercial hydrogenation process. It was developed back in 1901 by the German chemist W. Normann, an employee of the Leprince & Siveke factory [71, 72], and the first setup for the production of saturated fats by catalytic hydrogenation in the liquid phase were built by 1909 in Germany and England [73]. Almost simultaneously, in 1909–1910, catalytic hydrogenation of vegetable oils was developed in Russia at the Krestovnikov brothers' soap factory in Kazan, as well as at the Persits' oil mill plant in Nizhny Novgorod [14, 74]. S.A. Fokin, M.V. Vil'bushevich, K.A. Rozhdestvensky, and other engineers and chemists were directly involved in organizing these industrial processes in Russia. In particular, S.A. Fokin developed a nickel-silicate catalyst for the domestic hydrogenation process [74]. In addition to the hydrogenation of unsaturated fats and oils, the Ni/diatomite catalysts have found application in other large-scale processes, such as hydrogenation of naphthalene to tetralin and decalin, as well as phenol to cyclohexanol [68, 69], the industrial implementation of which was first carried out in Germany back in 1917 due to the urgent demand of the German chemical industry for synthetic solvents [75–78].

Another important type of nickel hydrogenation catalysts is the Ni/Al_2O_3 system which is obtained by coprecipitation of nickel and aluminum hydroxides from solutions of their salts, followed by heat treatment and reduction in a stream of hydrogen. The composition and preparation method of these catalysts were developed in 1914 at Badische Anilin & Soda Fabrik (BASF) [79]. In 1924, the outstanding Russian and Soviet chemist N.D. Zelinsky showed that the Ni/Al_2O_3 catalyst prepared by coprecipitation is very effective in hydrogenating the benzene ring of aromatic compounds and is comparable in activity to platinum or palladium catalysts under optimal reaction conditions [56]. An important conclusion from this study by N.D. Zelinsky was that aluminum oxide in the catalyst composition acts not only as an inert support, but as a modifier of the properties of nickel. It should be noted that V.N. Ipatieff, in his works on mixed catalysts [26, 80], has already pointed out the positive effect of alumina on the catalytic properties of a nickel hydrogenation catalyst. Apparently, these were the first observations of bifunctional catalysis. Beginning in the 1940s, numerous structural studies of the Ni/Al_2O_3 catalytic system were carried out, and, thanks to the employment of physical methods, a complex chemistry of the formation of catalytically active phases was established at all stages of catalyst synthesis [81–83]. Thus, it was shown that the composition of compounds formed during coprecipitation with alkali metal carbonates depends on the Ni:Al molar ratio, the pH value, the rate of addition of the precipitating agent, and other factors. Under certain conditions, the so-called Feitknecht compound with the composition of $Ni_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$ is precipitated, from which the $Ni_6Al_2O_9$ oxide phase is formed during further heat treatment. Subsequent reduction of this mixed oxide yields metallic nickel crystallites containing small nickel aluminate particles. Despite the fact that the results of a large number of research works have already allowed the formation of a conception of the genesis, structure, and hydrogenation performance of Ni/Al_2O_3 catalysts, however intensive studies of these catalysts are still ongoing [84, 85]. In practical terms, the Ni/Al_2O_3 catalysts have very diverse applications. As an actual example, we can point to the industrial process of benzene hydrogenation to cyclohexane [69, 86]. A two-stage scheme of this process ensures the production of cyclohexane of high purity (up to 99.88%). A 30–45 wt % Ni/Al_2O_3 catalyst is used at the first hydrogenation stage, and a 0.2–1.0 wt % Pt/Al_2O_3 catalyst at the second one.

An important stage in the evolution of nickel hydrogenation catalysts was the development of skeletal nickel and later of skeletal catalysts based on iron, cobalt, and copper. In 1925, the American engineer M. Raney patented a method for preparing a nickel catalyst, which consisted of removing silicon from a nickel-silicon alloy by treating the latter with an alkali solution [87]. Two years later, M. Raney modified this preparation method by using a nickel-aluminum alloy with approximately equal fractions of both metals [57]. According to this method, aluminum is completely removed from the alloy by leaching. In 1929, the Soviet chemists A.A. Bag, D.F. Volokitin, and T.P. Egupov developed a skeletal nickel hydrogenation catalyst for the preparation of which, unlike Raney nickel, a Ni–

Al alloy containing 27% Ni and 73% Al is used, and when it is treated with a dilute alkali solution, aluminum is only partially removed [58, 88]. Further studies, a review of which can be found, e.g., in [89–93], showed that the activity of skeletal nickel catalysts depends on the conditions of alkaline treatment of the initial alloy and the degree of aluminum leaching. The skeletal nickel catalysts most active in hydrogenations can contain up to 20 wt % Al. Part of the aluminum remaining in the catalyst after leaching is included in the aluminum hydroxide which is located on the surface of nickel crystals and has a promoting effect on skeletal nickel during hydrogenation. Skeletal nickel catalysts have been shown to be versatile, i.e. they can be used for hydrogenation of various organic compounds [2, 88–92], and at present these catalysts find very wide application not only in research works, but also in industrial processes, such as hydrogenation of benzene to cyclohexane [68, 69, 94], acetone to isopropyl alcohol [95], glucose to sorbitol [69, 93], and adiponitrile to hexamethylenediamine [69, 93].

Another unsupported nickel hydrogenation catalyst, which is also widespread in organic synthesis, is metallic nickel powder precipitated from an aqueous solution of $NiCl_2$ with zinc dust and treated (activated) with an acid or alkali solution. Such a catalyst was first proposed in 1951 by the Japanese chemist Y. Urushibara when he developed a method for the reduction of estrone to estradiol [61]. It has been shown in a number of works that nickel catalysts obtained by this method exhibit high catalytic performance in the hydrogenation of a wide range of organic compounds [96–98]. The procedure for activating the precipitated nickel with acid or alkali is a necessary step in the preparation of these catalysts. Precipitated and non-activated nickel was studied in hydrogenation reactions long before Y. Urushibara, but its catalytic activity was low [51, 98]. It was found that during activation, the basic zinc chloride, which is formed on the surface of nickel during the precipitation, dissolves, and the greatest degree of zinc removal is achieved upon activation with solutions of acids, for example, acetic acid. On the whole, in terms of catalytic properties, Urushibara nickel is comparable to some kinds of skeletal nickel catalysts under the same reaction conditions.

Noble Metal Catalysts

As mentioned above, fine powders (blacks) of platinum and palladium were the first to be used as catalysts for the hydrogenation of organic compounds [7–11]. At the beginning of the 20th century, S.A. Fokin and R. Willstätter intensively evolved the method of liquid-phase hydrogenation in the presence of noble metal blacks [36–42]. To obtain these blacks, several procedures based on the reduction of noble metal compounds dissolved in water have been developed [2]. For example, according to the Loew method, which is quite widespread in laboratory practice, platinum black is prepared by liquid-phase reduction of platinum chloride with formaldehyde, followed by the neutralization of resulting acids and the aging of a platinum precipitate with its filtration and washing [99]. Later, this method was improved by R. Willstätter, who also found that platinum black is active in hydrogenations if it contains a certain amount of oxygen [41, 100]. Noble metal blacks were very often used in catalytic research works of the 20th century. Among them, we note the well-known studies of N.D. Zelinsky on the hydro- and dehydrogenation catalysis of hydrocarbons [101], which formed the basis for the catalytic reforming of petroleum fractions, as well as the works of D.V. Sokol'sky and his school [102–104], the most important results of which were the conception of the hydrogenation mechanisms of organic compounds on the surface of metal catalysts and the theory of optimization of hydrogenation catalysts [105].

At present, the noble metal blacks are rarely used for the hydrogenation of organic compounds, and preference is given to supported catalysts, among which the Pd/C system is the most widespread both in laboratory research and in industry[2]. Apparently, the catalyst of this type was first employed to hydrogenate organic compounds in 1914 by German chemists C. Mannich and E. Thiele [107–109][3]. In their studies, they used a 2 wt % Pd/C catalyst obtained by shaking calcined animal charcoal with a solution of H_2PdCl_4 and hydrogen, followed by washing and drying. When studying this palladium catalyst in the hydrogenation of acetophenone derivatives and unsaturated fats and oils, C. Mannich and E. Thiele showed that the carbon support significantly increases the absorption capacity of palladium to hydrogen (as compared with the bulk metal), that provides to the Pd/C catalyst high activity in the hydrogenation of organic compounds. In addition, it was obvious that the supported Pd/C catalyst has an advantage over palladium black also from the viewpoint of saving expensive palladium,[4] since the distribution of metal particles on the support surface makes it possible to increase the fraction of the active surface available for reacting molecules. The method for preparing Pd/C catalysts (impregnation) proposed by C. Mannich and E. Thiele has become widespread and is still used in various versions [2, 113, 114]. Traditionally, special types of activated carbons obtained from vegetable or coal raw materials are applied as supports for Pd/C catalysts. In modern

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[2] As of 2011, the proportion of hydrogenation reactions performed using Pd/C catalysts was 75% [106].

[3] Note also that in 1908 the Russian chemist E.I. Orlov used a coke-supported nickel-palladium catalyst for conversion of synthesis gas to ethylene [110]. In 1914, G. Verona-Rinati used a coke-supported palladium catalyst for hydrogenation of oils, but he did not provide any data on this catalyst [111].

[4] For reference, in 1910 the price of palladium was \$54 per troy ounce [112], which was more than 2.5 times higher than the price of gold.

studies, various carbon nanomaterials, such as carbon nanotubes, carbon nanofibers, graphene, and carbon nanospheres, are often used for the synthesis of Pd/C catalysts [106, 115, 116]. The influence of the carbon support nature and the preparation conditions of the supported Pd/C systems on their catalytic properties in hydrogenation reactions was revealed at the dawn of their practical use [117]. The relative inertness of carbon supports and the weakness of the palladium–carbon interaction in comparison with, e.g., palladium catalysts based on the oxide supports [118] until recently did not allow explaining adequately a number of regularities in the formation and structure of Pd/C catalysts. Only relatively recently, owing to the application of a set of physical methods and model calculations, it was established that the supported Pd/C system exhibits a wide range of interactions that determine the catalytic properties of palladium-containing active sites, depending on the structure of the carbon support and its surface chemistry [116, 119–122].

In practical terms, the Pd/C catalysts find a wide variety of applications, examples of which are industrial hydrogenation of phenol to cyclohexanone [69, 123], aromatic nitro compounds to the corresponding anilines [68, 124], benzoic acid to cyclohexanecarboxylic acid [69, 125], as well as hydropurification of terephthalic acid [68]. In addition, Pd/C catalysts are indispensable in the production of pharmaceuticals [92, 126] and fragrances [127].

Among other supported palladium catalysts widely used in organic synthesis we note the so-called Lindlar catalyst, which is a 5 wt % $Pd/CaCO_3$ system modified with a lead salt, most often lead acetate, and quinoline. This catalyst was developed in 1949 by the Swiss chemist H. Lindlar, an employee of the F. Hoffmann-La Roche pharmaceutical company [60, 128]. The procedure for preparing the Lindlar catalyst [129] consists in the impregnation of precipitated calcium carbonate with a solution of H_2PdCl_4, followed by reduction of the supported precursor by treatment with a solution of sodium formate. The wet catalyst is then impregnated with a $Pb(OAc)_2$ solution and dried. Quinoline is added to the reaction mixture during the catalyst use. H. Lindlar showed that the catalyst he developed exhibits high selectivity in the partial hydrogenation of alkynes to *cis*-alkenes.[5] In order to establish the reasons for the high selectivity of the Lindlar catalyst in the hydrogenation of alkynes, numerous studies of its structure were undertaken using a set of physical methods. As a result of the investigations carried out in the 1980s, it was possible to identify various components (metallic Pd, $PbCO_3$, Pd–Pb intermetallics), which are formed on the support surface during the preparation of the Lindlar catalyst [131, 132]. Later, using model calculations, it was shown that lead, modifying palladium, prevents the formation of palladium hydrides, which are involved in undesirable over-hydrogenation to alkanes, and quinoline isolates palladium centers and minimizes oligomerization reactions [133]. Currently, the Lindlar catalyst is used both in laboratory practice [134] and in organic synthesis, for example, in the production of vitamins A and E [135, 136].

Among the platinum catalysts, which are very often used in many hydrogenation reactions of organic compounds, we note the so-called Adams catalyst, the composition of which is usually expressed by the molecular formula PtO_2. This catalyst was developed in 1922 by the American chemist R. Adams when he studied platinum black prepared by the Willstätter method [55, 137]. In developing the catalyst, R. Adams took into account two considerations: first, platinum black is usually active as a hydrogenation catalyst only if it contains oxygen [42, 100]; second, platinum oxides are formed upon absorption of oxygen by platinum black [138]. In the “classical” version, the synthesis of the Adams catalyst is very simple and consists in fusing H_2PtCl_6 and $NaNO_3$ until the evolution of gases is complete (at 500–550°C), followed by washing the cooled mass with water [55, 139, 140]. In numerous papers published by R. Adams and coworkers in the Journal of the American Chemical Society from 1923 to 1928 (references can be found, for example, in [140]), it was shown that the platinum catalyst obtained by this method can be used for hydrogenation of a wide range of organic compounds. In the 1940s, the procedure for the preparation of Adams catalyst was improved during the development of its large-scale production (the Johnson Matthey and May & Baker chemical companies) [141]. Studies of the structure of the Adams catalyst showed that it actually consists of Pt, α-PtO_2, and $Na_xPt_3O_4$ (platinum bronze) [142]. Under the hydrogenation conditions, α-PtO_2 is completely reduced by hydrogen to metallic platinum, which is the really active catalyst for hydrogenation. $Na_xPt_3O_4$ is also a catalytically active component, although it is only partially reduced under hydrogenation conditions. At present, the Adams catalyst is widely used in the processes of organic synthesis, for example, at the stages of hydrogenation in the production of pharmaceuticals [16, 126].

Adams’ idea, which consisted in the possibility of obtaining hydrogenation catalysts by a simple fusion method, was further evolved in the works of the Japanese chemist S. Nishimura [2, 62, 143–145]. In 1960, by fusing a mixture of H_2PtCl_6, $RhCl_3$, and $NaNO_3$, he obtained a Rh_2O_3–PtO_2 mixed oxide, which exhibited a very high activity in aromatic ring hydrogenation, surpassing in this parameter similarly obtained rhodium and platinum catalysts under the same reac-

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[5] In fact, Lindlar’s approach to the partial poisoning of a palladium catalyst in order to forcibly limit the reaction was not new and resembles, in particular, the procedure proposed in 1921 by K.W. Rosenmund for a $Pd/BaSO_4$ catalyst intentionally poisoned with sulfur-containing compounds to increase selectivity in the hydrogenations of acyl chlorides to aldehydes [130].

tion conditions. At present, the Nishimura catalyst (with 70–90 wt % rhodium) is sometimes used in organic synthesis for the selective hydrogenation of carbo- and heterocyclic aromatic compounds at room temperature and atmospheric pressure [2, 146].

Concluding the brief history of the development and study of hydrogenation catalysts, we note that we have considered only some of the most well-known catalysts. For example, we were forced to omit consideration of copper, iron and cobalt catalysts. However, even from the examples presented, it is easy to see that the compositions and methods for the preparation of catalytic systems currently used in hydrogenation reactions were already developed in the middle of the 20th century. Certainly, in the field of catalytic hydrogenation, the process of accumulating new data, a significant part of which is presented in patent sources, still continues. Many researchers, as well as the authors of this essay, admit that the preparation of catalysts is not only a field of science, but also of art.

Detailed studies of hydrogenation catalysts, which are ongoing due to new practice requirements, make it possible to confidently form conception about their genesis, structure, and performance in hydrogenation reactions. It is hoped that in the future, the results of these studies will become the foundation for the development of new methods to the targeted synthesis of effective catalysts, which will completely exclude the use of the “trial and error” approach [147], although the latter will be sorely missed by some professional catalytic chemists.

CONCLUSION

The history of the evolution of catalytic hydrogenation is indicative in that it clearly demonstrates how the catalytic reactions initially performed in the laboratory scale and the catalysts synthesized for these purposes are successfully introduced into industrial production. Laboratory methods for the hydrogenation of organic compounds, which were developed in the first quarter of the 20th century by P. Sabatier, V.N. Ipatieff, S.A. Fokin, R. Willstätter, and other chemists, were subsequently improved and eventually became the basis of industrial hydrogenation processes. In the second half of the 20th century, the laboratory hydrogenation methods have already become so mature and routine that the main techniques of hydrogenation and the design of the laboratory equipment have hardly changed over the past 50–60 years (see, for example, the classical monographs [2, 148–152]).

As for hydrogenation catalysts, it was already mentioned above that many of catalytic systems currently used in laboratory practice and on an industrial scale were developed in the first half of the 20th century. Note, however, that attempts to improve them are continued until now. In an applied aspect, one of the current trends in the improvement of hydrogenation catalysts is due to economic considerations and, in particular, consists in reducing the content of expensive noble metals while maintaining or even improving the catalytic performance. In addition, there have been recent attempts to restrict the use of catalysts that contain toxic components and can create environmental problems, for example, catalysts based on copper chromite. From the point of view of fundamental research in the field of hydrogenation catalysts, the directions of current work are still essentially reduced to the search for systems that are active, selective, and stable under optimal process conditions. In conclusion, it is advisable to list the main trends that are characteristic of recent research in the field of catalytic hydrogenation: (1) the use of nanostructured materials with controlled porosity and surface chemistry as catalyst supports, as well as a thorough study of interactions at the metal–support interface with the involvement of a set of modern physical methods (e.g., for metal-carbon catalysts, see [115, 116]); (2) creation and study of bi- and polymetallic catalysts with a pronounced synergistic effect, which leads to a multiple increase in activity and/or selectivity in comparison with monometallic analogs under identical reaction conditions [4, 153, 154]; (3) the employment of methods and approaches of nanochemistry for creating a controlled nanoarchitecture of catalysts to achieve high chemo- or stereospecificity in selective hydrogenation reactions [4, 155, 156].

ACKNOWLEDGMENTS

The authors are grateful to librarian E. G. Karnaukhova for her help in searching some hard-to-find sources.

FUNDING

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis (project AAAA-A21-121011490008-3).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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