*Russian Chemical Reviews* **67** (7) 587 – 616 (1998) © 1998 Russian Academy of Sciences and Turpion Ltd

UDC 541.128

# Heterogeneous hydrogenation catalysts

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**Abstract. The main types of heterogeneous catalysts used for hydrogenation, the methods for their preparation, and the structure and chemistry of their surfaces are considered, as well as the catalytic activity and the mechanism of action in the hydro genation of unsaturated and aromatic compounds, of CO, and of carbonyl compounds and in the hydrorefining of fuels. Chief attention is paid to supported Ni catalysts, to the methods for their preparation and physicochemical studies, and to the development of novel catalytic systems through modification. A novel type of catalyst for hydrogenation, *viz*. metal carbides, is described. Some aspects of the mechanochemical treatment of hydrogenation catalysts, including *in situ* methods, are discussed. Sulfide catalysts for hydrotreating are also discussed in detail. The bibliography includes 340 references**.

## I. Introduction

Catalytic hydrogenation includes a large group of addition reactions of hydrogen at unsaturated bonds C=C, C=O, C≡N, C≡C *etc*., as well as hydrogenolysis (cleavage and reduction) of C–C, C–O, C–S, and other bonds.

In addition to heterogeneous catalysts applied in large-scale processes, homogeneous metal-complex and hydride catalysts are also used (mostly, in fine organic synthesis). Enantioselective hydrogenation catalysts, basically metal-complex compounds of Ni, Co and other metals with optically active ligands, are also being increasingly used.

In 1991, of 1040 catalysts for oil processing produced by world industries the number of hydrogenation catalysts was 380.[1] However, modern technologies require more effective and less expensive hydrogenation catalysts. They can be designed only by development of novel scientific approaches to the preparation of supported catalysts and by the use of new physicochemical techniques.

Supported nickel catalysts of hydrogenation are the most widely used ones; they are followed by catalysts based on noble metals. Binary Ni–Mo, Ni–W, Co–Mo and Co–W catalysts are extensively employed in the processes of hydrotreating and hydrodesulfurisation. Metal carbides appear to be new promising catalysts.

This paper reviews certain problems related to the preparation, composition, and mechanism of action of heterogeneous catalysts of hydrogenation of unsaturated compounds (including aromatics), hydrogenation of CO and carbonyl compounds, as well as to the processes of hydrotreating. Primary attention is given to supported Ni catalysts, which have found increasing use in recent years not only in large-scale processes but also in fine organic synthesis. Catalysts based on noble metals (Pt, Pd, Ru, Rh, Ir), supported sulfide catalysts of hydrotreating and some novel hydrogenation catalysts, such as metal carbides, which have been extensively studied in recent years, are also the subjects of discussion. Some examples are given of the use of mechanochemistry techniques for preparing catalysts allowing the synthesis of environmentally safe motor fuels.[2]

At present, the most widespread are the following hydrogenation catalysts:

| Process | Catalyst |
|---|---|
| Hydrogenation of alkenes | supported Ni, Cu, Pt, Pd, Ru, and Rh |
| Hydrogenation of alkynes | supported Ni, Pd, Ni–Pd, Co–Pd, and Cu–Pd |
| Hydrogenation of aromatic hydrocarbons | supported Ni, Pd, Rh, Pt, and Co–Mo, Raney Ni |
| Hydrorefining of motor fuels | Ni, Ni–Mo, and Co–Mo on $Al_2O_3$ and kieselguhr |
| Hydrogenation of carbonyl compounds | skeletal and supported Ni and Co, supported Pd, Rh, and Pt, and Cu–Cr–O, Cu on kieselguhr |
| Hydrotreating (hydrodesulfurisation) | Ni–Mo, Ni–W, Co–Mo, Co–W, and Ru on $Al_2O_3$ and carbon, Mo and W carbides |
| Hydrogenation of niriles | supported Ni, Pd, and Pt |
| Hydrogenation of CO and $CO_2$ (methanation) | supported Ni, Cu, Co, Fe, Pt, and Rh, Pt mesh, Mo and W carbides |

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Received 25 August 1997
*Uspekhi Khimii* **67** (7) 656 – 687 (1998); translated by V D Gorokhov

This review is confined to heterogeneous hydrogenation catalysts and leaves out consideration of numerous homogeneous systems, as well as Raney catalysts (Ni, Co, Cu, and others) and co-precipitated catalysts.

## II. General characterisation of hydrogenation catalysts

### 1. Conventional hydrogenation processes and catalysts

The first industrial hydrogenation process used a nickel catalyst discovered by Sabatier in 1897.[3,4] Other well known hydrogenation catalysts were proposed later: Group VI–VIII metals, including platinum group metals, both on supports and as components of complex oxide systems, as well as Raney metal catalysts.

The results of Ipat'ev's studies of catalytic hydrogenation reactions under pressure dating back to the beginning of this century have served as the basis for the development of processes that are widely used in modern industries. Many specific hydrorefining catalysts have been developed that were obtained by impregnation or co-precipitation (Al–Co–Mo, Ni–Mo, sulfide Ni–W–S catalysts, *etc*.) and proved to be resistant to catalytic poisons present in crude oil (S-, N-, and O-containing compounds).[5]

Production of catalysts for the synthesis of organic compounds is rather limited. Relatively large-scale industrial processes of this type are hydrogenation of fats, 2-ethylhexenal, acetylene (for its removal from ethylene), hydrogenation of benzene to cyclohexane required for the manufacture of caprolactam, and some others. Hydrogenation catalysts are increasingly used for the production of drugs and physiologically active compounds. Important properties of this category of catalysts are high selectivity, extended lifetime, and the fact that they meet environmental requirements. Such characteristics are basically displayed by supported metal (Ni, Pt, Pd, and Ru) catalysts, and co-precipitated Cu–Cr and Ni–Cr catalysts.

Hydrogenation of benzene to cyclohexane may be used as an example illustrating the trends for the use of particular catalysts depending on the strictness of requirements for the final product purity.[4,6] Cyclohexane of high purity (99.88% and above) is used for the manufacture of caprolactam and fibres based on it, and for nylon-6. In the USA alone the cyclohexane output in 1992 was $1.363 \times 10^6$ m$^3$ (Ref. 7).

Since the beginning of this century benzene has been traditionally hydrogenated on nickel (Raney Ni, impregnation catalysts) and on supported platinum group metals. In early industrial processes carried out under high pressure and at high temperature, the main reaction was accompanied by side reactions: cracking with production of n-hexane, isomerisation of cyclohexane to methylcyclopentane, isomerisation and cracking with the formation of lower hydrocarbons.[4]

A two-stage scheme gives the best results in the production of high-purity cyclohexane: in the first stage, a supported Ni catalyst is used (30%–45% Ni/$Al_2O_3$), while in the second stage, a supported Pt catalyst (0.2%–1.0% Pt/$Al_2O_3$) is used. Here, the purity of cyclohexane is 99.57%–99.88%.[8]

An important contribution to the development of hydrogenation catalysts has been made by D V Sokol'skii and his associates.[9,10]

In our country, much attention was given to co-precipitated Ni–Cr catalysts enabling the production of high-purity cyclohexane in a few stages in tubular reactors provided the technological requirements are strictly observed. Such catalysts were prepared by precipitation of Ni and Cr nitrates with a sodium carbonate solution at room temperature. This was followed by filtration, washing of the precipitate to remove nitrate ions, drying, calcination, pelleting, and activation in a flow of hydrogen.[11] The contents of Ni and $Cr_2O_3$ were 48 mass %–63 mass % and 37 mass %–52 mass %, respectively. The disadvantages of this and other techniques for preparing Ni–Cr catalysts are their multistage character, cumbersome filtration equipment, large volumes of waste water from the washing stage, *etc*.

In this connection, a sewage-free method was proposed for producing Ni–Cr catalysts[11] that included the stage of mixing $Ni(NO_3)_2$ and $(NH_4)_2Cr_2O_7$ solutions with subsequent drying and calcination of the resulting mixture by spraying it over a heated inert packing in the fluidised bed reactor system at 310–340 °C, pelleting, and reduction.

A multistage synthesis of Ni–Cr and co-precipitated Al–Co–Mo, Al–Ni–W and Ni–W catalysts used in oil refining[5,12] is complicated, and the technology of catalyst preparation is also complex. Besides, these catalysts are insufficiently active and require large quantities of active additives. Even at a high Ni percentage in Ni–Cr catalysts the active surface does not exceed 25–30 m$^2$ g$^{-1}$, while their thermostability is preserved only up to 250–280 °C,[9,11] which imposes definite restrictions on technological processes.

The method of impregnation of supports possessing specific structures and properties yields more active Al–Ni–Mo and Al–Co–Mo catalysts.

### 2. Modern trends in the development and application of new hydrogenation catalysts

In the 1980s, studies were undertaken aimed at developing supported Ni hydrogenation catalysts the activity of which and other parameters were not inferior to those of skeletal catalysts. Such properties are displayed, for example, by Euro-Ni-1 catalyst (25% Ni/$SiO_2$) developed by a large group of investigators headed by Coenen.[13–15] This catalyst has been prepared by homogeneous precipitation in which part of the nickel forms hydrosilicate on the support. The specific surface of the active metal reaches 113–182 m$^2$ g$^{-1}$ (Ref. 15). Homogeneous precipitation of Ni was carried out in the presence of urea on a water-suspended microspherical silica gel, which was prepared by direct flame pyrolysis of $SiCl_4$.[14] In the presence of $SiO_2$, the pH of an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ does not exceed 5.3–5.5, whereas in its absence the pH reaches 5.8 during precipitation of nickel hydroxide and remains constant.

The existence of a strong interaction between Ni and $SiO_2$ in the preparation of the catalyst is evident from the difficulty of reduction of Ni species, especially in comparison with the non-supported $Ni(OH)_2$. Complete reduction of the Euro-Ni-1 catalyst requires temperatures above 400 °C, up to 600 °C.[14]

In the deposition of Ni on $SiO_2$, the development of the surface may take place due to the formation of intermediate nickel hydrosilicate.[14] However, this depends on the conditions, Ni : $SiO_2$ ratio, and the reactivity of $SiO_2$. Along with Euro-Ni-1, in recent years novel technologies allowed preparation of Ni/$SiO_2$ catalysts with a lower metal content (10 mass %–15 mass %) for the hydrogenation of acetone.[16] In these catalysts, the specific surface of Ni does not exceed 10–30 m$^2$ g$^{-1}$.

Other attempts aimed at increasing the specific surface of Ni on supports with a concomitant decrease in its content down to 4%–10% have also been undertaken.[17,18] To this end, use was made of both the impregnation technique and organometallic complexes, modifying the surface of $SiO_2$ and $Al_2O_3$ supports, in organic solvents. According to the available data,[18–20] the active surface of Ni may reach 124 and 197 m$^2$ g$^{-1}$ at its content of 4.8% and 10%, respectively.

In the 1980s, great interest arose in Russia in the so-called 'sorptional' catalysts.[19–21] The method of their preparation consisting of binding of organometallic complexes to the surface of the support, is rather complex and expensive. Nonetheless, this technique may be successfully used for the preparation of Pd catalysts with a unique mechanical strength, which is achieved by proper selection of supports, while the size and structure of metal particles may be controlled.[21,22]

In recent years, public concern about environmental problems has become especially acute in many countries. For example, the

US 'Clean Air Act', of 1992 rigorously limits the content of carcinogenic aromatic compounds, sulfur and other noxious compounds in motor fuels (both hydrocarbon- and alcohol-based).[23–32] New requirements stimulated the rapid development of refining of various fuels thus making the role of hydrogenation catalysts very important.

To meet all normative requirements under the conditions of a total ban on the use of tetraethyllead in gasoline, it is necessary to restructure the entire oil refinery sector; specifically, to replace reforming by other processes of high-octane gasoline production.[2,24,25,28] The size of the required investment amounts to hundreds of billion dollars.[30] There are doubts whether this task may be coped with at all.[5]

Nowadays, along with studies aimed at replacing reforming by alkylation, skeletal isomerisation, and synthesis of oxygenates allowing an increase in the octane number of gasoline, hydrogenation of aromatic and unsaturated hydrocarbons is extensively studied (to remove their excess from petroleum fractions), and the appropriate catalysts of hydrorefining of motor fuels are being developed and improved.

The content of aromatic hydrocarbons in gasoline and diesel fuel fractions can vary within broad limits. Fractions from direct petroleum refining contain from 20 vol.% to 40 vol.% of aromatic compounds, while diesel fractions after cracking range from 40 vol.% to 70 vol.%.

Hydrotreating of directly distilled gasoline involves mainly co-precipitated Al–Co–Mo catalysts capable of removing sulfur. These catalysts ensure only partial hydrogenation of aromatic compounds[5,12,31] and are insufficiently active in general for the hydrogenation of aromatic and unsaturated compounds. In some cases, Ni–W–Al or Ni–Mo–Al catalysts are more suitable for this purpose.

In major modern catalytic upgrading technologies, the directly distilled gasoline is supplemented with products of secondary processing of heavier fractions, which are even more enriched in aromatic hydrocarbons and alkenes (gasoils of catalytic cracking, hydrocracking, reforming, pyrolytic gasoline). Therefore, catalytic hydrodearomatisation and hydrogenation of unsaturated hydrocarbons, which are also used for alkylation, have become highly important for the production of high-quality and ecologically clean reformulated gasoline, jet and diesel fuels. In the preparation of jet fuels by hydrodearomatisation of kerosene, the co-precipitated Ni–W sulfidised catalysts proved to be the best of the known Co–Mo, Ni–Mo, and Ni–W systems.[5,12] In such catalysts, the content of tungsten reaches 20 mass % – 30 mass %; hence, they are rather expensive and their practical application is limited.

In recent time, much attention has been given to new types of supported Co–Mo, Ni–Mo, and Ni–W catalysts, as well as to the catalysts based on noble metals.[5,12,31–40]

Sulfur-resistant catalysts are widely used in both single- and two-stage processes for hydrogenation of aromatics.[31,38–40] It was found[31] that the Ni–W/$Al_2O_3$ catalyst is poisoned by sulfur more intensely than Ni–Mo/$Al_2O_3$. Therefore, two-stage hydrorefining involves the Ni–Mo catalyst in the first stage (mainly, hydrogenation of sulfur compounds), whereas in the second ('final' hydrogenation) stage low-percentage Ni–W catalyst *e.g.*, (6%Ni + 20%$WO_3$)/$Al_2O_3$ is used.[39]

Since the late 1980s a number of companies dealing with hydroprocessing of motor fuels have been developing new Ni–W catalysts on supports.[31–35,39] A common shortcoming of all proposed catalysts is the rather high content of $WO_3$; furthermore, effective hydrotreating on these catalysts requires high pressures (up to 10 MPa) and temperatures (up to 360 °C).[35,39]

Thus, at present the most attractive and inexpensive catalysts for the hydrogenation of unsaturated compounds (including aromatics) are supported Ni-containing catalysts modified with W or Mo oxides.

The nickel-based catalysts are also successfully used in other processes, *e.g.*, for the hydrogenation of CO into methane and other hydrocarbons.[41–43] Most catalysts of CO methanation are also prepared on supports ($Al_2O_3$, $Cr_2O_3$, kieselguhr, Mg-containing spinels). In addition to nickel, the role of active component may be played by Co, Pt, and Pd; however, the resulting systems are less active than the modified Ni-containing catalysts. Investigation of CO methanation has become topical due to attempts to adapt this process for the large-scale production of clean gaseous fuels through gasification of low-grade coals,[44] as well as for the realisation of chemical-energetic transfer and the use of heat from nuclear power stations and other industrial fields.[45] Effective methanation of CO has been found to require[46] thermally and mechanically stable Ni catalysts possessing the largest possible specific surface. These requirements can be met using appropriate supports supplemented with structure modifiers and promoters.

Until the 1980s, the long-term operation of a catalyst was believed to be associated with a sufficiently high content of an active metal (up to 35 mass %). For this reason, preference was given to co-precipitated rather than to impregnated catalysts.[46] However, the results of recent studies disprove this belief. At present, there is a trend for the use of modified low-percentage Ni catalysts (0.8 mass % – 8.0 mass % Ni) on supports both for the hydrogenation of unsaturated and aromatic compounds[34,39] and for the methanation of CO.[47–49]

## 3. Catalysts for the hydrotreating of motor fuels

According to the estimates of experts,[50] the oil reserves will substantially decrease and their quality will worsen by the year 2000. As pointed out above, further use for motor transport of fuels with excess levels of aromatic compounds and alkenes may result in air pollution hazardous to humans.[23,25]

Upgrading technologies for motor fuels (gasoline, diesel, and kerosene distillates) involve a number of catalytic processes that ensure the transformation of directly distilled crude oil or products of petroleum processing into high-quality fuels meeting rigorous norms for the levels of toxic admixtures, primarily reactive aromatics and alkenes. The actual content of aromatic hydrocarbons in the diesel fractions of petroleum is considerably higher than the mentioned norms and reaches 80% – 95%. In the 1980s, they were mostly removed by extraction, while nowadays preference is given to catalytic methods of dearomatisation.[5,12,31,32,35–37] This improves both the environmental and operational parameters of diesel fuels. Thus, the decrease in the content of aromatic compounds from 46.5% to 30% increases the cetane index of diesel fuel to the allowed level (from 31 – 34 to 40 – 46).[51]

Many reports[31,37,40,50] describe new catalytic processes for dearomatisation of different types of diesel fuel. The Arosat and Synsat processes developed by the Lummus Co. make it possible to reduce more than 50% of aromatic components of raw materials by the combined application of two catalysts designed by the Criterion Co. in a stationary layer under a relatively low pressure.[32] The resulting diesel fuel meets the European standards (content of aromatics, 20% – 25%; cetane index, 40 – 45).

The catalysts of the Criterion Co. offer four ways for the decrease in the content of aromatic compounds in diesel fuel.[32]

1. Single-stage hydrogenation under high pressure (103 atm) and a moderate flow rate (1.0 $h^{-1}$). When supported catalysts (Ni, Ni–W, or Ni–Mo on $Al_2O_3$) are used, the level of aromatic compounds in raw materials can be > 50%.

2. Hydrocracking under high pressure (100 – 140 atm) at a moderate flow rate with the use of Ni-containing catalysts on different supports ($Al_2O_3$, aluminosilicates, zeolites). This one- or two-stage process is most popular.

3. Two-stage hydrogenation under pressure ranging from medium to high (83 – 105 atm.) with the use of supported noble metal catalysts in the second stage. The pressure is determined by the conditions of the first stage aimed at maximum removal of heteroatom-containing components by drastic hydrotreating on $Al_2O_3$-supported catalysts (Co–Mo, Ni–W, and other).

4. Single-stage hydrogenation under low pressure and small flow rate (the Synsat process). In this process, the above-mentioned combination of Ni-containing catalysts on supports is used. The catalysts are placed in the reactor in such a way that the products obtained in the first catalytic layer improve their characteristics upon passage through the second layer. Under a pressure of 43 atm and a flow rate of 0.5 $h^{-1}$ the degree of saturation of aromatic hydrocarbons present in the diesel fraction reaches 40% – 50%. When it is necessary to reduce the level of aromatics below 10% (for preparing a high-quality jet fuel), it is sufficient merely to increase the pressure. Realisation of the Synsat process requires relatively modest expense.

Modern catalytic processes for hydrorefining diesel fuels are more efficient, flexible and economical than the extraction used earlier for the increase in cetane index. The efficiency and simplicity of hydrodearomatisation are provided by the use of catalysts that in most cases refer to supported nickel contacts.

Nishijima *et al.*[52] reported a two-stage process of hydrorefining of middle and heavy distillates with using new catalysts. Heteroatom-containing compounds are removed in both stages. In the first stage, hydrogenation takes place, whereas in the second stage the remaining aromatic component undergoes hydrocracking.

Fundamental physicochemical studies allowed the development of two types of industrial catalysts on supports for single- and two-stage hydrorefining. The composition of the catalysts obtained, predominantly Ni-containing ones, is presented in Table 1. Catalysts were modified in order to make them suitable for hydrogenation or hydrocracking. Changes in the character of hydrogenation were brought about by the use of specific supports. As regards their hydrogenation activity in the presence of sulfur-containing compounds, the $Al_2O_3$-supported catalysts form the following series: Ni – W > Ni – Mo > Co – Mo.

**Table 1**. Catalysts for the two-stage hydrotreating of diesel fuels.[52]

| Active component | Support | Content of active components (mass %) | | | | Process |
|---|---|---|---|---|---|---|
| | | CoO | NiO | $MoO_3$ | $WO_3$ | |
| Co – Mo | γ-$Al_2O_3$ | 0 – 6 | – | 10 – 30 | – | hydrogenation |
| | USY [a] – $Al_2O_3$ | 0 – 5 | – | 10 – 25 | – | hydrocracking |
| Ni – Mo | γ-$Al_2O_3$ | – | 0 – 6 | 10 – 30 | – | hydrogenation |
| | $SiO_2$ – $Al_2O_3$ | – | 0 – 3 | 0 – 15 | – | hydrocracking |
| | $TiO_2$ – $Al_2O_3$ | – | 0 – 3 | 0 – 15 | – | " |
| | USY [a] – $Al_2O_3$ | – | 0 – 5 | 10 – 25 | – | " |
| | ZSM-5 – $Al_2O_3$ | – | 0 – 3 | 0 – 15 | – | " |
| | Mordenite – $Al_2O_3$ | – | 0 – 3 | 0 – 15 | – | " |
| Ni – W | γ-$Al_2O_3$ | – | 0 – 6 | – | 16 – 48 | hydrogenation |
| | USY [a] – $Al_2O_3$ | – | 0 – 5 | – | 16 – 40 | hydrocracking |

[a] USY is an ultrastable zeolite of Y type.

Physicochemical studies pointed to a different behaviour of Ni – W and Ni – Mo catalysts on $Al_2O_3$. They possess higher hydrogenation activity at a smaller and larger degree of sulfidation of tungsten and molybdenum, respectively. Consequently, the choice of a Ni-containing catalyst for a single-stage hydrotreating depends on the content of sulfur in the raw material.

Similar results were obtained earlier [31] in the studies of Ni – W and Ni – Mo catalysts for hydrodearomatisation of diesel fuel fractions containing up to 70% of aromatic compounds. The ratios of the rate constants for hydrogenation on Ni – Mo and Ni – W catalysts were 100 : 90 (1.7% sulfur) and 100 : 225 (0.14% sulfur).

The trend for maximum decrease in the content of sulfur in motor fuels of all types (down to 0.01% – 0.05%) will favour wider use in the near future of two-stage hydrotreating in which the first stage provides for profound hydropurification of fuel from sulfur, while in the second stage aromatic compounds undergo hydrogenation on efficient Ni – W catalysts. At present, platinum catalysts (0.6%$Pt/Al_2O_3$) are used in such processes at a residual sulfur concentration of 1.5 ppm.[31,40] In the pressure range of 4.5 – 6.0 MPa, at temperatures 320 – 400 °C, and at flow rates of 0.75 – 1.0 $h^{-1}$, the degree of hydrogenation of the aromatic component is 60% – 70%.

The Haldor Topsøe Co. has also developed single- and two-stage hydrotreating refinement processes [40] for producing high-quality diesel fuels (the so-called City Diesel) with the levels of aromatic compounds below 10 mass % and sulfur below 5 ppm. In the two-stage process, the first stage is based on the use of common sulfidised Co – Mo, Ni – Mo, and Ni – W catalysts, while the second stage relies on the Pt- and Pd-zeolite catalysts. The latter are more resistant to sulfur than the bimetallic catalysts Pt – $Re/Al_2O_3$, Pt – $Sn/Al_2O_3$, Pd/LaY, and others. The catalyst designed for the final hydrogenation preserves its activity at levels of sulfur up to 1000 ppm and nitrogen up to 50 ppm. After the first stage, the diesel oil contains 10 ppm of sulfur, less than 1 ppm of nitrogen and 18 vol.% of aromatic compounds, and the cetane index is 52. After the second stage, the nitrogen content remains at the same level, the sulfur content drops below 1 ppm, the level of aromatics decreases down to 4 vol.%, and the cetane index is 55.5. It is seen that the most significant removal of aromatic compounds is achieved in the second stage.

According to earlier estimates,[36,50] by the year 2000 the predominant type of fuel produced will be low-sulfur fuel (sulfur content 0.05 mass % instead of 0.1 mass % – 0.3 mass %) with a reduced content of aromatics. To achieve this, it was recommended:

(1) to restrict the content of high-boiling components in the diesel fuel since sulfur is most difficult to remove from fractions with b.p. > 315 °C;

(2) to conduct hydrotreating refinement at relatively low temperature, reduced flow rate, and high hydrogen pressure;

(3) to remove aromatic compounds on supported Ni – Mo or Ni – W catalysts.

These predictions are somewhat at variance with the critical need for additional resources of diesel and jet fuels.[53]

The proportion of the diesel fuel and gasoline consumed is known to shift in favour of the former.[54] The need for the jet fuel also increases, while its production by direct distillation and hydrotreating refinement of crude oil fractions cannot meet the demand.[55,56] For this reason, in some countries specialists propose to raise the limiting boiling point of diesel fuels to 360 – 370 °C [55] and to include in the diesel fuel some gasoline fractions, as well as secondary products of petroleum refining (gas oils from hydrocracking, fracturing, coking, *etc.*) that will unavoidably lead to a poorer quality of the final products. In gasoils from the secondary oil refining, the content of aromatic compounds reaches 46% – 87%, while the cetane index does not exceed 25 – 39. Hydrogenation of such feed stocks improves their quality but makes them as expensive as synthetic liquid fuels. Hydrogenation of coal is equally expensive, while the products of its liquefaction contain up to 54% of aromatics.[54]

The ways of expanding the production of high-quality diesel and jet fuels have been discussed.[53] It was pointed out that, in addition to the above methods, the processes of motor fuel production from alkenes (the MOGD † process of Mobil Co.) and from synthesis gas formed upon coal gasification (the Sasol process), are promising as well as the processes based on natural gas conversion (SMDS ‡ of Shell Co. and the Mossgas process) and gasification of any hydrocarbon raw material.[57 – 66]

Selective oligomerisation of light alkenes to heavy isoalkenes over zeolite-based catalysts (ZSM-5, ZSM-12, H-offretites and

† Mobil Olefins to Gasoline and Distillates.
‡ Shell middle distillate synthesis.

other) (the MOGD process) allows preparation of gasoline or middle distillates with upgraded characteristics after the hydrogenation stage in which noble metals on supports are commonly used as catalysts.[57,58] After hydrogenation, the cetane index increases from 33 to 52, while the levels of aromatic compounds and sulfur become 2%–4% and 0.002%, respectively. These parameters are much better than those of diesel fuel from petroleum or coal (hydrogenation), while they remain inferior to the parameters of fuels from the synthesis-gas produced by the Fischer–Tropsch synthesis. For instance, low-temperature hydrogenation of CO on a Ru catalyst can yield diesel fuel that is predominantly composed of n-paraffins (72.4%) and is free of aromatics and sulfur. After the hydrostabilisation stage (removal of alkenes), the cetane index of the product is 90 and it may be used as a high-cetane component of the diesel fuel.[66]

As regards its characteristics, the jet fuel produced by the MOGD process differs favourably from the existing commercial fuels of petroleum origin. It contains as little as 4% of aromatic compounds (instead of 25%), 1% of alkenes (instead of 5%), and less than 0.002% of sulfur (instead of 0.3%–0.4%), while the proportion of paraffins and isoparaffins is 96%. However, the aircraft engines are continuously upgraded with more and more rigorous requirements for the fuel.

Catalytic hydroprocessing of raw oil is a method widely used for producing high-quality aircraft fuels with low sulfur content, increased thermal and oxidation stabilities, and upgraded environmental characteristics.[67,68] Earlier, hydrotreating of directly distilled fractions was mostly carried out[12] on Co–Mo–Al catalysts at 350–400 °C, 30–50 atm, and a raw material flow rate of 2–5 $h^{-1}$. The process of single-stage hydrorefinement of kerosene fractions reduced the level of sulfur, while the decrease in the level of aromatic compounds and alkenes was insignificant. The need for the hydrotreating of gasoils of secondary origin with a high content of aromatic compounds and alkenes, using the technology based on Co–Mo–Al catalysts that is popularly used in Russia, has necessitated an increase in the pressure in the system to 140 atm. To reduce the pressure down to 35–80 atm, the products of secondary refining were mixed with directly distilled fractions so that the percentage of aromatic compounds was 34%–36%.[56] However, even under a pressure of 83–85 atm, hydrotreating on the Co–Mo–Al catalyst was not sufficiently effective. The resulting product contained 18%–19% of aromatic compounds, which is considerably higher than the level admissible for jet fuels.

Two-stage processes in which hydrodesulfurisation (*e.g.*, on a Co–Mo–Al catalyst) and hydrodearomatisation (*e.g.*, on supported Ni–Mo or Ni–W catalysts) are conducted separately (see above) are efficient. In Western technologies, in the second stage the sulfur-free raw materials are hydropurified from aromatic hydrocarbons and alkenes on Pt- or Pd-containing catalysts since the exhaustive hydrogenation on Ni catalysts with oxide additives of the $MoO_3$ or $WO_3$ type requires elevated pressures.[40]

Studies of benzene hydrogenation and thiophene hydrogenolysis on Ni–W–Al catalysts have shown [69] that both processes take place in the same active centres that are poisoned with hydrogen sulfide. The rate of benzene hydrogenation may be increased 30–70-fold under non-steady-state conditions and after pretreatment of the catalyst with hydrogen. The results obtained made it possible to develop a process of dearomatisation of petroleum fractions in a non-steady-state regime.

The production of environmentally clean gasoline is much more problematic. The products of catalytic reforming yielding a high-octane gasoline contain large quantities of aromatic hydrocarbons and alkenes. For this reason, reforming should be replaced by other processes. Even under the conditions of catalytic cracking, current technologies yield on average 29.7% of aromatic compounds (which is 20%–25% higher than the required level) and more than 5 mass % of alkenes (up to 30%).

In order to produce high-octane gasoline, attempts are made to use processes of skeletal isomerisation, alkylation, synthesis and addition of oxygenates. Hydrodearomatisation and hydrogenation of alkenes as gasoline components attracted less attention, though these processes will in the near future be among the leading methods in the technologies of oil refining targeted at the production of environmentally clean motor fuels.[23,24,29,70] In these processes a special role is played by supported Ni-containing catalysts. The possibility of their upgrading and the relatively low production cost (by an order of magnitude lower than that of Pt- or Pd-containing hydrogenation catalysts) make them rather attractive subjects for further studies.

## 4. CO Hydrogenation catalysts

Like hydrorefining, catalytic hydrogenation of CO and $CO_2$ is highly interesting from the environmental viewpoint and may be used for large-scale production. Carbon mono- and di-oxides are contained in the exhaust gases from power stations and different chemical industries. The simplest reaction of CO hydrogenation (methanation)

$$CO + 3H_2 \longrightarrow CH_4 + H_2O,\ \Delta H_{298} = -206.4\ \text{kJ mol}^{-1} \quad (1)$$

allows an energetically advantageous production of a valuable fuel, *viz.* methane, that is used further in gas turbines. In connection with the depletion of natural gas resources studies are being undertaken as to the possibility of the environmentally clean coal gasification with subsequent CO methanation.[44,71–73] In the first decade of the 21st century, important facilities for coal gasification and methanation are expected to be put into operation.[72–74] This requires the development of new technologies and active catalysts.

This review leaves out other reactions of CO hydrogenation that yield various products (paraffins, alkenes, alcohols,[75] aldehydes, *etc.*) depending on the catalysts applied and the conditions of the process.

Catalytic methanation finds applications in chemo-energetic cycles where atomic (nuclear reactors) or solar energy is used.§[74,76] The thermochemical cycle includes the exothermic reaction of methanation (1) and endothermic reactions of conversion of the methane produced

$$CH_4 + H_2O \longrightarrow CO + 3H_2, \quad (2)$$

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2, \quad (3)$$

which are conducted in reactors with heat withdrawal or supply, respectively. These reactions require active and highly selective catalysts. Specifically, only the catalysts inhibiting side reactions in which CO can be consumed are suitable for methanation:

$$CO + H_2O \rightleftharpoons CO_2 + H_2,\ \Delta H_{298} = -41.5\ \text{kJ mol}^{-1}, \quad (4)$$

$$2CO \rightleftharpoons CO_2 + C,\ \Delta H_{298} = -171.7\ \text{kJ mol}^{-1}. \quad (5)$$

Common and widespread Ni catalysts for reactions (1)–(3) are rapidly deactivated, and it was proposed to replace them by noble metals on supports.[74] The major difficulties are associated with carbonisation in reactions (1)–(3), particularly, in the methanation at low $H_2$:CO ratios. On noble metals, the carbonisation is considerably less pronounced, especially in an excess of water vapour due to the reaction

$$C + H_2O \longrightarrow CO + H_2. \quad (6)$$

Reaction (6) is best accelerated by Ru catalysts, while Rh is more suitable for methanation.[74]

Thermodynamic calculations show that it is advantageous to obtain methane in reaction (1) at temperatures not exceeding 550–600 °C. The yield of $CH_4$ is increased at higher pressure and $H_2$:CO ratio. At low $H_2$:CO ratios and temperatures up to 600 °C, the common Ni and Ru catalysts may be replaced by an expensive rhodium catalyst (0.5%$Rh/Al_2O_3$).[74]

The activity of metals on supports in the methanation reaction strongly depends on the mode of the catalyst preparation and

§ See also V N Parmon *Catal. Today* **35** 153 (1997).

conditions of its pretreatment and reduction. In this respect, Ni and Co catalysts have been studied in most detail. In the methanation reactions, supported catalysts containing Ni on metal oxides (MgO, $Cr_2O_3$, $ThO_2$, $ZrO_2$, $MoO_3$, $SiO_2$, $Al_2O_3$), promoted by Cu (0.1% – 0.3%), promoted by alkali metals, and Ni sulfide on $Al_2O_3$ are the most efficient.[75]

The specific activity of Group VIII metals on $Al_2O_3$ supports decreases in the following series: Ru > Ni > Co > Rh > Pd > Ir. It is noteworthy that the Ni catalyst with a well developed surface is highly active and rather selective in the methanation reaction. In some cases, depending on the mode of preparation, the nature of the support, and other factors, the Ru catalyst proves to be more efficient.[75]

A Ni catalyst with a highly developed surface is applied for the selective CO methanation in the presence of $CO_2$.[77] On a number of catalysts, *viz*., 0.5%Ru/α-$Al_2O_3$, Raney nickel of ICI (30%Ni – 18%Al – 52%$Al_2O_3$), 58%Ni/kieselguhr (Harshaw), 47%Ni/$Al_2O_3$ (CCI), and 32%Ni/$Al_2O_3$ (Girdeer, G-65), selective hydrogenation of CO in a mixture 0.3%CO + 80%$H_2$ + 19.7%$CO_2$ can be carried out at atmospheric pressure and at 125 – 300 °C.[77] In all cases, the maximum conversion occurs in the temperature range 200 – 250 °C.

Some catalytic systems including Ni, Fe, Rh and Ru are more active and selective in the reaction of $CO_2$ methanation than in reaction (1).[78, 79] For example, the rate of $CO_2$ methanation on a Ni/MgO catalyst is higher than that of CO methanation, especially after the catalyst has been reduced at 600 °C.[77] Examples of higher activity and selectivity of different metal catalysts in the hydrogenation of $CO_2$ are reviewed.[80]

Inui and Takeguchi[81] described a Ru-containing supported Ni catalyst of methanation with a low content of components (3%Ni, 2.5% $La_2O$, and 0.7%Ru). The catalyst has a meso-macro-bimodal porous structure with finely dispersed components and displays a very high activity in the reaction of $CO_2$ methanation. The role of Ru in this catalyst is explained by its involvement in the hydrogen spillover to the active Ni centres.

Numerous studies and reviews are devoted to the problems of the catalyst formation and the mechanism of CO hydrogenation.[75, 82–86] Krylov *et al*.[85] consider in detail the results of studies into the formation mechanism of the active centres of Fe catalysts for the Fischer – Tropsch synthesis and of Ni catalysts of methanation and their effect on the catalytic activity and selectivity.

Much attention is given to the investigation of the formation of active centres in finely dispersed metal particles obtained by decomposition of carbonyl clusters on oxide supports. The carbonyl clusters interact with the hydroxyl groups of the support forming bridging bonds with the metal (M) atoms in a lower oxidation state:

$$\geq Al-OH + M^{2+}(CO)_n \longrightarrow \geq Al-OM(CO)_{n-1}\rceil^{+} + CO + H^{+}. \quad (7)$$

Active and selective contacts can be obtained by deposition of carbonyl complexes [*e.g*., $Co_2(CO)_8$] and a number of complexes with organic ligands on γ-$Al_2O_3$. In this case, the hydroxyl cover of the support is of critical importance.[85] Some complexes are oxidised to form $Co^{2+}$ particles which aggregate into clusters on the surface. Heating under an inert gas atmosphere favours formation of a cluster containing 3 or 4 Co atoms. Further heating to 220 °C leads to dimerisation of the complex with subsequent formation of metal particles. To increase the activity of a catalyst in the CO hydrogenation, it is necessary to have large $Co^0$ clusters. As to selectivity, it is increased when oxidised Co species that are produced on the hydroxylated $Al_2O_3$ surface upon deposition of low-nuclear complexes are present on the surface. Carbonaceous ligands present in the cluster inhibit the process of hydrogen spillover and impede the complete hydrogenation of CO to $CH_4$. The use of carbonyl clusters containing two different metals allows the preparation of catalysts with new properties. For example, hydrogenation catalysts prepared from Co – Fe carbonyl clusters manifest the activity of cobalt and the selectivity of iron.

High-resolution electron microscopy and X-ray phase analysis *in situ* were used to study the mechanism underlying the formation of Ni catalysts of methanation.[85, 87] In contrast to hydrogenation on Fe or Co, the hydrogenation of CO on Ni yields only methane. After the dissociation of CO on the Ni surface, the consecutive transformations $C \rightarrow CH \rightarrow CH_2 \rightarrow CH_3$ take place. Active carbon exists on the surface in a rather narrow temperature range: it is not formed below 200 °C since there is no CO dissociation, while above 450 °C it is rapidly transformed into inactive graphite. The methanation rate at the Ni (100) face is higher the larger the carbon concentration on the surface, and the yield of higher hydrocarbons is larger the higher the CO concentration.[84]

Two nickel specimens were shown to behave differently[85, 87] under the conditions of CO methanation. Nickel oxide obtained by a plasmochemical technique forms cubic crystals with the most developed face (100). Under the reaction conditions this face is the site of epitaxial growth of cubic Ni crystals, while the polycrystalline carbide $Ni_3C$ is formed only in later stages. NiO prepared by decomposition of $NiCO_3$ is composed of lamellar crystals with the developed face (111) on which nickel carbide builds up epitaxially, whereas the phase of metallic nickel appears only after heating to 283 °C and decomposition of carbide. No direct correlation between the methanation rate and the carbide content was established. The reaction occurs most likely at the Ni/NiO interface (possibly, on NiO defects).

The nature of the support influences the catalytic properties of Co and Ni in hydrogenation of CO to methane and its homologues.[86] Thus, the activity and selectivity of supported metal catalysts depend on the nature and acid-base properties of the support. The specific catalytic activity of supported Co catalysts decreases in the following series of supports: $SiO_2$ > $TiO_2$ > $ZrO_2$ > BeO > $Cr_2O_3$ > $Al_2O_3$ > MgO > $WO_3$, while that of supported Ni catalysts decreases in the order: $ZrO_2$ > $TiO_2$ > BeO > MgO > $Al_2O_3$ > $SiO_2$ > $Cr_2O_3$ > $WO_3$.

The heat of adsorption of carbon monoxide ($q_{CO}$) and, consequently, catalytic activity and selectivity strongly depend on the mean size of metal particles. According to quantum-chemical calculations,[88] the M – CO bond is weakened on transition from small clusters to large crystallites. Co/$SiO_2$ (mean particle size $d$ = 32 nm) and Ni/$WO_3$ catalysts ($d$ = 97 nm) are the most active in the reaction of CO hydrogenation. Co/$WO_3$ and Ni/$WO_3$ catalysts ($d$ = 60 and 120 nm, respectively) manifest noticeable activities only at $T$ > 300 °C.[89] The only reaction product is methane. These data indicate that the optimum sizes of Co and Ni particles are different. Prokhorenko *et al*.[86] explain this by the difference in their $q_{CO}$ values. The heat of CO adsorption on Co must be lower than that on Ni, and this was confirmed experimentally. In order to have similar $q_{CO}$ values for both metals, the nickel particles should be larger than those of cobalt. At small $q_{CO}$ values, the filling of the Co and Ni surfaces is insignificant and the selectivity is low. With the increase in $q_{CO}$, the extent of filling increases as well as the probability of non-linear stages of reactions of CO leading to the formation of higher hydrocarbons.

However, the heat of CO adsorption is not the only factor affecting the selecitivy.[86] For example, Co/$ZrO_2$ and Co/$SiO_2$ have virtually the same degree of dispersion ($d$ = 97 and 103 nm, respectively), though their selectivities differ by 34%. Transformations of an intermediate compound are supposed to involve the support and to occur at the metal/support interface. The increase in the acidic character of the support on transition from $ZrO_2$ to $WO_3$ results in an increase in the selectivity of methane formation to 100%.

## 5. Catalysts for hydrogenation of carbonyl compounds

Catalysts for the hydrogenation of carbonyl compounds (aldehydes, ketones, and carboxylic acids) present in alcohols as admixtures are of commercial interest. In particular, this reaction is used for hydrorefining of alcohol-based motor fuels. Hydro-

genation of aldehydes and ketones is also of an independent significance since it allows the preparation of alcohols free of by-products. For example, 2-ethylhexanol is produced from 2-ethylhexanal on an industrial scale.[90,91]

The first industrial hydrogenation of aldehydes on copper catalysts dates back to the 1920s. However, after the appearance of Raney nickel (1925) most processes of hydrogenation of aldehydes were modified to use catalysts of this type. The industrial importance of techniques for the alcohol production from aldehydes increased after the discovery of oxosynthesis in 1938.[90]

In parallel, a strong impetus was given by the production of plastics [specifically, poly(vinyl chloride)], where respective alcohols are used as plasticisers. Lower alcohols are used as solvents, while higher alcohols are used in the production of detergents. In 1992, the world production of alcohols was (millions of tons): n-butanol, 1.7; isobutanol, 0.4; 2-ethylhexanol, 2.4; higher alcohols, 0.2.[90]

Despite the very high activity of Ni-containing catalysts, they prove sometimes to be unsuitable for the hydrogenation of aldehydes, especially when high selectivity of the process is required. Thus, the preparation of n-butanol from crotonaldehyde proceeds more selectively on copper catalysts. In addition, Ni unlike Cu, often catalyses splitting of CO from saturated aldehydes:

$$R^1R^2CHCHR^3CHO \xrightarrow{H_2} R^1R^2C\,CHR^3 + CO + H_2. \qquad (8)$$

When a Ni catalyst is sufficiently active, subsequent hydrogenation of alkenes occurs with the predominant formation of alkanes.

Modified Ni catalysts on supports are free of these shortcomings. Their activity may be reduced using such supports as $SiO_2$ subjected to high-temperature treatment, or employing a special impregnation technique of $Na^+$-containing $SiO_2$, and calcinating the specimens additionally at 600–700 °C.[16] To this end, $TiO_2$ may also be used as a support.[90] The high activity of Ni and Ni–Cu catalysts allows their use in liquid-phase reactions, which facilitates the removal of heat released during the reaction.

In addition to Cu and Ni, supported Co and noble metals (Pt, Pd, Ru, and Rh) are also applied for the hydrogenation of carbonyl compounds. Of all noble metals only palladium is a component of catalysts for the selective hydrogenation of α,β-unsaturated aldehydes to saturated ones. Furthermore, along with nickel, palladium ensures complete hydrogenation of unsaturated aldehydes, *e.g.*, 2-ethylhexenal.[91]

## III. Nickel hydrogenation catalysts

### 1. Methods for preparation

Industrial production of nickel catalysts relies basically on precipitation of components from aqueous solutions and suspensions and on impregnation of specially prepared supports with aqueous solutions of active metal compounds. The activity of hydrogenation catalysts prepared by the impregnation of supports is usually higher than that of catalysts produced by co-precipitation.[9,12,22]

In the late 1980s, the relevant literature (especially the Russian) opposed the impregnation and 'sorptional' catalysts.[17–20] In our opinion, the technology for the preparation of the latter does not differ substantially from impregnation. It consists of the deposition of an active component on a support from different solutions (including non-aqueous ones) using organometallic compounds. In this case, optimally distributed active centres are formed on the support surface, and their characteristics are best suited for hydrogenation.

Generally, the procedure for the preparation of Ni catalysts includes the stages of impregnation, drying, dehydration, activation (calcination), reduction, and passivation.

The preparation of precipitated and impregnated Ni catalysts involves the following processes.[92]

1. Impregnation of supports ($Al_2O_3$, $SiO_2$, carbon, zeolite) with a salt solution, *e.g.*, nickel nitrate. Then the catalyst is dried and calcined at high temperature (400–500 °C) in air.

2. Mixing of precipitated active hydroxide $Ni(OH)_2$ with a hydrogel of the support. The mixing lasts for 20–30 h, followed by extrusion, drying, and calcination.

3. Deposition of one precipitate onto another. For instance, nickel hydroxide is precipitated with ammonia from a nickel nitrate solution in the presence of a suspension of hydrated alumina. The precipitate is filtered off, thoroughly washed, dried, and calcined at 500 °C for 2 h in air.

4. Co-precipitation. For example, a boiling solution of sodium silicate is slowly added to a nickel nitrate solution. The precipitate is filtered and washed. Also, ammonia may be added to a mixed solution of nickel and aluminium nitrates at 70 °C. Then the precipitate is filtered off, washed, dried, and calcined.

5. Hydrothermal treatment of mixed precipitates. A mixed paste of $Ni(OH)_2$ and $SiO_2$ is heated with water vapour in an autoclave for 25 h at 250 °C and 50 atm; the precipitate is filtered off, dried, and calcined.

6. Superhomogeneous co-precipitation. Three salt solutions, *e.g.*, $Ni(NO_3)_2$, $NaNO_3$, and $Na_2Si_2O_5$, are mixed to form a supersaturated solution. Under intense stirring, a homogeneous precipitate is formed which is separated, washed, dried, and calcined.

Prior to their use in reactions, the catalysts are reduced with hydrogen (sometimes with the reaction mixture) at 400–500 °C. The catalysts prepared by impregnation are the easiest to reduce, while those obtained by co-precipitation and hydrothermal treatment undergo reduction with more difficulty. In the supported catalysts the specific surface of the active nickel is usually 100–120 $m^2\ g^{-1}$, whereas in the precipitated catalysts it varies from 20 to 70 $m^2\ g^{-1}$ (*cf.* Ref. 93). Depending on the treatment and reaction conditions, the metal particles on supports have sizes from 2 to 10 nm.[94,95]

In recent years, efficient catalysts on supports have been prepared using the so-called CVD (chemical vapour deposition) technique. This consists of fixation of a metal in a layer of finely dispersed particles with the aid of vapour-phase adsorption of intermediate compounds, *e.g.*, metal acetylacetonates, which are subject to subsequent decomposition on the supports.[96] In this case, the surface is the first formation site for catalytic precursors, ensuring high metal dispersion upon their subsequent decomposition. The Amoco Co. proposed the use of CVD method for binding the silanol groups in zeolite matrices to prepare metal oxide catalysts of the Fe/Mo/support type. German scientists prepared catalysts for hydrogenation and a number of other processes in which Pt, $Cr_2O_3$, and $V_2O_5$ are fixed on $SiO_2$ or $Al_2O_3$.[96]

Active film structures of the metal–oxide type on supports, the analogues of metal-ceramic films, in which metal particles are regularly distributed over the surface, were also designed.[97,98] Fixation of metal on supports is ensured by co-precipitation of salts of an active metal (Pd, Pt, *etc.*) and salts of higher carboxylic acids (resinates, stearates, abietates, and others) from organic solvents. Similar structures can also be prepared using aqueous solutions of inorganic salts and compounds of noble metals in the presence of water-soluble polymers, colloidal oxide solutions, *etc.* The common feature of all these techniques is the formation of a film on the surface of a support.

The preparation by this method of highly selective catalysts for the hydrogenation of acetylene that are suitable for large-scale hydropurification of ethane–ethylene fractions from acetylene admixtures has been patented,[99] as well as of catalysts of oxidation, isomerisation, and dehydrogenation.[100–104] The preparation of film catalysts is based on a specific combination of several conventional techniques.[97–100] This leads not only to regular distribution of active components in the surface layer of the support and high dispersity of metal particles, but also to the thermal stability of the catalysts.

Nonetheless, impregnation from aqueous solutions still remains an industrially preferable way of preparing the hydrogenation catalysts on supports. This takes advantage of the recent developments in the field of formation of the catalyst active phase. For example, it was established that if conditions favouring retention of a metal in the ionic form in supports ($Ni/Al_2O_3$, $Ni/SiO_2$) are met, this favours the preparation of active and stable Ni hydrogenation catalysts.[15, 104] In particular, two-stage deposition of nickel should be applied: the first stage consists of the incorporation of difficultly reducible $Ni^{2+}$ ions into the support as a result of ion exchange, and the second stage includes physical sorption of a readily reducible salt. The $Ni^{2+}$ ion appears to be the centre of crystallisation and stabilisation of Ni crystallites. Heating of a $Ni/TiO_2$ system often leads to a decrease in the active surface of nickel due to coating of the crystallites with metal oxide.[101, 102] This may be regarded as a manifestation of a strong metal–support interaction (SMSI) effect. The SMSI effect is enhanced in the presence of hydrogen which affects the activity and selectivity of catalysts.

## 2. Influence of the preparation procedure on the structure, physicochemical properties, and activity of catalysts

Principal factors that affect the catalytic and physicochemical properties of impregnated low-percentage $Ni/Al_2O_3$ catalysts have been studied systematically.[47, 49, 103–111] The conditions for the realisation of major stages in the preparation of these catalysts were shown to be related to their structure, activity, selectivity, and the degree of nickel reduction and dispersion. For example, the active surface of nickel and the proportion of the reduced metal are increased by the increase in the $H_2$ flow rate during reduction. Passivation of the reduced $Ni/Al_2O_3$ catalyst at room temperature in a flow of nitrogen containing 1% of air prevents ageing and bulk oxidation of nickel, which may result from its contact with the atmosphere.

The first stage in the preparation of impregnated nickel catalysts is highly important. When a support is impregnated with an aqueous solution of a salt (or salts) precursors appear on the support surface and in its bulk, and their formation is influenced by the electrolyte concentration, pH of the medium, and ionic strength of the solution.[105, 112–114] The first stage is supposed to generate several forms of isomorphically substituted nickel in the support lattice. At low pH, aluminium oxide is solubilised, which favours isomorphic substitution in the final forms.

The effect of pH on the concentration of nickel precipitated from a $Ni(NO_3)_2$ solution onto $Al_2O_3$ is illustrated by the data presented in Table 2.

The concentration of electrolyte, ionic strength, and pH of impregnation solution influence not only the content of Ni in the catalyst, but also the amount of active nickel precursors and hence the physicochemical properties and the hydrogenation activity of the catalysts formed.[103, 105]

**Table 2**. Dependence of the Ni content in a catalyst on pH of the impregnation solution of $Ni(NO_3)_2$.[103]

| [Ni] in the solution (mass %) | pH | [Ni] in the catalyst (mass %) [a] |
|---|---|---|
| 0.7 | 1 | 0.2 |
| | 3 | 1.2 |
| | 5 | 2.1 |
| 2.9 | 1 | 3.5 |
| | 3 | 4.1 |
| | 5 | 3.0 |
| 5.2 | 1 | 6.6 |
| | 3 | 8.3 |
| | 5 | 7.3 |

[a] With respect to the mass of the $Al_2O_3$ support.

**Table 3**. Content of nickel in supported catalysts, its specific surface ($S_{Ni}$), and dispersity ($D_{Ni}$).[103]

| [Ni] (mass %) | $S_{Ni}$ /m$^2$ g$^{-1}$ | $D_{Ni}$(%) |
|---|---|---|
| 0.8 | 5.2 | 94 |
| 1.2 | 5.7 | 70 |
| 2.1 | 5.6 | 40 |
| 3.0 | 6.0 | 29 |
| 3.5 | 6.0 | 26 |
| 4.1 | 5.7 | 21 |
| 6.6 | 5.1 | 12 |
| 7.3 | 5.2 | 11 |
| 8.3 | 5.3 | 10 |

The procedure for the preparation of $Ni/Al_2O_3$ catalysts affects their structure, activity, and selectivity, *e.g.*, in the hydrogenation of CO.[47, 49, 103–108] Temperature-programmed desorption (TPD) of $H_2$ and its interaction with CO allowed us to obtain data on the accessibility of surface Ni centres to $H_2$ and CO at various conditions of preparation of low-percentage catalysts. Surprisingly, the variation of Ni content from 0.8 mass % to 8.3 mass % proved to have little effect on the adsorption of $H_2$ and the active nickel surface calculated from the results obtained (Table 3). However, the metal dispersity varies noticeably depending on the concentration of nickel precipitated and precipitation conditions, *i.e.*, it decreases at higher concentrations.

At the same time, the analysis of temperature-programmed CO desorption spectra points to the existence of two types of adsorptional and reactive centres. The specimen with 0.8% of Ni is an exception, since its spectrum has a single peak at 260 °C. In all other cases, low-temperature (at 150–200 °C) and high-temperature peaks were observed. The increase in Ni content to 2.3% increases the portion of CO desorbed in the low-temperature range. In the case of specimens containing 2.3%–7.3% of Ni, the contribution of both peaks is nearly the same. According to Kester and Falconer,[48] the two CO peaks correspond to two types of active centres of different composition on the surface of the Ni catalyst. The low-temperature peak is supposed [48, 105] to correspond to NiO, while the high-temperature peak corresponds to $NiAl_2O_4$. Stronger metal–support bonding is predominant in catalysts with low Ni content.[105] Low pH values facilitate isomorphic substitution of Ni in the octahedral lattice of $Al_2O_3$, which favours the predominant existence of this metal in the $NiAl_2O_4$ form. Only this structure was revealed in the 0.8% $Ni/Al_2O_3$ specimen.

The results reported by Huang and Schwarz [103] are at variance with those obtained by Tsai *et al.*[112] who have found that the increase in Ni content results in an increase in its specific surface calculated from the CO adsorption from 3.9 to 15.8 m$^2$ g$^{-1}$. The increase in Ni concentration from 0.8% to 2.1% is accompanied by a decrease in the degree of Ni dispersity, also calculated from the CO adsorption, from 70% to 31%, which then remained nearly constant (27%–35%).

The catalytic activity and selectivity of the $Ni/Al_2O_3$ specimens described above in the reaction of CO hydrogenation are closely related to their composition and conditions of preparation. This allows the prediction of their catalytic properties.[104] The limiting stage of the methanation is determined by the type of active centres prevalent on the surface. According to Huang and Schwarz,[47] the process of CO methanation includes the following stages:

1) $CO_{ads} \rightleftharpoons CO_{gas}$,

2) $CO_{ads} \longrightarrow C_{ads} + O_{ads}$,

3) $C_{ads} + O_{ads} \longrightarrow CO_{gas}$,

4) $CO_{ads} + O_{ads} \longrightarrow CO_{2\ ads}$,

5) $H_{2\ gas} \longrightarrow 2H_{ads}$,

6) $CO_{ads} + (2 + x)H_{ads} \longrightarrow CH_{x\ ads} + H_2O$,

7) $2CO_{ads} \longrightarrow C_{ads} + CO_{2\ ads}$,

8) $CH_{x\ ads} + (4-x)H_{ads} \longrightarrow CH_{4\ gas}$.

Investigation of the surface interaction of CO and $H_2$ on $Ni/Al_2O_3$ catalysts with variable Ni content by X-ray photoelectron spectroscopy (XPES), thermoprogrammed reaction (TPR)[113] and other methods confirmed that in the case of prevalence of $NiAl_2O_4$ centres on the surface (catalysts with low Ni content) the methanation rate is determined by the rate of CO dissociation [stage (2)]. On catalysts with high Ni content, in which nickel is in the form of particles, the methanation rate is determined by that of hydrogenation of the $CH_x$ fragments [stage (8)].[47] If the reaction of methanation is regarded as being structure-sensitive, then the changes in its mechanism are well explained by the lower degree of Ni dispersity and the increase in its content from 0.8 mass % to 8.0 mass %.

XPES and TPR[113] studies have shown that $NiAl_2O_4$ centres predominate on an $Ni/Al_2O_3$ catalyst with 0.8% Ni, while $Ni + NiAl_2O_4$ centres predominate on a catalyst with 6.5% Ni.

Contrary to the CO methanation, the hydrogenation of aromatic hydrocarbons cannot occur on active centres of the $NiAl_2O_3$ type in which Ni is structurally bound. This requires that the active centres were formed by finely dispersed Ni particles on a support. Kester *et al.*[115] consider the hydrogenation of aromatics as structure-insensitive reactions. There are fundamental difficulties that prevent the preparation of long-lived Ni catalysts on $\gamma$-$Al_2O_3$ with the Ni content below 5% for the hydrogenation of aromatic compounds. The point is that local overheating taking place during the exothermic reactions of hydrogenation induce the formation of inactive surface spinel and hence the absorption of the active component.[48,116–118] This explains why the industrial Ni catalysts of hydrogenation usually contain considerable quantities of metal (up to 65%) and include oxide promoter additives (Table 4) diminishing the SMSI effect.

**Table 4**. Industrial nickel catalysts for hydrogenation.

| Composition of the ctalyst | | | Specific surface /$m^2\ g^{-1}$ | Pore volume /$cm^3\ g^{-1}$ |
|---|---|---|---|---|
| Ni (mass %) | additive | support | | |
| Catalyst of Harshaw Co. (USA) | | | | |
| 60–65 | – | clay | 155–165 | 0.22 |
| 40 | – | $Al_2O_3$ | 160 | 0.69 |
| 68 | – | special support | 125 | 0.35 |
| 46 | – | " | | |
| 14 | $WO_3$ | $Al_2O_3$ | 140 | 0.38 |
| Catalyst of BASF Co. (Germany) | | | | |
| 4–10 | $WO_3$ | active clay | – | – |

Nickel catalysts on other types of supports (*e.g.*, $SiO_2$) modified by Ti, Zr, and Ce oxides also manifest low activity in the hydrogenation of benzene provided the SMSI effect is realised.[116,119] They are one order of magnitude less active than a catalyst analogous in composition [7%$Ni/SiO_2 - TiO_2(ZrO_2)$], prepared by precipitation of $Ni(OH)_2$, which is free from the SMSI effect.

The technique of homogeneous precipitation was used to prepare a highly efficient Ni catalyst (Euro-Ni-1) containing 25 mass % of Ni.[13–15] In this case, the major part of nickel is in the form of hydrosilicate. Therefore, it was necessary to activate the catalyst at elevated temperatures in a flow of hydrogen (Table 5).

The maximum degree of reduction of nickel (96%) is achieved at 630–650 °C, though in this case its specific surface is somewhat decreased, possibly because of sintering. Nonetheless, it exceeds nearly eightfold the surface of Ni in a precipitated Ni–Cr catalyst containing 50 mass % – 60 mass % of Ni. The main part of the active component is bound by the support ($SiO_2$), which results in the formation of new surface phases. This means that this method cannot yield industrial low-percentage, highly active nickel hydrogenation catalysts on the $SiO_2$ support.

**Table 5**. Effect of temperature on the extent of Euro-Ni-1 catalyst reduction and the specific surface of nickel.[15]

| Temperature of reduction /°C | Extent of reduction (%) | $S_{Ni}$ /$m^2$ (g Ni)$^{-1}$ (see [a]) | $S_{Ni^0}$ $m^2$ (g $Ni^0$)$^{-1}$ (see [b]) |
|---|---|---|---|
| 430–450 | 85 | 181 | 213 |
| 500 | 90 | 181 | 201 |
| 630–650 | 96 | 113 | 118 |

[a] Total specific surface of nickel. [b] Specific surface of totally reduced nickel.

Romero *et al.*[120] showed that the specific surface of unmodified $Ni/SiO_2$ and $Ni/Al_2O_3$ catalysts and their capacity to absorb $H_2$ during thermal treatment or under hydrogenation conditions decrease very rapidly on heating to 650–750 °C. Thus, after treatment at 650–750 °C, the overall specific surface of an $Ni/SiO_2$ catalyst diminishes from 199 to 159 $m^2\ g^{-1}$, and the absorption of $H_2$ becomes more than twice as low.

Transmission electron microscopy data showed that the size of Ni particles increases from 2.9 to 6.8 nm. After an analogous thermal treatment, the Ni particles in the $Ni/Al_2O_3$ catalyst are enlarged from 2.7 to 9.3 nm, though in this case the overall specific surface and $H_2$ absorption do not change as strongly as upon the thermal treatment of $Ni/SiO_2$. In both cases the degradation of porous structures takes place. Thermal treatment of $Ni/SiO_2$ and $Ni/Al_2O_3$ decreases the specific surface of Ni by 70% and 25%, respectively.

Thermal inactivation of supported Ni catalysts can be caused by the growth of Ni crystallites, degradation of a support, metal–support interaction, or by combinations of these factors.

## 3. Effect of the nature of supports on the catalytic properties and specific surface of catalysts

The chemical nature of supports and their structure influence the activity and selectivity of hydrogenation catalysts.[116–119]

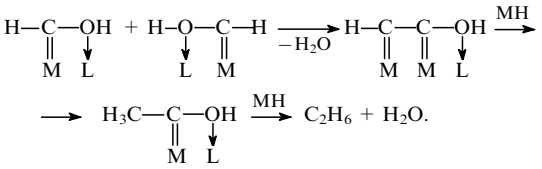
Pavlenko *et al.*[117] investigated the adsorption and catalytic properties of Ni catalysts deposited on $ZrO_2$, MgO, $TiO_2$, and $SiO_2$ in the reaction of CO hydrogenation (Table 6).

**Table 6**. Kinetic and thermodynamic parameters of CO hydrogenation on supported nickel catalysts.[117]

| Catalyst | Mean size of Ni particles /nm | $T$ /K | Maximum pore radius /nm | $E$ /kJ $mol^{-1}$ | $q_{CO}$ |
|---|---|---|---|---|---|
| $Ni/ZrO_2$ | 97 | 495 | 137.0 | 43 | 45 |
| | 97 | 508 | 198.0 | 43 | 45 |
| | 97 | 533 | 292.0 | 43 | 45 |
| $Ni/TiO_2$ | 103 | 526 | 55.0 | 59 | 46 |
| | 103 | 545 | 92.0 | 59 | 46 |
| | 103 | 561 | 128.0 | 59 | 59 |
| Ni/MgO | 1 | 471 | 2.3 | 93 | 101 |
| | 1 | 495 | 7.2 | 93 | 101 |
| | 1 | 506 | 12.0 | 93 | 101 |
| $Ni/SiO_2$ | 6 | 498 | 1.5 | 52 | 76 |
| | 6 | 498 | 3.4 | 52 | 76 |
| | 6 | 498 | 8.1 | 52 | 76 |

The heat of adsorption $q_{CO}$ increases as the dispersity of Ni increases. This is in agreement with the results of quantum-chemical calculations [88] according to which the metal–CO bond becomes weaker on transition from the primary clusters to large crystals reaching a constant strength at a mean size of Ni particles 10–20 nm. The specific catalytic activity of specimens at 220 °C decreases in the following order of supports: $ZrO_2$ > $TiO_2$ > > MgO > $SiO_2$, *i.e.* there is no direct correlation with the size of crystallites. The selectivity of formation of higher hydrocarbons depends on the nature of the support and varies in the same order, while that of methane formation varies in the opposite direction.

Thus, the nature of the support affects mainly the size of the crystallites and the heat of CO adsorption $q_{CO}$, which in turn influence the reaction parameters. There are other factors, too. Thus, according to Huang and Schwarz,[49, 107] with the same metal dispersity, the selectivity of CO hydrogenation depends on the acid-base properties of supports. This dependence can be determined, for example, by the intermediate interaction of the surface complexes $CH_xOH$ bound through an oxygen atom to acidic Lewis centres (L) at the metal–support interface




(9)

According to this scheme, the selectivity of formation of higher hydrocarbons should depend on the strength of CO molecule bonding ($q_{CO}$) and the energy of acid–base interaction.

The influence of the nature and acidity of supports on the properties of Ni-containing catalysts and the metal state in them is clearly manifested in the formation of industrially important bifunctional catalysts containing from 0.5 mass % to 2.0 mass % of Ni.[120–123] Depending on the differential acidity of supports, *i.e.*, on the ratio of the Brønsted (B) to Lewis (L) centres, catalysts are formed with different activity and selectivity in reactions of hydroisomerisation, aromatisation, and hydrogenolysis. The acidic properties of zeolite supports influence the dispersity of nickel, the extent of its reduction and the magnitude of the SMSI effect, which in turn affects the activity and selectivity of catalysts.

Hoang *et al.*[121] investigated the state of nickel in the Ni-containing catalysts by IR spectroscopy of adsorbed CO and $NH_3$, thermoprogrammed reduction, chemisorption of $H_2$ and $O_2$, and thermoprogrammed desorption of $NH_3$. When zeolite is impregnated with a nickel salt solution at pH 1.8, ion exchange of B-centres in the channels of zeolite occurs. The nickel fixed in these centres is difficult to reduce; it remains mainly in the NiO form and hence cannot be determined by IR spectroscopy of adsorbed CO. Impregnation of zeolite with a nickel salt solution at pH 4.8 results in the formation of metallic Ni localised mostly outside the channels. In these two cases, the Ni-zeolite catalysts manifest different activity and selectivity in reactions of aromatisation, dehydrocyclisation, and hydrogenolysis of n-hexane.

The acidity of the support and concentration of B- and L-centres also influence the state of Ni in a reduced catalyst (Table 7). In absence of L-centres on the surface (specimen I), NiO particles are formed that interact strongly with the support, the extent of their reduction being a minimum. The presence of even a small number of L-centres (specimen II) leads to the formation of reduced particles $Ni^0$, which are less dispersed than those in specimen III with the maximum quantity of L-centres. The specimen III contains highly dispersed Ni particles. In all cases, part of the Ni interacts with the B-centres to form presumably $Ni(OH)^+$ ions, which are not reduced to $Ni^0$.[121]

Similar results were reported by Romero *et al.*[120] who used physicochemical methods to study the metal incorporation into zeolite. The use of a number of additives, *e.g.*, nickel acetylacetonate, and impregnation of zeolite with a Ni salt solution

**Table 7**. Effect of the acidity of the support on the state of nickel in a Ni/HZSM-5 catalyst after reduction.[121]

| Specimen $g^{-1}$ | [Ni] (mass %) | Concentration of acidic centres | | Extent of reduction of Ni (%) | Ni dispersity (%) | $S_{Ni}$, $/m^2$ - |
|---|---|---|---|---|---|---|
| | | B [a] | L [b] | | | |
| I | 0.5 | 1.8 | 0 | 3 | – | – |
| II | 0.5 | 1.6 | 0.09 | 75 | 6.2 | 0.15 |
| III | 2.0 | 1.1 | 0.38 | 75 | 4.8 | 0.48 |

[a] Determined from the absorption band of adsorbed $NH_3$ (1460 $cm^{-1}$) in the IR spectrum. [b] Determined from the absorption band of adsorbed $NH_3$ (1610 $cm^{-1}$) in the IR spectrum.

produces catalysts possessing different acidity, which influences the metal state, activity and selectivity of contacts in the process of hydrocracking of n-paraffins.

Analogous conclusions about the effect of the character of distribution of acidic centres over the support with regard to the strength of these centres on the metal state, activity, and selectivity were drawn from a number of studies dealing with the preparation of Pt, Pd, and Ni catalysts on zeolite supports.[124–127] These catalysts are applied for dearomatisation in installations for hydrorefining of diesel fuels.[40] According to Hoang *et al.*,[121] the acidic function of the support controls the formation of the active surface of nickel. Impregnation Ni catalysts are less active than those obtained by ion exchange, since the extent of Ni dispersity is lower in the former case.

The use of a set of physicochemical methods (IR spectroscopy of adsorbed CO, ferromagnetic resonance, chemisorption of $O_2$ and $H_2$, thermoprogrammed desorption of $NH_3$) made it possible to reveal the effect of strong interaction of Ni with zeolite supports of the Y type characterised by the different extent of $Na^+$ exchange for $NH_4^+$ ions and hence by different total acidity.[127]

With the increase in the extent of ion exchange, the total acidity increases with simultaneous appearance of a trend for a larger size of Ni particles and a smaller number of *d*-electrons per nickel atom.

The results obtained allowed one to make a conclusion on the formation of nickel clusters on the surface of zeolite supports and a substantial role of electronic factors in this process. By controlling the formation of clusters, including SMSI regulation, one may prepare highly efficient Ni catalysts with different active centres enabling the occurrence of specific reactions involving $H_2$.

Studies of the effect of the surface nature, porous structure and support crystallinity on the formation and properties of Ni catalysts are of considerable interest.[49]

Table 8 presents the main characteristics of $Al_2O_3$ specimens of different origin (Degussa, Engelhardt, and Kaiser products) used to prepare impregnation catalysts of composition 6%Ni/$Al_2O_3$.

The preparation of catalysts involves several stages. In the first stage, the support is brought into contact with an electrolyte, which results in adsorption of precursors, most frequently by ionic adsorption. There are two ways of cation adsorption on the support surface. If the support is protonated, *i.e.*, it contains no heterometallic ions, the ion adsorption may be realised by treating the support with a solution containing metal ions at a sufficiently high pH. Then the surface $H^+$ ions are exchanged for metal ions, *e.g.*, $Ni^{2+}$, following the scheme

$$2Al^{3+}OH_s^- + Ni_{aq}^{2+} + 2OH_{aq}^- \rightleftharpoons [Al^{3+}O^{2-}]_2Ni_s^{2+} + 2H_2O.$$

An increase in pH shifts the equilibrium to the right, and the concentration of metal ions may prove to be insufficient for precipitation of the metal in the form of hydroxide.

In the first stage, upon contact with an $Ni(NO_3)_2$ solution at pH 5 the support is partially dissolved and interacts with the electrolyte, whose pH is thus changed, and a portion of $Al^{3+}$ ions

**Table 8**. Effect of the type of support on pH of the impregnation solution and Ni adsorption from solution.[49]

| Type of support | $S_{sp}$ /$m^2\ g^{-1}$ | X-Ray crystallinity /rel. units | pH at zero charge | Pore volume (from $N_2$) /$cm^3\ g^{-1}$ | $Al^{3+}$ concentration /ppm [a] | Solubility /rel. units (see [b]) | Ni adsorption | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | g (g $Al_2O_3$)$^{-1}$ | /rel. units |
| Degussa | 97 | 1.8 | 5.2 | 0.003 | 0.26 | 1.00 | $3.25 \cdot 10^{-4}$ | 1.0 |
| Engelhardt | 195 | 1.4 | 6.8 | 0.54 | 0.84 | 13.51 | $4.39 \cdot 10^{-3}$ | 13.5 |
| Kaiser | 200 | 1.0 | 9.3 | 0.5 | 2.87 | 35.08 | $1.14 \cdot 10^{-2}$ | 35.0 |

[a] Concentration of $Al^{3+}$ in the electrolyte formed upon $Al_2O_3$ solubilisation and ion exchange with $Ni^{2+}$. [b] Solubility of $Al_2O_3$ in an $Ni(NO_3)_2$ solution at pH 5.0.

pass into solution. Here, ion exchange can take place with participation of both the OH groups and the surface cations. The hydroxy groups are donors of protons, while the hydrolysed cations are donors of hydroxyls. The departing $Al^{3+}$ cations are substituted by hydrogen as a result of hydrolysis. Subsequently, the $Al^{3+}$ ions are readsorbed. A mixed adsorption leads to the formation of nickel aluminate on the surface.

As is seen in Table 8, the crystallinity (ordering) of the structure of $Al_2O_3$ and its solubility in the electrolyte change in opposite directions: solubilisation of a support with a deformed lattice occurs more easily. Transition of $Ni^{2+}$ ions from solution to support may be explained by ion exchange with a neutral or negatively charged surface of $Al_2O_3$ and incorporation of $Ni^{2+}$ into the deformed lattice of $Al_2O_3$. The ion exchange requires a definite pH at which $Al_2O_3$ is dissolved in the electrolyte. The larger the number of $Al^{3+}$ ions passing into solution, the more deformed the support lattice, which facilitates incorporation of $Ni^{2+}$ into the support. The most soluble $Al_2O_3$ of Kaiser Co. adsorbs the largest quantity of $Ni^{2+}$, whereas the $Al_2O_3$ of Degussa Co. has the lowest solubility and adsorbs the smallest quantity of $Ni^{2+}$. The order of $Ni^{2+}$ adsorbability on various supports is the reverse to the order of their crystallinity.

The efficiency of a catalyst is substantially dependent not only on the quantity of adsorbed $Ni^{2+}$, but also on the size of its active surface and the structure of the latter. The catalysts of the Kaiser and Engelhardt companies have similar pore sizes. However, according to Ghen *et al.*,[49] the adsorption of $Ni^{2+}$ from aqueous solutions and treatment with $HNO_3$ do not affect the structure of the support of Kaiser Co., but modify the structure of $Al_2O_3$ of Engelhardt Co.

Thermoprogrammed reduction (TPRd) of catalysts with hydrogen reveals differences between the porous (Engelhardt and Kaiser) and non-porous (Degussa) specimens. The TPRd spectrum of the Ni catalyst on the Degussa support has no high-temperature peak, whereas the catalysts on the porous supports are characterised by two peaks (at 141–149 and 223–230 °C), though their ratio for the two above-mentioned specimens is not the same. It may be suggested that the catalyst on the Degussa support possesses only the exchangeable surface Ni and centres of the NiO type. The presence of two peaks in the spectrum of TPRd on this catalyst is indicative of the presence on the surface of reduced nickel ($Ni^0$) and nickel aluminate, *i.e.* a surface compound carrying incorporated Ni. $Al_2O_3$ of Kaiser Co. has very little surface Ni and much incorporated Ni in comparison with $Al_2O_3$ of Engelhardt Co. The quantity of surface (exchangeable) nickel decreases in the order Degussa > Engelhardt > Kaiser, which correlates with the data on crystallinity, solubility, and adsorption.

The porous structure of the support was shown [128] to influence the extent of metal reduction. On the $Al_2O_3$ support with a smaller pore size, the mean size of metal particles and the quantity of $H_2$ sorbed in the low-temperature range are larger.

The readily reducible nickel oxides are believed [129] to be localised in small pores, while the oxides that are difficult to reduce occupy large pores. The oxides of the first type are close in their structure to the bulk-distributed NiO and interact very weakly with the support. The reduction-resistant oxides may occur as small crystallites and as surface compounds. The next section is concerned with the effect of the porous structure of supports on physicochemical and catalytic properties of modified nickel catalysts studied by one of the authors of this review.

There are two peaks in the TPR spectra of CO for all reduced samples. It is supposed that the low-temperature peak corresponds to the CO adsorbed on Ni,[49] whereas the high-temperature peak is associated with the CO spillover on $Al_2O_3$ or with its adsorption on a surface nickel compound. In the spectrum of the catalyst on the porous support of Kaiser Co. with an abnormally small specific surface of nickel ($S_{Ni} = 2.17\ m^2\ g^{-1}$), the low-temperature peak is smaller than that in the spectrum of the catalyst on the support of Engelhardt Co. ($14.89\ m^2\ g^{-1}$). The low-temperature peak is larger ($14.22\ m^2\ g^{-1}$) in the case of the sample on the non-porous support of Degussa Co.

Thus, by selecting the type and porosity of a support, one can control the formation of precursors of active Ni centres, the extent of metal reduction, and hence the activity and selectivity of a catalyst in specific hydrogenation reactions, and regulate thermostability and physicochemical and catalytic properties of impregnation catalysts.

## 4. Effect of modifiers and promoters on the properties of catalysts

The mode of support preparation and its nature substantially influence the activity, selectivity and physicochemical properties of supported catalysts; however, the strongest effect is achieved by the use of promoters and modifiers.

According to Roginskii,[130] modification, unlike promotion, is 'a more complicated phenomenon associated with more profound and complex changes in the catalytic properties and specific action of additives' the introduction of which induces 'not merely changes in the absolute magnitude of activity, but also a profound modification of the surface quality'. This can result in a change in the reaction route, *i.e.*, not only in the catalyst activity, but also in its selectivity. This concerns, for example, the modified Ni catalysts of hydrogenation, if the additives, as shown below, 'can react with the surface layer of the solid'.

The application of modern physicochemical methods allows a scientifically sound selection of modifiers and promoters for preparing efficient hydrogenation catalysts for any purpose.

At present, Ni-containing catalysts of hydrogenation are prepared mostly on supports, such as $Al_2O_3$, $SiO_2$, aluminosilicates, zeolites, *etc.*, which are modified by oxides.[5, 12, 20, 116, 131] Modifiers, which are for the most part inorganic additives ($SiO_2$, zeolites, Mg, Zr, and Ti oxides, boric and phosphoric acids), are introduced into supports by precipitation or impregnation techniques. This results in the enhanced thermostability and mechanical strength of the support. The activity and selectivity of the catalyst change insignificantly when the additives introduced do not affect the extent of nickel dispersity, the degree of its reduction and the magnitude of SMSI.

The fact that thermal treatment influences, as has been shown above, the dispersity and structure of supported Ni catalysts makes topical the enhancement of thermostability by modification. For example, addition of 3%–10% of BaO to $\gamma$-$Al_2O_3$ inhibits sintering and improves thermostability of the support.[12]

Addition of phosphoric acid to aluminium hydroxide favours an increase in the total porosity and the proportion of micropores. Other modifiers are also used.

Stabilisation of the existing Ni-containing centres, and creation of newer ones, often requires that considerable quantities of modifying oxide additives (up to 20 mass % – 40 mass %) be incorporated into the catalyst.[12, 132] Thus, the addition of 5% of $B_2O_3$ to the $NiO-Al_2O_3$ system leads solely to a lower concentration of $Ni^{3+}$ ions that are not reduced to the metallic state. Addition of 10% of $B_2O_3$ precludes the formation of $Ni^{3+}$ ions and stabilises $Ni^{2+}$ ions (a sample with $3\%Ni/Al_2O_3$), though even in this case a large portion of nickel remains in the form of surface oxide associates, whose reduction to the metallic state is problematic.

An analogous situation is observed in the modification of $\gamma$-$Al_2O_3$ with oxides, such as $WO_3$ and $Cr_2O_3$, and zeolites. With hydrogenolysis of thiophene as an example Surin *et al.*[133] described the promoting effect of zeolite on the hydrotreating catalyst, $Ni-Mo/Al_2O_3$. Studies involving a set of techniques (DTA, TG, EPR, FMR) showed that zeolite forms thermostable compounds with molybdenum and interacts with $\gamma$-$Al_2O_3$. Introduction of zeolite in the Ni—Mo catalyst favours more uniform distribution of acidic centres, which exerts a substantial effect on the formation of an active hydrogenation phase: a more dispersed phase is formed upon reduction of nickel molybdates.

In recent years there has been a much greater use of nickel catalysts modified by surface hydrides formed in the process of catalyst preparation [13–15, 134] and of the above-mentioned sorptional catalysts. The latter catalysts are highly dispersed, thermostable, and very active in hydrogenation processes, although the method of their preparation is not well-suited to industrial conditions because it includes decomposition on supports of organometallic compounds of elements belonging to Groups IV–VII (Mo, W, Re, and Sn) or Group VIII.[18–22, 110, 116, 134] The most probable reason for the enhanced thermostability is the interaction of the active component with low-valent ions to form metal–metal bonds between cations of these modifiers and the metal of organometallic compound:[135]

$$\equiv(O)_x\cdot E^{x+} + M(\pi\text{-}C_4H_7)_2 \longrightarrow \equiv(O)_x\cdot E^{x+}M(\pi\text{-}C_4H_7)_2,$$

$$\equiv(O)_x\cdot E^{x+}M(\pi\text{-}C_4H_7)_2 \longrightarrow \equiv(O)_x\cdot E^{x+}M^0 + 2C_4H_8,$$

where $M(\pi\text{-}C_4H_7)_2$ is the organometallic compound; $M^0$ is the metal; $E^{x+}$ is the modifying element of Group IV–VII.

Certain procedures developed for preparing sorptional catalysts, including nickel-containing ones, make it possible to reach a degree of dispersion close to the atomic state.[18–22] Slinkin *et al.*[116] described a process for preparing nickel catalysts based on ternary oxide systems $Ni-SiO_2(MO_2)$ synthesised by the alkoxide technology. Catalysts prepared by precipitation from alcoholic or aqueous solutions and promoted with Ti, Zr, and Ce oxides were used for comparison. The extent of nickel dispersion in these catalysts and others obtained from the ternary systems using organometallic compounds proved to be much the same. However, due to the absence of a SMSI effect, the activity of the precipitated catalysts $7\%Ni/SiO_2-10\%TiO_2(ZrO_2)$ in the hydrogenation of benzene proved to be one order of magnitude higher than that of the systems synthesised by chemical mixing, where the SMSI effect takes place. In their capacity to stabilise high-dispersity crystals of nickel, the modifiers form the following series:[116] $CeO_2 > ZrO_2 > TiO_2$.

A highly dispersed Ni catalyst for benzene hydrogenation was prepared by modifying the support surface with an organolithium compound from methanolic solution:[18]

$$\equiv OH,\ \equiv OH + CH_3Li \xrightarrow{-CH_4} \equiv OLi,\ \equiv OLi \xrightarrow[-LiCl]{NiCl_2} \equiv O-NiCl,\ \equiv O\diagdown\!\diagup Ni$$

In accordance with this scheme the so-called grafted $Ni/SiO_2$ catalysts with 0.8 mass% – 4.6 mass% of metal were prepared. Physicochemical and catalytic studies of such catalysts showed that they possess a number of advantages compared to the impregnation systems of similar composition. The degree of reduction of the grafted catalysts at 250–400 °C does not reach 100%, and the size of Ni particles in them ranges from 4.8 to 8.5 nm, while it is 12.5 nm in the impregnation catalysts with 100% reduction. The maximum activity of grafted catalysts in the reaction of benzene hydrogenation is observed at 350–360 °C, which is 12–15 times larger than that of impregnation systems.[18]

The drawbacks of the method of support modification with organometallic compounds include a narrow set of compounds possessing satisfactory solubility even in organic solvents, complexity of their synthesis, high explosive tendency and fire hazard of the process, and the need for special pretreatment of supports.[13]

However, this method makes it possible to modify the support surface at the atomic level and to form active metal centres with a predetermined environment.

In our opinion, a method for preparing low-percentage Ni catalysts of hydrogenation by impregnation with mixed inorganic complex salts from aqueous solutions is more promising.[136–145] In all cases, the role of modifier or active phase is played by heteropolycompounds (HPC) with anions of the general formula $[H_wA_xB_yO_z]^{n-}$, where A = Ni or Co; B = Mo, W, or V. Their decomposition yields supported Co—Mo, Ni—W, and Ni—Mo catalysts;[146] they may also be used as modifiers of Ni-containing catalysts.[136–145]

Heteropolycompounds with anions $[NiM_6O_{24}H_6]^{4-}$ (M = Mo or W) were synthesised to prepare hydrogenation catalysts of this type aimed at modelling the known Co—Mo, Co—W and Ni—W catalysts of hydrotreating.[146] Their decomposition on the surface yielded the active phase. Previously, this type of salt and acid were mostly applied as catalysts of oxidation, hydration–dehydration and some other processes.[147–151]

Supported Ni—Mo and Ni—W catalysts prepared by impregnation of their support with heteropolycompounds were tested in reactions of hydrodesulfurisation and hydrogenation.[146, 152] They were found to be less active than the industrial Ni—Mo and Ni—W catalysts. This is rationalised by the lower content of Ni which cannot be increased because in this case HPC are used as an ordinary active phase.

In the 1980s, one of the authors of this review designed nickel catalysts of a fundamentally new type on different supports (activated carbon, $Al_2O_3$, and $SiO_2$) in which HPC of different composition ($HPC_1$, $HPC_2$, $HPC_3$, *etc.*) play the role of modifiers.[136–143] They were tested in a broad spectrum of reactions (hydrogenation of alkenes, aromatic compounds, aldehydes, ketones, and CO; hydrogenation of coal; hydrodemethylation of toluene; hydrocracking of petrol fractions; dehydrogenation of cycloalkanes). It was shown that they possess high and controllable activity and selectivity. Common distinctive features of these catalysts are low metal content (2% – 6% Ni), modifying salts on the surface of a support and a well-developed surface of metallic nickel with high dispersity. These catalysts exhibit high thermostability, and the procedures for their preparation match technological demands.

Table 9 presents values of the specific surface of nickel ($S_{Ni}$), its dispersity ($d_{Ni}$), and the degree of reduction ($\alpha$) in modified catalysts of the new type on $\gamma$-$Al_2O_3$ with different HPC modifiers and, for comparison, in some industrial Ni catalysts of hydrogenation.

The extent of reduction of modified samples reaches high values, despite the fact that the reduction conditions are considerably milder (400 °C, 6 h) than, for example, those for the Euro-Ni-1 catalyst.[15] In some cases, the $\alpha$ value for modified catalysts with low Ni content (*e.g.*, $2\%Ni-HPC_1$) reaches 100%. As noted above, this index is not reached for non-modified $Ni/Al_2O_3$ catalysts, since in these a fraction of the Ni is incorporated into the lattice forming a spinel.

**Table 9**. Specific surface of nickel, its dispersity, and the extent of reduction in HPC-modified and some industrial catalysts.

| Catalyst | [Ni] (%) | $S_{Ni}$ /m$^2$ (g catalyst)$^{-1}$ | $d_{Ni}$ [a] /Å | α (%) |
|---|---|---|---|---|
| Ni – $HPC_1/Al_2O_3$ | 4 | 220 | 26 | 70 |
| Ni – $HPC_2/Al_2O_3$ | 4 | 334 | 17 | 87 |
| Ni – $HPC_3/Al_2O_3$ | 4 | 56 | 100 | 87 |
| Ni – Cr | 48 – 63 | 25 – 27 | | |
| Euro-Ni-1[b] | 25 – 52 | 181 | 48 – 56 | 85 – 96 |
| $Ni/Al_2O_3$ (Exson) | 8 – 10 | 197 | 34 | |

[a] Found from $H_2$ adsorption. [b] Reduction for 10 – 26 h at 630 °C.

The HPC-modified catalysts with 2% – 4% of nickel manifest enhanced activity in the hydrogenation of mono- and bi-cyclic aromatic hydrocarbons, and their selectivity reaches 100%. Hydrogenation of toluene on HPC-modified Ni catalysts with 2% – 4% of Ni occurs considerably more easily than on industrial Ni – Cr catalysts with 50% of Ni (Fig. 1).[138]

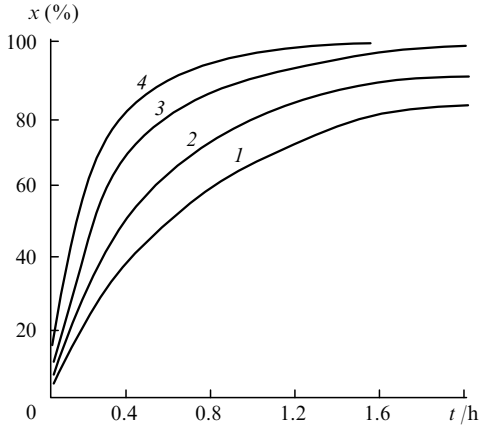



**Figure 1.** The extent of toluene hydrogenation *vs.* time on an industrial Ni – Cr catalyst (*1*) and modified $Ni-HPC_2/Al_2O_3$ catalysts with 2 mass %, 3 mass %, and 4 mass% of Ni [(*2*) – (*4*), respectively].

The catalyst $Ni-HPC_1/Al_2O_3$ with 2% of Ni is more active at 3 MPa and 220 °C than its analogue with 4% of Ni, and complete hydrogenation of benzene on this catalyst occurs within a contact time less than 0.1 h.[140]

These results confirm direct participation of HPC in the formation of active centres of hydrogenation. This follows in particular from the data on the formation of HPC oxometallates, and the formation of W-containing hydrogen bronze upon reduction of highly dispersed particles in the $Pt/WO_3$ system.[141, 150, 152]

Preparation of modified Ni – HPC catalysts on carbon supports is accompanied by the formation of an active phase in which Ni particles are distributed uniformly. Figure 2 presents microphotographs of modified and non-modified catalysts on a carbon support with a specific surface of 600 m$^2$ g$^{-1}$. In the absence of HPC the Ni particles are nonuniformly distributed, and their size exceeds that of particles in the modified catalyst.[138] In the catalyst 4%Ni – HPC/C reduced at 300 – 420 °C, the size of particles can be as small as 5 – 7 Å, and in the catalyst on $\gamma$-$Al_2O_3$ they can be even smaller. To achieve optimum dispersity of Ni (5 – 7 Å) and maximum reduction, it is necessary to have specific HPC concentration and a Ni : HPC ratio on each support. Complete reduction of Ni is possible at a low metal content (2% – 4%). In this case, nickel virtually does not interact with $\gamma$-$Al_2O_3$ since it is distributed on the modifier surface. Catalysts $Ni/\gamma$-$Al_2O_3$ containing less

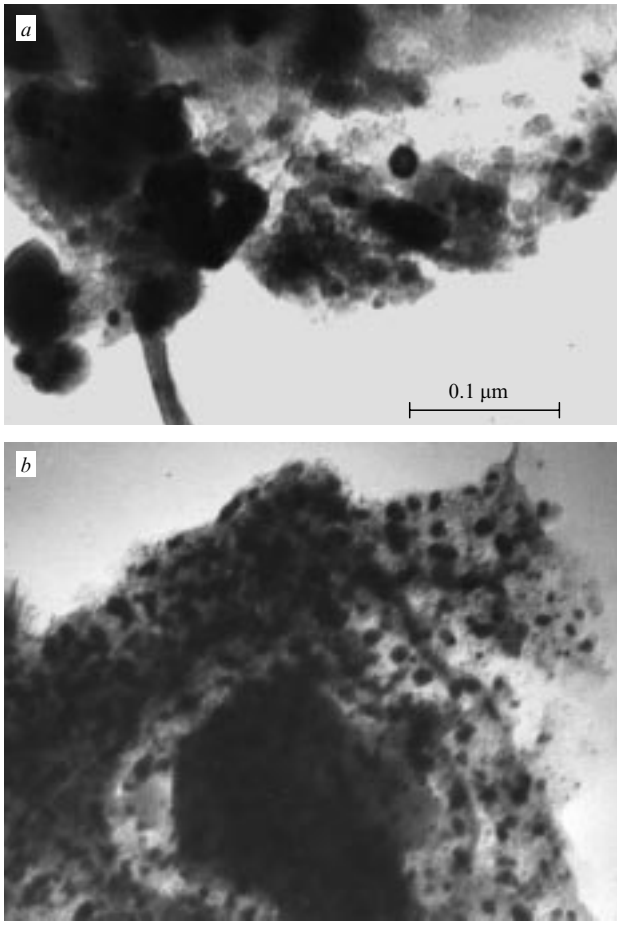



**Figure 2.** Microphotographs of reduced (at 400 °C) catalysts containing 4% of Ni on carbon supports in the absence of modifier (*a*) and the presence of $HPC_1$ (*b*).

than 5% of metal are virtually inactive in hydrogenation of benzene because of the difficulty in reducing NiO that is in contact with $Al_2O_3$.

Modification of the $Ni/Al_2O_3$ catalyst containing 4% of Ni with heteropolycompounds shifts the range of CO hydrogenation towards higher temperatures (250 – 400 °C) and substantially diminishes the $CO_2$ concentration in the products on total CO conversion.[139] The transition of centres of type A (Ni/NiO) to centres of type B (Ni/NiO) ensures selective hydrogenation, which occurs at a lower temperature. In the absence of a modifier, the centres of the B type are possibly not formed at all.

The assumption of the different structure of Ni centres on modified and non-modified catalysts was confirmed by the analysis of electronic spectra of diffuse reflection. It was shown that Ni catalysts modified by HPC have two types of $Ni^{2+}$ ions with different crystalline fields, while $Ni^{3+}$ ions are absent. Spectral parameters do not correspond to the compound $NiAl_2O_4$, which shows that the modifier is involved in the distribution of nickel and that the direct interaction between Ni and $Al_2O_3$ is absent.

The $B_2O_3$ modifier added in quantities considerably larger (up to 10 mass % – 20 mass %) than HPC influences the thermostability of catalysts since it destroys the Ni – O – Ni clusters, inhibits the formation of spinel with $Al_2O_3$, and stabilises the $Ni^{2+}$ ions on the surface.[132] Addition of $B_2O_3$ to the $Ni/Al_2O_3$ system strongly decreases the concentration of $Ni^{3+}$ ions, which form the oxide associates Ni – O – Ni and alters the acid-base properties of a catalyst.

Heteropolycompounds serve not only as chemical modifiers, they also influence the microporous structure of catalysts.

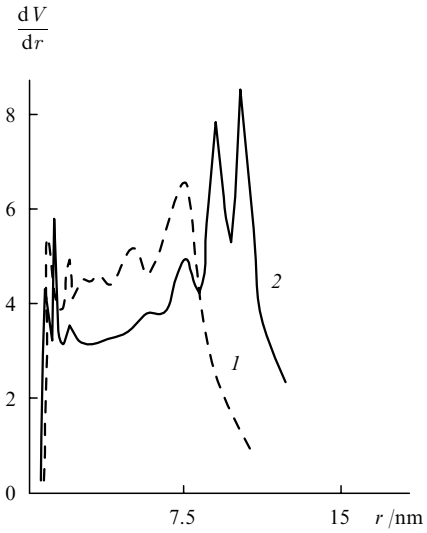



**Figure 3.** Changes in the porous support structure after formation of the active phase of Ni catalyst in the presence of HPC: (*1*) $\gamma$-$Al_2O_3$ support after thermal treatment; (*2*) $Ni-HPC_1/Al_2O_3$ catalyst.

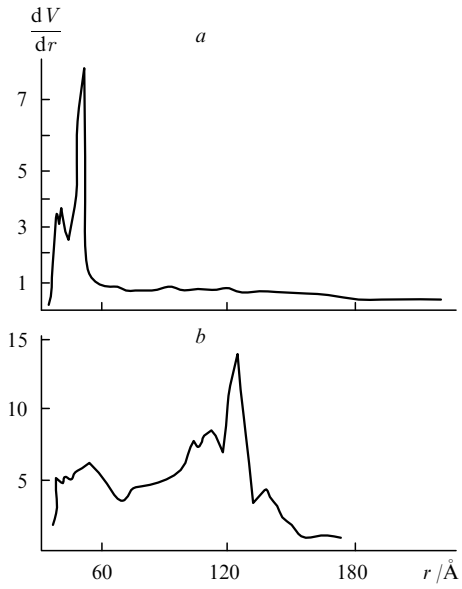



**Figure 4.** Distribution of the volume of pores in the supports $\gamma$-$Al_2O_3$ of the X type (*a*) and $Al_2O_3$-1 (*b*).

Figure 3 shows changes in the porous structure of $\gamma$-$Al_2O_3$ after introduction of HPC in the preparation of a Ni hydrogenation catalyst. The presence of micropores 20–30 Å in diameter influences rather favourably the activity of catalysts for the hydrogenation of aromatic hydrocarbons. The micropores are the sites where readily reducible nickel oxides are formed, after activation with hydrogen the oxides are transformed into highly dispersed metal particles, which ensure rapid hydrogenation of benzene. By modifying the porous support structure with HPC, one can prepare active and selective catalysts for the hydrogenation of aromatic and carbonyl compounds or CO methanation.

Table 10 presents some characteristics of HPC-modified catalysts with the same content of nickel and supports used for their preparation by impregnation. The supports were $\gamma$-$Al_2O_3$ with a predominant pore size of 9–12 nm ($Al_2O_3$-1) or $Al_2O_3$ of the X type ($X_1$, $X_2$, $X_3$) with a pore size of 1–3 nm. Figure 4 shows the dependence of changes in the volume of pores ($V$) as a function of their radius ($r$) for the supports of the X type and $Al_2O_3$-1.

The data presented in Table 10 show that the catalysts based on supports with similar total porosity (specimens 1, 4 and 8) and volume of micropores (specimens 1 and 4) exhibit different activities. The catalyst No. 9 prepared on the support with the largest volume of micropores is the most active in hydrogenation of benzene but is little active in the hydrogenation of acetone. On the contrary, specimens 2 and 3 prepared on $Al_2O_3$-1 are not very active in the hydrogenation of benzene and highly active in the hydrogenation of acetone. The modified Ni catalysts with a well-developed microstructure (the predominant pore size 1–3 nm) were shown to have active centres of benzene hydrogenation and those with large pores (9–12 nm) — to contain active centres of acetone hydrogenation.

Dehydration of modified samples under conditions of thermoprogrammed heating in the temperature range 50–700 °C yields water as the sole product. Modification with HPC substantially alters the properties of the initial surface of $Al_2O_3$. Specifically, hydrophilicity of the catalysts prepared was found to be higher than that of initial $Al_2O_3$ over all the measurement range. After deposition of Ni on modified $Al_2O_3$, the liberation of adsorbed water in the thermolysis takes place in the temperature intervals 50–100 °C, 200–300 °C, ~ 400 °C, 500–600 °C, and even near 700 °C. The most actively modified Ni catalysts possess an increased capacity for $H_2O$ (12% and more). They are characterised by the presence of water removable only in the high-temperature range.[153]

## IV. Catalysts based on noble metals

The Ni-containing catalysts are less expensive than those based on noble metals (Pt, Pd, Ru, Rh, Ir, and Os). However, for a number of industrial hydrogenation processes preference is given to the latter because of their high catalytic activity allowing operations at lower temperature and pressure. The lifetime of these catalysts often extends to several years. Pd, Pt, Ru, and Rh catalysts and

**Table 10**. Effect of the porous structure of supports on the activity of Ni catalysts in the hydrogenation of benzene and acetone.

| Entry | Catalyst or support | $S_{sp}$ /$m^2$ $g^{-1}$ | Total porosity /$cm^3$ $g^{-1}$ | Microporosity /$cm^3$ $g^{-1}$ | Rate constant of benzene hydrogenation /$h^{-1}$ $cm^{-3}$ | Degree of acetone conversion (%) |
|---|---|---|---|---|---|---|
| 1 | $Al_2O_3$-1 | 170 | 0.59 | 0.10 | – | – |
| 2 | $Ni-HPC_2/Al_2O_3$-1 | – | – | – | 0.40 | 80 |
| 3 | $Ni-HPC_5/Al_2O_3$-1 | – | – | – | 0.12 | 60 |
| 4 | $X_1$ | 193 | 0.42 | 0.11 | – | – |
| 5 | $Ni-HPC_2/X_1$ | – | – | – | 0.86 | – |
| 6 | $X_2$ | 214 | 0.45 | 0.14 | – | – |
| 7 | $Ni-HPC_2/X_2$ | – | – | – | 1.16 | 20 |
| 8 | $X_3$ | 201 | 0.51 | 0.20 | – | – |
| 9 | $Ni-HPC_2/X_3$ | – | – | – | 1.44 | 12 |

bimetallic systems are of special interest. The use of special supports makes it possible to bring the content of noble metals down to 0.01% – 0.005% and thus make catalysts less expensive, while preserving their qualities.[154–157]

Modern physicochemical methods allow the investigation into the mechanism of action of these catalysts, optimisation of their composition, and development of methods for controlling the metal dispersity on the support surface. Some catalysts based on noble metals are resistant to poisoning with S- and N-containing compounds.[158, 159]

## 1. Hydrogenation of CO

A number of studies (see, *e.g.*, Refs 160 — 163) showed that supported Pt, Pd, Ir, Ru, and Rh catalysts allow one to bring about the methanation of CO under atmospheric pressure. Hydrogenation of CO under elevated pressure in the presence of $Pt/Al_2O_3$, $Pd/Al_2O_3$, and especially $Ru/Al_2O_3$ and $Rh/Al_2O_3$ (in contrast to Ni-containing catalysts) leads to the formation of alcohols and other oxygenated compounds [164–166]

$$CO + 2H_2 = CH_3OH,$$

$$2CO + 4H_2 = C_2H_5OH + H_2O,$$

$$2CO + 3H_2 = CH_3CHO + H_2O.$$

The Fischer – Tropsch synthesis may be also carried out on $Ru/Al_2O_3$ and Ru catalysts on specially selected supports to produce higher ($C_5 – C_{20}$) hydrocarbons (with selectivity up to 81%) as well as methane, $C_1 – C_5$ alcohols, and $C_{21} – C_{40}$ hydrocarbons.[167–170]

$$nCO + 2nH_2 \longrightarrow [-CH_2-]_n + nH_2O,$$

$$2nCO + nH_2 \longrightarrow [-CH_2-]_n + nCO_2.$$

Industrial processes (Sasol-II, SMDS, and Gulf Badger) on Ru-containing catalysts allow selective formation of a diesel fraction of synthetic liquid fuel or higher paraffins the cracking of which affords high-quality diesel and rocket fuels.[167, 170]

During the period 1987 – 1990, the catalytic activity of platinum group metals on supports in the reaction of CO hydrogenation, its mechanism and kinetics were systematically studied.[117, 118, 163] The dispersities (mean size of metal particles, $d_{mean}$) of the catalysts studied, their activities ($k$), and selectivities are presented in Table 11.

**Table 11**. Certain characteristics of different metal catalysts for the CO methanation ($p_{CO}$ = 20 kPa, $p_{H_2}$ = 50 kPa, $T$ = 275 °C).

| Catalyst | $d_{mean}$ /nm | $10^7\,k$ /mol m$^{-2}$ s$^{-1}$ | Selectivity of methane formation (%) |
|---|---|---|---|
| $Ru/Al_2O_3$ | 4.4 | 6.7 | 87 |
| $Rh/Al_2O_3$ | 2.5 | 5.5 | 94 |
| $Ni/Al_2O_3$ | 2.4 | 4.7 | 96 |
| $Pt/Al_2O_3$ | 3.9 | 0.4 | 99 |
| $Ir/Al_2O_3$ | 6.8 | 0.2 | 100 |
| $Pd/Al_2O_3$ | 5.0 | 0.1 | 100 |

As seen in Table 11, the specific catalytic activity decreases and the selectivity increases in the series Ru → Rh → Ni → Pt → Ir → Pd. The catalytic activity decreases as $q_{CO}$ increases.[163] The $q_{CO}$ values determined from kinetic data increase in the following series: Ru < Rh < Ni < Pt ≪ Ir < Pd.[161, 171] On the whole, the specific catalytic activity of platinum group metals and nickel is lower the larger the size of the metal particles (*cf.* Table 11).

The effect of the phase structure of the support ($Al_2O_3$) was studied for Rh catalysts.[172] Rhodium was deposited on δ-, θ-, and α-$Al_2O_3$ with specific surfaces from 5 to 90 m$^2$ g$^{-1}$. In these catalysts, rhodium was found to be present in three forms: encapsulated, strongly interacting, and non-interacting with the support. The maximum extent of dispersity (11%) was reached on α-$Al_2O_3$ at low Rh content (< 1 μmol m$^{-2}$). At higher Rh content (> 1 μmol m$^{-2}$), the extent of dispersity was below 3%. The activity of a catalyst is enhanced if α-$Al_2O_3$ is used as a support, if $Al_2O_3$ is treated with water vapour prior to Rh deposition, and if the content of deposited rhodium is low.

## 2. Hydrogenation of carbonyl compounds

The similarity of the processes underlying hydrogenation of CO and carbonyl compounds on platinum group metals was reported in different studies.[161, 167–171] The character of the dependence of specific catalytic activity on the heat of adsorption of the reactant proved to be nearly the same in both cases. The same holds for the influence of dispersity: the heat of adsorption of reactants increases with a decrease in the size of crystals leading to a lower catalytic activity. The mechanisms underlying the hydrogenation of CO and acetone were supposed to be similar (the Langmuir – Hinshelwood mechanism):

$$1)\ CO + Z \rightleftharpoons ZCO,$$

$$2)\ H_2 + 2Z \rightleftharpoons 2ZH,$$

$$3)\ ZCO + ZH \longrightarrow ZCOH + Z,$$

$$4)\ ZCOH + ZH \longrightarrow \text{hydrogenation products}$$

and

$$1')\ (CH_3)_2CO + Z_a \rightleftharpoons Z_a\cdot OC(CH_3)_2,$$

$$2')\ H_2 + 2Z_H \rightleftharpoons 2Z_HH,$$

$$3')\ Z_a\cdot OC(CH_3)_2 + Z_HH \longrightarrow Z_a\cdot HOC(CH_3)_2 + Z_H,$$

$$4')\ Z_a\cdot HOC(CH_3)_2 + Z_HH \longrightarrow \text{hydrogenation products}$$

($Z$, $Z_a$, and $Z_H$ are the catalyst active centres).

The limiting stages are the addition of the first hydrogen atom to an adsorbed CO molecule or to the >CO group of acetone, respectively, with the formation of a 'semi-hydrogenated' reactant form.

However, certain differences also exist: in the CO hydrogenation, the most active catalyst is Ru, while the hydrogenation of carbonyl compounds is best catalysed by Pt. Some investigators believe [167–171] that the reason for this difference consists in the stronger binding of C and O atoms ($q_{>CO}$) in a complex of the type



compared to the carbonyl compound binding ($q_{CO}$) in the complex



and thus $q_{>CO,\,opt} < q_{CO,\,opt}$. According to approximate estimates, $q_{>CO,\,opt} \simeq 20$ kJ mol$^{-1}$ and $q_{CO,\,opt} \simeq 100$ kJ mol$^{-1}$. These differences are reflected in the series of catalytic activity and selectivity. Table 12 presents data on the dispersity of metals of the platinum group and nickel deposited on $Al_2O_3$ and their specific activities in the acetone hydrogenation. The specific activities of catalysts with similar metal dispersion decreases in the order: Pt > Ir > Rh > Ni > Ru > Pd. The position of individual metals in this series depends on both their chemical nature and the dispersity. Hydrogenation of the carbonyl group of a ketone is a structure-sensitive reaction. This means that the probability of multipoint adsorption of complex molecules and the rate of their hydrogenation depend on the size, shape, and arrangement of microcrystals on the support. Possibly, the adjacent sites of the support surface take part in the substrate activation due to hydrogen spillover.[165]

**Table 12**. Specific activity of some catalysts in the acetone hydrogenation reaction and the deposited metal dispersity.

| Catalyst | $d_{mean}$ /nm | $10^7 k$ /mol m$^{-2}$ s$^{-1}$ | $q_{CO}$ /kJ mol$^{-1}$ |
|---|---|---|---|
| $Pt/Al_2O_3$ | 3.9 | 44 | 12 |
| $Ir/Al_2O_3$ | 6.8 | 11.7 | 20 |
| $Rh/Al_2O_3$ | 2.5 | 7.7 | 15 |
| $Ni/Al_2O_3$ | 2.4 | 7.5 | 85–25 |
| $Ru/Al_2O_3$ | 4.4 | 700 | 30 |
| $Pd/Al_2O_3$ | 5.0 | 0 | – |

## 3. Hydrogenation of unsaturated hydrocarbons

In some cases, noble metals rather than nickel are preferred as catalysts for the hydrorefining of motor fuels (dearomatisation, hydrogenation of alkenes).[29,40] Catalysts based on noble metals are more active and more resistant to poisoning by sulfur compounds. Platinum and palladium deposited on $Al_2O_3$ are easily deactivated at a sulfur concentration below 1 ppm;[173] however, their resistance to sulfur poisoning increases on acidic supports, such as zeolites.[158,159] For instance, 98% of the products of dodecane hydrocracking are alkanes on Pd/LaY under $H_2S$ pressure of 63 kPa, *i.e.* when all palladium would be expected to pass to PdS; the catalyst activity and selectivity remain virtually unaltered.[159] Such an unusual behaviour of this noble metal is explained by the SMSI effect or changes in the electronic state of palladium upon its interaction with the acidic centres of zeolite.[158]

Platinum catalysts are prepared by ion exchange or impregnation of the support with a solution of $Pt(NH_3)_4Cl_2$; its cation binds to an acidic centre of zeolite $\equiv Al-O^-$. The next important stage consists of the formation of centres $2(\equiv Al-O^-)Pt^{2+}$ upon calcination in air. On subsequent reduction with hydrogen, platinum becomes involved in clusters of the type $m(\equiv Al-O-H)\cdots Pt_n$. The clusters are in close contact with strong acidic centres, which makes possible the transfer of electrons from this noble metal and leads to the formation of electron-deficient metal particles ($Pt^{\delta+}$), which are responsible for the specific properties of this catalyst.[174]

In most cases, hydrogenation is conducted on supported palladium catalysts. Table 13 presents the data from studies of the hydrogenation reactions of CO, aldehydes, and unsaturated hydrocarbons on $Pd/TiO_2$ catalysts prepared by different methods and differing in the size of particles and the active surface of the metal.[176]

The data in Table 13 indicate that the rates of CO hydrogenation and low-temperature hydrogenation of propionaldehyde to propanol increase with the Pd dispersity. However, in the hydrogenation of the C=C double bonds in ethylene, butadiene, and acrolein the reverse order of activity is observed, being particularly noticeable in the hydrogenation of the conjugated bonds of butadiene.

The relationship between the catalytic properties of supported palladium and its dispersity is widely discussed in the literature.[174–184] In some reports, this phenomenon is explained by changes in the electronic state of Pd resulting from the SMSI effect,[175,179] while in others, by the participation of both the catalyst and the support in the reaction.[180] Table 13 shows three Pd catalysts on the same support ($TiO_2$), which possess different activities and selectivities. Therefore, according to Barbier *et al.*,[173] the reason for the differences should be sought in the properties of the particles of palladium itself: in variations of their size, shape, electronic structure, and the nature of their interaction with the molecules subject to hydrogenation. For example, in the adsorption of CO an electron is transferred from Pd to CO, while in the adsorption of ethylene it is transferred in the opposite direction. This results in inverse dependences of the catalytic activity of $Pd/TiO_2$ on the degree of metal dispersity in different hydrogenation reactions.

Highly dispersed palladium is more active in the hydrogenation of electron-acceptor compounds, whereas the low dispersed palladium is more active in the hydrogenation of electron-donor compounds. As was shown above (see Table 11), $Pd/Al_2O_3$ is the least active catalyst of CO methanation. The metal in bulk is also weakly active in this reaction.[181] Consequently, in $Pd/TiO_2$, palladium forms clusters or small particles which are endowed with special properties different from those of bulk Pd or Pd on $Al_2O_3$. Of all the catalysts listed in Table 13, the strongest Pd–support interaction may be expected for the first specimen, which is characterised by a well-developed active surface and small particle size. In this case, an effect of the SMSI type is possible.

## 4. Bimetallic and modified catalysts

Considerable interest arose in bimetallic catalysts on supports in connection with the development of sulfur-resistant hydrogenation catalysts based on noble metals. For example, combination of Pt and Pd deposited on zeolite is known [183,184] to enhance sulfur tolerance, the optimum Pt : Pd ratio being equal to 1. The support used was zeolite of the Y type with a high Si/Al ratio (Shell), and mordenites, borosilicates, and Y- and β-zeolites (Amoco).

The Haldor Topsøe company has developed two types of catalysts for the two-stage hydrotreating of petroleum fractions: $Ni-Mo/Al_2O_3$ for the first stage and TK908 containing a supported noble metal for the second stage.[185] The latter was in operation for 5600 h and the extent of its deactivation was less than 1% after 1000 h, despite the fact that the content of sulfur in raw materials reached 1000 ppm and that of nitrogen reached 50 ppm.

Ru–Pd catalysts prepared by impregnation of a support with salts of both metals are highly active. These catalysts were used to study the hydrogenation of benzene.[186]

Bastiaux *et al.*[187] described in detail a new approach to the preparation of highly selective bimetallic catalysts for the hydrogenation of alkynes and dienes in the hydrorefining of pyrolysis gases and petroleum fractions. Industrial Pd catalysts were substantially upgraded by promoting them with a second metal. The choice of the second metal promoter was made on the basis of modern theories of homogeneous catalysis and of current concepts of changes in ligand mobility in organometallic compounds.[188] Alkanes, alkenes, and alkadienes localised on the surface of Pd catalysts may be regarded as ligands which form strong bonds with palladium in the absence of promoters, thus

**Table 13**. Mean activity (catalyst turnover) of different $Pd/TiO_2$ catalysts in the hydrogenation of CO, aldehydes, and alkenes. [176]

| Catalyst characteristics | | | | Mean catalyst activity in hydrogenation | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| [Pd] (%) | $S_{sp}$ m$^2$ g$^{-1}$ | $d$ /nm | H : Pd | CO (methanation) | CO in $CH_3OH$ (230 °C) | C=O bond in propionaldehyde (80 °C) | $C_2H_4$ (80 °C) | C=C bond in acrolein (80 °C) | $C_4H_6$ (80 °C) |
| 5.5 | 207 | 4.5–6.5 | 0.32–0.67 | $7.3\times10^{-4}$ | $4.3\times10^{-4}$ | 0.16 | 380 | 0.09 | 150 |
| 5.2 | 9 | 186 | 0.17 | $2.8\times10^{-4}$ | $4.0\times10^{-5}$ | $4.5\times10^{-3}$ | 500 | – | 680 |
| 4.4 | 9 | 295 | 0.067 | $5.5\times10^{-4}$ | 0 | $4.5\times10^{-3}$ | 580 | 0.4 | $1.05\times10^{3}$ |

decreasing the catalyst's activity. The strength of the alkyl–metal bond may be reduced by the addition of an electron-donor compound or a metal promoter which favours higher selectivity of acetylene hydrogenation.[187] New procedures for the preparation of highly selective bimetallic hydrogenation catalysts with controlled dispersities were developed using recent progress in the field of inorganic synthesis and synthesis of organometallic compounds.[189,190] Higher yield of the target product and higher stability of catalysts are achieved by modification of the electronic properties of palladium by the second metal. This approach was employed to prepare the industrial catalyst LT-279 for the selective hydrogenation of acetylene in an ethane–ethylene fraction.[187]

As noted above, the selectivity of acetylene hydrogenation may be considerably increased by preparing Pd catalysts on supports in the form of active film structures of the cermet type.[99] In this case, the electronic properties of palladium are modified in a different way, namely, due to the formation of a surface catalyst layer with incorporated modifying oxide additives ($Al_2O_3$). To this end, a simple technique may be used, such as impregnation, which is inapplicable for the production of bimetallic catalysts. The latter are synthesised by making recourse to a more complex technology using, *e.g.*, organometallic compounds or vapour condensation of two metals on a support.[187]

Film-type Pd catalysts modified with $Al_2O_3$ in their surface layer contain 0.1%–0.3% of Pd. They are thermostable and may be subjected to oxidative regeneration. Metal particles are formed in them on the surface of $\gamma$-$Al_2O_3$ supplemented with a thermostable alumina oxide in the ratio $Pd : Al_2O_3 = 1 : 1$. Alteration of Pd properties leads to higher catalytic activity in the reaction of acetylene hydrogenation, which allows one to conduct it at low temperature (30 °C), low $H_2 : C_2H_2$ ratio (2 : 1), and high flow rates (up to 10 000 $h^{-1}$), with a substantial increase in the selectivity of $C_2H_2$ hydrogenation, *i.e.*, the same effects as with bimetallic catalysts. Modification of film-type palladium catalysts is brought about by adding very small quantities of oxide ($Pd : Al_2O_3 = 1 : 1$), and the procedure for their preparation is much simpler than that of bimetallic catalysts.

As for the selectivity of acetylene hydrogenation, the $Al_2O_3$-modified Pd (0.1%Pd) is more than twice as effective as its industrial analogue MA-15 (0.5%Pd).[99] On a bimetallic LT-279 catalyst, transformation of acetylene increases by no more than 10%–20% compared to that on a common Pd hydrorefining catalyst.[187]

Selective hydrogenation of unsaturated hydrocarbons can be performed on new highly dispersed $Pt/MoO_3$ and $Pt/WO_3$ catalysts in which the metal particles interact on the surface with the modified support.[152] The ultradispersed $MoO_3$ and $WO_3$ particles obtained in a plasma reactor are reduced in a stream of hydrogen at 300 °C. Subsequent interaction with Pt or Pd leads to hydrogen bronzes, which serve as hydrogen reservoirs for hydrogenation.[191,192] The hydrogen bronzes are formed upon deposition of 0.2% Pt on $MoO_3$ or 0.1% Pt on $WO_3$ owing to spillover of $H_2$ from the metal centres to the support under the hydrogenation conditions. This results in changes in the specific surface and the size of particles that form the centres active in the hydrogenation of alkenes. The molybdenum and tungsten bronzes themselves (without hydrogen) can also catalyse ethylene hydrogenation.[193]

## V. The mechanism of hydrogenation on metal catalysts

The mechanism of catalytic hydrogenation, in particular the sequential formation of different surface compounds, has been reviewed recently.[194] Hydrogenation is assumed to involve atomic hydrogen formed upon dissociation of $H_2$ on metals, such as Ni, Pt, Pd, and others. This assumption is confirmed by an intense isotope exchange

$$H_2 + D_2 \rightleftharpoons 2HD$$

and formation of monodeuterioethane $C_2H_5D$ upon deuteriation of ethylene. On oxides, in particular on ZnO, deuterioethane $C_2H_4D_2$ is formed from ethylene, which indicates the participation of molecular hydrogen in this reaction. However, other data[195] point to the possibility of participation of both atomic and molecular hydrogen in the hydrogenation on metals.

Numerous forms of adsorbed alkenes were detected on the surface of metals that were found to compete for the active centres. Strongly bound forms of the type $CH_3-CH=M$, $CH_3-C\equiv M$, *etc.* are hydrogenated at high temperatures, whereas at low temperatures only weakly bound forms of the $\pi$-type and $\pi$-allyl complexes undergo hydrogenation.

The hydrogenation rate may be varied by regulating the strength of alkene adsorption. For example, modification with alkylsilanes increases the activity of ZnO 20- and 150-times in the hydrogenation of butadiene and pentadiene, respectively.[195] This is explained by a steric effect: bulky alkylsilanes prevent strong adsorption of dienes, but do not hinder hydrogen adsorption.

It is suggested that the centres of hydrogen activation involved in hydrogenation are localised on the metal surface. Therefore, the larger the surface of a metal the higher should be its catalytic activity. If the size of metal crystallites has no effect on the specific activity of a catalyst, the catalysed reaction is called structure-insensitive. The hydrogenation of the C=C bond in alkenes is an example of such reactions. On the contrary, the hydrogenation rates of an aromatic ring, the C=O and C≡C bonds, and conjugated compounds of the butadiene type depend on the metal dispersity and hence such hydrogenations are regarded as structure-sensitive reactions.

Investigation of hydrogenation of cinnamaldehyde on $Ru/Al_2O_3$ showed a decrease in the specific rate constant for the C=C bond hydrogenation with an increase in the metal dispersity.[196] This indicates that this reaction requires a planar adsorption of substrate, *e.g.*, in the form of a $\pi$-complex. At the same time, the rate constant for the C=O bond hydrogenation increased with increase in the metal dispersity. Evidently, this reaction requires point-type adsorption ($Ru\cdots O=C\lhd$). The adsorption coefficient of the C=O bond of cinnamaldehyde is independent of dispersion, while the adsorption coefficient of the C=C bond decreases with an increase in the metal dispersity.

Apparently, intermediate semi-hydrogenated forms can manifest properties of free radicals ($C_2H_5^{\bullet}$ from $C_2H_4$, $C_3H_7^{\bullet}$ from $C_3H_6$, *etc.*).[197]

Small palladium particles with a size < 2.5 nm (Pd/MgO, $Pd/Al_2O_3$, $Pd/SiO_2$, Pd films and Pt black) are less active than larger particles,[95,198–200] and they become totally inactive when their size is < 1 nm. This is explained by the fact that very small particles cannot dissolve hydrogen. Sintering of particles leads to enhancement of the catalyst's activity and selectivity in the hydrogenation of unsaturated compounds.

The hydrogen necessary for the hydrogenation can be accumulated not only on the surface but also in the bulk of the metal. The properties of the surface- and bulk-absorbed hydrogen differ considerably. For example, in the hydrogenation of CO and $CO_2$ on $Pd/Al_2O_3$, Pd black, and Pd foil the bulk hydrogen favours formation of oxygenated compounds, $CH_3OH$ and $CH_3CHO$, while the surface hydrogen favours formation of $CH_4$ and other hydrocarbons.[201]

Other phases of a complex catalyst can also absorb hydrogen and deliver it rapidly to the compound subject to hydrogenation. Hydrogenation reactions often require the activation of both hydrogen and the compound to be hydrogenated. The latter process can be brought about on another phase. The unsaturated compound can also be localised on the metal, although covering of the surface of the metal prevents adsorption of $H_2$ and hampers the delivery of hydrogen in quantities necessary for hydrogenation. Hydrogenation can occur as a result of alternating interactions of different components of a catalyst with hydrogen and the compound to be hydrogenated and hydrogen spillover from

one component to another. The latest data on hydrogen spillover have been reviewed recently.[202]

Hydrogen exchange between the metal phase and the support occurs with participation of acidic centres of the support. This was proved by experiments on the poisoning of $Pt/Al_2O_3$ catalysts with ammonia under the conditions of butadiene hydrogenation.[203] The results are interpreted by the authors as a redox process

$$Pt^0 + (Al-OH) \longrightarrow (Al-O)^{n-} + Pt^{n+} + \tfrac{1}{2}H_2.$$

The increase in the catalyst crystalline lattice parameter in the course of hydrogenation may be regarded as an indirect evidence of hydrogen dissolution. The use of neutron diffraction revealed the intercalation of hydrogen into the ZnO phase in CO hydrogenation on a Cu–ZnO catalyst.[204] Such an intercalation leads to the formation of a solid solution of Cu in ZnO in which half of the copper ions are replaced by protons. Carbon monoxide is adsorbed on copper, while hydrogen, though also being activated on copper, is involved in the hydrogenation from the subsurface ZnO layer.

Neutron diffraction also revealed the dissolution of hydrogen in the $CuCrO_2$ catalyst.[205] The defects $\square_{Cu^{2+}}$ stabilise the dissolved hydrogen. The catalyst has in its bulk two types of hydrogen: atomic hydrogen H in the lattice interpoint space and hydrogen in the form of the OH groups resulting from $Cu^{2+}$ exchange for $H^+$.

The intercalation of hydrogen into the lattice of $CeM_xO$ catalyst (M = Cu and Ni; $0 < x < 5$) was proved by X-ray, XPES, EPR, and DTG methods.[205] The intercalation of H atoms and reduction of $Ce^{4+}$ to $Ce^{3+}$ results in the extension of the $CeO_2$ lattice:

$$2Ce^{4+} + 2O^{2-} + H_2 \longrightarrow 2Ce^{3+} + 2OH^-,$$

$$2OH^- \longrightarrow H_2O + O^{2-} + \square,$$

$$H_2 + O^{2-} + \square \longrightarrow OH^- + H^-,$$

$$Ni^{2+} + O^{2-} + H_2 \longrightarrow Ni^0 + H_2O + \square,$$

$$2Ce^{4+} + Ni^0 \rightleftharpoons 2Ce^{3+} + Ni^{2+}.$$

In the above consideration of Ni supported catalysts, we repeatedly mentioned the existence of two types of active centres on the surface: metallic (Ni) and oxidised ($Ni^{2+}$) centres. Different centres are already formed in the preparation of a catalyst, *e.g.*, upon incorporation of NiO into the lattice of $\gamma$-$Al_2O_3$. Nonmodified catalysts with a Ni content of 3.2%–4.4% were studied by the method of TPR of carbon monoxide.[206] The degree of Ni reduction at 500 °C did not exceed 25%. Two types of CO adsorption were observed, which followed from the two peaks of methane formed upon hydrogenation. The methanation proceeds according to the following scheme:

$$\begin{array}{l} CO\,(A) + 3H_2 \xrightarrow[E = 51]{} CH_4\,(A) + H_2O \\ \uparrow E < 51 \\ CO\,(B) + 3H_2 \xrightarrow[E = 145]{} CH_4\,(B) + H_2O \end{array}$$

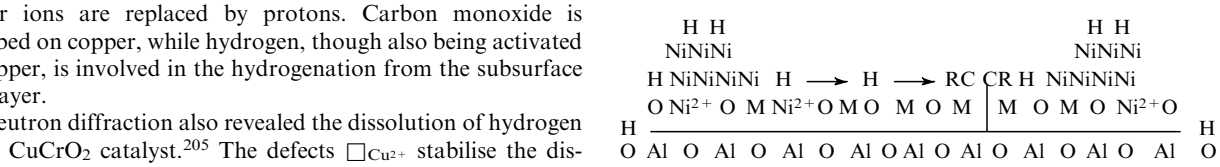
(values of $E$ are given in kJ $mol^{-1}$).

The conversion of CO (B) into CO (A) at temperatures below 250 °C proceeds very slowly, but upon completion of this transition, CO (A) is rapidly hydrogenated at 142–247 °C. Thus, the rate of methanation on low-percentage $Ni/Al_2O_3$ catalysts is determined by the rate of B → A conversion, *i.e.* of Ni atoms interacting with NiO, into the Ni centres on the metal surface. Hydrogenation of CO (B) requires a considerably higher activation energy than that of CO (A).

The presence of centres with Ni in different oxidation states is also characteristic of HPC-modified Ni catalysts on supports. We consider here a possible hydrogenation mechanism on such catalysts.

The hydroxylic cover formed on an HPC-modified surface differs substantially from that of the initial support and a binary Ni catalyst. It is homogeneous and depends on the type and concentration of the modifier and metal concentration.

Heteropolycompounds (HPC) are directly involved in the formation of metal-containing active centres. Judging from electron microscopy (see Fig. 2), at the optimum HPC concentration the active phase is regularly distributed thus creating seeds of Ni microcrystal formation and stabilising the metal formed upon reduction. Nickel particles are distributed in the defect layer of the modifier where $Ni^{2+}$ can also be present. They have no direct contact with the support and are exceptionally thermostable: the specific surface of the metal is not changed up to 600 °C. Hydrogen is adsorbed on the Ni surface and diffuses to the modifier (M) surface following the spillover mechanism with the possible participation of the hydroxy groups of the modifier, as shown below (the arrows indicate the direction of spillover):




An unsaturated organic compound seems to be adsorbed on the modifier phase. Thus, the functions of the two catalyst's phases *viz.*, Ni and HPC, are different. Presumably, $Ni^{2+}$ ions formed from the metal are incorporated into the HPC structure. The initial activation of hydrogen takes place on the Ni particles:

$$2Ni + H_2 \longrightarrow 2NiH \text{ (or } 2Ni + 2H).$$

Then a reversible reaction occurs.

$$2H + Ni^{2+} \rightleftharpoons Ni + 2H^+.$$

This results in the formation of very small Ni particles, which in some cases cannot be detected even by electron microscopy. HPC can interact with the organic compound with transfer of the accumulated hydrogen

$$2H^+ + R + Ni \longrightarrow RH_2 + Ni^{2+}.$$

Probably, the active hydrogenation centres of unsaturated compounds and aromatics differ from those of CO and carbonyl compounds.

## VI. Carbide catalysts

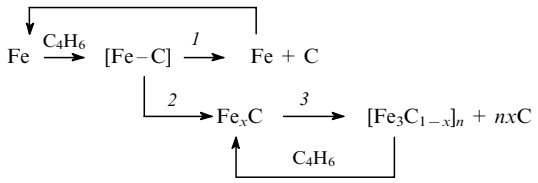
Boudart and Levy[207] were among the first investigators to study the catalytic properties of carbides. They showed that $Mo_2C$ possessed an unusually high catalytic activity close to that of platinum in reactions of hydrogenation and isomerisation. Nearly the same activity was found in tungsten carbide. These compounds are formed upon reactions of Mo or W salts or oxides with hydrocarbons. For example, a powder of tungsten carbide with a specific surface of 3.5 $m^2\ g^{-1}$ can be obtained in the reaction of $WCl_5$ vapour with butane at 1.3 kPa and 1340 °C.[208] On the surface of tugsten carbide there is polymeric carbon, which decreases its hydrogenation activity. Adsorption of oxygen facilitates adsorption of $H_2$ by inducing the formation of islets of tungsten bronze, $H_xWO_3$, on the surface which is possibly a hydrogen reservoir. Under the conditions of catalysis the $WO_3$ oxide is not reduced. Thus, the catalytic activity is apparently manifested not by the carbide itself, but rather by a biphasic structure.

The interaction of $MoO_3$ with a $CH_4 + H_2$ mixture at 630 °C produces a powder of $Mo_2C$ of hexagonal structure with a specific surface ranging from 50 to 100 $m^2\ g^{-1}$.[209] This also has a polymeric carbon on its surface which is removed under the hydrogenation conditions. A metastable carbide $\alpha$-$Mo_2C_{1-x}$ ($x = 0-0.5$) with a specific surface of 200 $m^2\ g^{-1}$ and particle size of 3 nm was prepared in the TPR mode by the reaction of $MoO_3$ with ammonia and methane.[210] First, the reaction $Mo_3 + NH_3$ yields nitride $Mo_2N$, which is then transformed into

carbide upon reaction with a $CH_4 + H_2$ mixture. When some platinum is added to $MoO_3$, the temperature of the synthesis is reduced by 100–150 °C and a thermodynamically stable but less active $Mo_2C$ is formed. Carbides can also be synthesised by carbidisation of the supported oxide $MoO_3/Al_2O_3$.[211]

It is also known [210,211] that in the reactions involving hydrocarbons the carbides are precursors of the 'coke', *i.e.*, graphite-like formations, which cover the surface of the catalyst and poison it.

The coke results from realisation of the so-called carbide cycle.[212,213] For example, the interaction of Fe with $C_4H_6$ involves the following transformations:




Depending on the conditions, either the metal phase or the carbide phase may be stable. Pathway (*1*) is the catalytic formation of carbonaceous deposits on the metal phase; pathway (*2*) is the transformation of a carbide-like phase (Fe–C) into the genuine carbide phase *via* an intermediate carbide-like compound; pathway (*3*) is the formation of carbon on the stable carbide phase. The carbide phase is stable at low temperatures, while at high temperatures the metal phase is stable, *i.e.*, the pathway (*1*) is predominant.

Molybdenum carbide was used to prepare catalysts for the hydrodesulfurisation.[214] The surface layer was sulfidised, while the carbide remains the support.

Numerous hydrogenation reactions occur at low temperatures, where the carbide phase is stable. This raises the question whether one should seek to prepare the carbide phase with a large specific surface in the synthesis of catalysts for hydrogenation. This problem has been investigated using iron and nickel catalysts for the CO hydrogenation (the Fischer–Tropsch synthesis).[85,87,215–218]

The most detailed studies were concerned with the catalysts based on the oxides $\alpha$-$Fe_2O_3$ or $\gamma$-$Fe_2O_3$ as the initial phase.[87,216,217] The use of $\alpha$-$Fe_2O_3$ allowed the preparation of an active catalyst yielding basically methane and a small propotion of alkenes in the $CO + H_2$ reaction at 250–300 °C. The analysis of the phase composition of this catalyst showed that after the reaction it contained equimolar quantities of $\varkappa$-$Fe_5C_2$ and $Fe_3O_4$. On the contrary, the use of $\gamma$-$Fe_2O_3$ led to a system totally inactive as a catalyst composed of $Fe_3O_4$, $Fe_3C$, and $\alpha$-Fe. During catalyst preparation according to the Bell–Boudart reaction, a considerable quantity of $CO_2$ is released; however, under stationary catalysis conditions hardly any release occurred, which was indicative of the lack of carbon formation.

An investigation into the catalytic activity together with the application of X-ray phase analysis *in situ* and Mössbauer spectroscopy made it possible to trace the sequence of catalyst formation based on $\alpha$-$Fe_2O_3$ under the reaction conditions used.[216] First, $\alpha$-$Fe_2O_3$ is transformed into a defective magnetite $Fe_3O_4$ possessing low activity in the hydrogenation reactions. A sharp increase in the activity and selectivity (for $C_2$–$C_4$ hydrocarbons) occurs at the moment the $\varkappa$-$Fe_5C_2$ carbide phase appears. With an increase in the $\varkappa$-$Fe_5C_2$ : $Fe_3O_4$, ratio the catalytic activity of $Fe_3O_4$ steadily increases, while the selectivity of alkene formation passes through a maximum.

Electron microscopy studies [87,216] showed that the general morphology of particles remained unaltered under the reaction conditions. The particles are overgrown with amorphous carbon; however, the latter does not seem to block the active centres. The size of the $Fe_3O_4$ and $\varkappa$-$Fe_5C_2$ particles is $\sim$ 60 nm and $\sim$ 25 nm, respectively. The most interesting finding is evidence of intercalation of the carbide formed in the $Fe_3O_4$ lattice. In addition to electron microscopy, the electronographic analysis of selected sites and the anisotropy of the Mössbauer spectra confirm the formation of such a structure. The active centres of CO hydrogenation were supposed to be localised at the carbide–oxide interface. The higher the proportion of intercalated carbide the more extended the interface and the higher the catalytic activity. The maximum yield of alkenes is formed at an equal percentage of $Fe_3O_4$ and $\varkappa$-$Fe_5C_2$ phases.

Jung and Thomson [219] undertook an analogous study of the formation of CO hydrogenation catalysts based on $\alpha$-$Fe_2O_3$ using the X-ray phase analysis *in situ*. The results obtained are also in favour of the initial formation of non-stoichiometric magnetite, the establishment of steady-state activity after the appearance of the $Fe_5C_2$ carbide phase, and the formation of magnetite and carbide phases in approximately equal proportions under steady-state conditions. These authors attribute the permanent activity of the catalyst produced to the presence of a single stable carbide phase. In another study,[220] where the initial phase was metallic iron, they detected the formation of a mixture of $\varepsilon'$-$Fe_{2.2}C$ and $Fe_{2.5}C$ carbides.

Investigations into CO hydrogenation by Mössbauer spectroscopy using the system 64% $Fe_2O_3$ + 5% Cu + 1% $K_2O$ + 30% kaolin revealed that under the reaction conditions the oxide $Fe_3O_4$ and carbide $\varkappa$-$Fe_5C_2$ are formed, which were further transformed into $\varepsilon'$-$Fe_{2.2}C$. Rao *et al.*[221] presume that the carbide formation is a necessary but insufficient condition for the manifestation of catalytic activity. A catalyst with the maximum carbide content was not the most active.

An investigation of an Fe–ZSM-5 system by Mössbauer spectroscopy and X-ray phase analysis [217] revealed that the initial catalyst comprised $Fe^{3+}$-containing particles 5–15 nm in size. Treatment with hydrogen reduces 90% of iron to $\alpha$-Fe. Under the conditions of CO hydrogenation, small spinel clusters, goethite $\alpha$-FeOOH and $\varkappa$-carbide were formed. Under the same conditions, in an Fe–Mn–zeolite system small clusters of inverted spinel, $\varkappa$-carbide, and MnO were formed.

In analogous studies of a nickel catalyst for the CO hydrogenation (methanation),[85,87,218] two procedures for preparing the initial NiO phase were considered: (1) a plasmochemical method yielding cubic NiO crystals possessing numerous point defects with the most developed plane (100); (2) decomposition of $NiCO_3$ yielding lamellar crystals with the most developed plane (111). Reduction by hydrogen of the former specimen leads to the epitaxial formation of metallic nickel. Under the conditions of the $H_2$ + CO reaction, polycrystalline carbide $Ni_3C$ is formed in a later stage. This is followed by the formation of a three-phase system metal + carbide + oxide, which is active in the CO methanation. In the specimen prepared by the latter method, the epitaxy on the NiO plane (111) first induces the formation of hexagonal $Ni_3C$ single crystals which correspond in size to NiO crystallites. Upon reaching its critical size, the carbide crystal liberates the NiO surface for the build-up of the next particle. In this case, the metal nickel phase appears only after a temperature increase to 283 °C, which may be due to carbide decomposition. The rate of CO hydrogenation is higher in the latter than in the former specimen; nonetheless, no direct correlation between the reaction rate and the carbide content was found.

The formation of carbides was also observed on a cobalt catalyst in the Fischer–Tropsch synthesis.[222] It occurs under the conditions of CO hydrogenation according to the Boudart reaction. Subsequently, the participation of carbides in the synthesis is possible due to direct interaction with hydrogen or intermediate interaction with water. In the presence of carbides, the selectivity of the process is shifted towards the synthesis of higher hydrocarbons.

Thus, it is systems in which the oxide–carbide phases can be formed under the reaction conditions that are the active hydrogenation catalysts. Most recent studies have shown that the formation of oxycarbide structures favours the reactions with the participation of unsaturated compounds on tungsten and molybdenum carbides.

Many recent studies[223–226] were devoted to the studies of hydrogenolysis of 2-methylpentane, n-hexane, and methylcyclopentene on tungsten carbide WC. This catalyst was synthesised by heating $WO_3$ in a mixture of 20% $CH_4$ + 80% $H_2$ in the TPR mode. In the process of reduction, intermediate species, *viz*., $W_{20}O_{58}$, $W_{18}O_{49}$, and $WO_2$, were produced and a carbon layer was formed. After heating in this mixture at 800 °C for 10 h, the carbon layer disappeared to give way to WC with specific surface 12 $m^2\ g^{-1}$ possessing a biporous structure (the pores 2 nm and 6 nm in diameter predominate). On WC, which is similar in its catalytic properties to Ru, Ir and Ni, cracking and, to a much lesser extent, isomerisation take place in the presence of hydrogen.

According to Leclercq *et al*.,[227] it is advantageous to prepare the tungsten carbide in two stages: first, carbidisation of metallic W or $WO_3$ with a mixture of 20% $H_2$ + 80% $CH_4$ at 650 °C produces $W_2C$ and a small amount of free C

$$2W + CH_4 = W_2C + 2H_2,\ CH_4 \longrightarrow CH_2 + H_2,\ CH_2 \longrightarrow C + H_2,$$

and then WC is formed at 800 °C in the reaction

$$W_2C + CH_4 = 2WC + 2H_2.$$

In the presence of $O_2$ at 100–300 °C a complex mixture containing oxycarbide phases, WC, $W_2C$, $WO_2$, and metallic tungsten is formed.[228] The properties of the catalyst are strongly changed, and it becomes similar to a bifunctional platinum catalyst and selectively accelerates skeletal isomerisation.

The development of procedures for preparing carbides with large specific surface (up to 200 $m^2\ g^{-1}$) should be regarded as an important achievement.[229–233] The hexagonal phase of $Mo_2C$ is formed upon interaction of activated carbon with $MoO_3$ vapour. The unconsumed carbon is burned in the bulk of the carbide and can enhance the mechanical strength of the catalyst grains. According to the XPES data, the surface is covered by carbide alone, though the contact with oxygen leads to the formation of an oxide film. The oxide oxygen cannot be removed from the $Mo_2C$ surface by heating in hydrogen at 850 °C without partial decarbidisation. To avoid this, the catalyst is treated with a mixture of $H_2$ plus a hydrocarbon. Alternatively $Mo_2C$ or WC is impregnated with small quantities of Group VIII metal salts which accelerate decarbidisation.

However, oxygen is not always a poison for carbide catalysts. A discovery was made owing to the accidental aspiration of air into a catalytic installation:[229–233] in the presence of hydrogen, the oxidised $Mo_2C$ catalyses isomerisation of n-hexane into methylpentanes and dimethylbutanes without formation of aromatic compounds. This makes it possible to reform hydrocarbons into high-octane and non-carcinogenic fuel. The most efficient catalyst was obtained by treating the carbide with air for 14 h at 350 °C. This resulted in the formation of an oxycarbide layer on the catalyst surface. According to the results of XPES, the major part of the molybdenum exists in the Mo(VI) state on the surface of this catalyst (in contrast to $Mo_2C$). X-Ray studies showed that its structure corresponds to that of $MoO_3$, but the oxygen vacancies $\square_O$ on the surface are filled with carbon atoms that block the formation of $MoO_2$.[195]

Such an oxycarbide possesses not only good selectivity, but also high activity and resistance to coking. It is 25 times as active as the $Pt/Al_2O_3$ catalyst but, unlike the latter, is little poisoned with the coke and retains its catalytic activity for a long time. The addition of methylcyclopentane to n-heptane results in slow deactivation of the catalyst due to blocking of active centres by the alkenes formed, which are readily hydrogenated. Moderate heating of the catalyst in an oxygen atmosphere is sufficient for its regeneration.[233]

High catalytic activity in the hydrogenation of isopropylbenzene is exhibited by molybdenum oxynitride. In this reaction its activity is increased due to carbidisation:[234] $MoN_{0.7}O_{0.7}$ is transformed into $MoC_{0.27}N_{0.14}O_{0.76}$.

## VII. Mechanochemical treatment of hydrogenation catalysts

In most cases, mechanochemical treatment of solids leads to their fragmentation and the appearance of various defects. Many investigators have used mechanochemical techniques for the treatment of catalysts, since the catalytic activity usually (though not always) increases with the surface area and the number of defects. It is important that the changes obtained are preserved under catalysis conditions.

Moroz *et al*.[235] studied the formation of defects in the mechanochemical treatment of a typical ZnO catalyst in a planetary centrifuge mill using stainless steel balls 0.5 cm in diameter. Electron microscopy and X-ray data showed that short mechanochemical impacts ($\tau < 180$ s) produce insignificant changes in the structure and size of the particles. At 180 s $< \tau <$ 600 s, one observes cracking of crystalline blocks, their mutual displacement, and rotation, relaxation of microdistortions in the direction (001) and their growth in other directions. At 600 s $< \tau <$ 1200 s the crystals begin to undergo disintegration into primary crystalline blocks 5–10 nm in size with the formation of secondary aggregates of globular shape 1000 nm in size along with relaxation of microdistortions arising as a result of crystal breakdown. Thus, the general picture is not reduced to a mere increase in the catalyst surface and defectiveness of its lattice.

Streletskii *et al*.[236] investigated the mechanism of changes induced by mechanical treatment of complex oxides with the perovskite structure. Powders of $BaTiO_3$ and $SrTiO_3$ were subjected to mechanical treatment in an eccentric mill with calorimetric measurement of the absorbed energy dose.[237] The increase in the absorbed energy dose led to an increase in the specific surface from 7–8 to 25 $m^2\ g^{-1}$, a decrease in the coherent scattering range (CSR) from 150 to 20 nm, and to the appearance of microdistortions and point defects (paramagnetic centres with a concentration up to $10^{18}\ g^{-1}$). Each particle of the powder was shown to consist of several CSR blocks, the overall area of CSR being $\sim 60\ m^2\ g^{-1}$. Only a small fraction of the mechanochemical energy is spent in generating the defects preserved after the completion of mechanical treatment. The temperature of sintering of particles after mechanical treatment decreases by 300 °C. When such a treatment is performed in water, the CSR size corresponds to the particle size, while microdistortions are insignificant.

The mechanism underlying the mechanochemical transformations depends on the chemical and electronic properties of solids.[238] In covalent dielectrics, *e.g*. in $SiO_2$, the defects after mechanical treatment are better preserved than in semiconducting metals. The application of mechanochemical techniques in the synthesis of catalysts can result not only in the formation of defects and an increased surface, but also in various chemical effects. In such a way one can prepare, for example, FeAl or FeW alloys, which cannot be formed in the usual processes because of the low mobility of the atoms, and even amorphous alloys. Recourse to mechanochemical treatment is often made in the synthesis of complex oxide systems from oxide mixtures, where the conventional thermal synthesis requires very high temperatures, which are difficult to achieve. Mechanochemical decomposition of salts and hydroxides may be used to prepare oxides with the preservation of the disordered state of their atomic structures.

There are some studies[85,215] of the effect of mechanochemical treatment on the properties of catalysts in CO hydrogenation. We have already mentioned the formation of the two-phase oxide–carbide system in the catalyst based on $\alpha$-$Fe_2O_3$ under the conditions of CO hydrogenation. A catalyst prepared from $\alpha$-$Fe_2O_3$ after its treatment at high pressure with shearing on the Bridgeman anvil was also studied. Such a mechanochemical treatment is known to form a great number of defects. The impact of the reaction medium on the 'defective' specimen is manifested

earlier than on the 'defect-free' one. In the first stage, the defective $\alpha$-$Fe_2O_3$ is rapidly transformed into magnetite, however its catalytic activity is lower than that of the defect-free specimen. Electron microscopy of the defective specimen reveals individual oxide and carbide particles and a small number of intercalated particles. The particle size in this specimen is smaller than that in the defect-free specimen, but the extension of the carbide – oxide interface, which determines the catalytic activity, is also smaller.

The CO hydrogenation reaction was also used for an investigation of the activity of amorphous, highly dispersed Fe – Ni – O alloys prepared by friction between two rapidly rotating discs made of iron and nickel. By modifying the friction conditions, it was possible to prepare an alloy of $Fe_{20}Ni_{20}O_{60}$ composition on the surface of which clusters are formed with a predominantly ionic type of Fe – O bonds, and an $Fe_{30}Ni_{40}O_{30}$ alloy in which, according to XPES and Auger spectroscopy, clusters with covalent-type of Fe – O bonds are prevalent. The former alloy is catalytically active in the CO hydrogenation to $CH_4$ and $C_2$ – $C_4$ hydrocarbons, while the latter proved to be inactive. Under catalysis conditions a non-stoichiometric oxide $Fe_3O_{4-x}$, carbide $FeC_y$ and metallic nickel are formed on the former alloy. The surface of the latter alloy is covered by a nonreactive oxide $FeO_x$, while in its bulk the spinel $NiFe_2O_4$ and a solid solution of iron in nickel are formed.

The formation of active centres of CO hydrogenation is crucially influenced by the type of chemical bonding. Iron carbide and oxide phases exist on the surface of active catalysts, while metallic iron does not take part in the active centre formation. In a binary alloy catalyst, iron is mostly in the oxidised state, while nickel is predominantly in the metallic state. The activation of $H_2$ seems to take place on Ni, whereas the CO activation occurs on $Fe^{n+}$.

The Fischer – Tropsch synthesis was brought about directly in a mechanochemical reactor by grinding the metal mixtures.[239] Grinding allows formation of amorphous alloys $Ni_{40}Zr_{60}$, $Ni_{60}Zr_{40}$, $Pd_{30}Zr_{70}$, $M_{30}Ti_{70}$ (M = Fe, Co, Cu), $M_{30}Ti_{70}$ (M = Ni, Pd), which catalyse the CO hydrogenation. The alloy $Ni_{30}Ti_{70}$ manifests 100% selectivity. Detailed studies of structural changes in Ni – Zr alloys in the course of CO hydrogenation showed that prolonged grinding results in the formation of ZrO, $ZrO_2$, Ni, and possibly $ZrH_2$ and ZrC phases. Zirconium oxides are formed due to CO dissociation on the segregated nickel. Hydrogenation of CO was also studied under the conditions of mechanochemical treatment of Ti, V and Zr hydrides. In contrast with the reaction on amorphous titanium and zirconium alloys, the formation of hydrocarbons on the above-mentioned hydrides proceeds without any induction period. The CO conversion reaches a stationary level and begins to decrease, when the hydrogen content in the metal becomes insufficient for the maintenance of the reaction stoichiometry.

Analogous work was done by Morozova *et al.*[240, 241] Powders of an amorphous alloy $ZrNi_{1-x}$ were treated in a vibrational mechanochemical reactor consisting of a cylindrical steel chamber filled with steel balls 6 – 7 mm in diameter.[242] The amorphous alloy was prepared in the same reactor by mechanochemical fusion of Ni and Zr. Experiments were carried out in the static and flow modes; in the first case, the products were analysed by mass spectrometry, while in the second case, by gas chromatography.

Under conditions of mechanochemical treatment, sorption of hydrogen rapidly increased with the dose of absorbed energy and reached a maximum. The quantity of sorbed hydrogen was approximately proportional to the zirconium content in the alloy. X-Ray phase analysis indicated that the reaction of hydrogen with zirconium and ZrNi yields $ZrH_2$ and $\alpha$-$ZrNiH_2$, respectively. After the termination of mechanochemical treatment, sorption of $H_2$ continued at a decreasing rate until a stoichiometric hydride was formed.

Under these conditions, chemisorption of CO increased proportionally to the absorbed energy and Zr content. It follows a dissociative mechanism and is accompanied by oxidation of Zr

$$CO + Zr \longrightarrow ZrO_xC_y \; (x = y, \; x + y < 1).$$

In addition, reversible sorption of CO occurs, which corresponds to the nickel content. At large doses of absorbed energy, zirconium oxycarbides are decomposed

$$ZrO_xC_y + CO \longrightarrow ZrC + ZrO_2 + C.$$

After saturation of the alloy with hydrogen, *i.e.*, after formation of $ZrH_2$ and $ZrNiH_2$, methane, some ethane and hydrogen are formed under the conditions of mechanochemical treatment in a CO flow:

$$ZrH_2 + CO \longrightarrow ZrO_xC_y + H_2 \longrightarrow ZrHC + ZrO_2 + CH_4,$$

$$\alpha\text{-}NiZrH_2 + CO \longrightarrow ZrHC + ZrO_2 + H_2 + CH_4.$$

After termination of mechnochemical treatment, the formation of methane continues at a decreasing rate. Such treatment may be conducted in the flow of a CO + $H_2$ mixture. In this case, the rate of methane formation is 5 – 10 times lower than that in the stepwise process (in the hydrogenation of CO with dissolved hydrogen) under the same conditions.

In the mechanochemical treatment of a NiZr alloy, graphite also undergoes hydrogenation with formation of methane (and ethane at a high dose)

$$\alpha\text{-}NiZrH_2 + C \longrightarrow ZrHC + Ni + CH_4.$$

Thus, in the process of mechanochemical treatment the dissolved hydrogen acquires mobility indispensable for the realisation of reactions both on the surface and in the bulk of a powder. Interestingly, nickel, which is a typical hydrogenation catalyst, is a ballast in this case, while hydrogen is activated with participation of zirconium. In addition to the inertial process of CO hydrogenation, an inertia-free mechanochemical process leading to the formation of short-lived intermediate compounds takes place on the surface.

## VIII. Sulfide catalysts for hydrotreating

### 1. Preparation of oxide precursors

In the first sections of this review mention was made of the use of Ni – Mo, Ni – W, Co – Mo and Co – W oxide catalysts for the hydrogenation of unsaturated compounds, especially for hydrotreating. However, industrial processes rely most widely on the application of sulfide hydrotreating catalysts prepared from oxide precursors.

The major components of sulfide catalysts for hydrotreating (hydrodesulfurisation, hydrodenitration, hydrodemetalation, hydrogenation of oxygenated and aromatic compounds in petroleum) are as a rule Co (or Ni) and Mo (or W). Nickel is cheaper than cobalt and ensures a higher hydrogenation rate but it favours rehydrogenation, which results in an increased hydrogen uptake and a lower octane number of the products. Tungsten is similar to molybdenum in its catalytic properties, but it is more expensive.

High activity is displayed by ruthenium, but this metal is very costly. The $NiRu/Al_2O_3$ catalyst is 30 times more active than $RuS/Al_2O_3$ in hydrogenation processes.[243]

A great number of studies (see, *e.g.*, reviews [5, 244, 245]) are devoted to the preparation of hydrotreating catalysts, their formation under conditions of catalysis and the mechanisms underlying the relevant reactions. The common practice is to use catalysts deposited on $\gamma$-$Al_2O_3$ or carbon. Catalysts on $\eta$-$Al_2O_3$ are more active than those on $\gamma$-$Al_2O_3$, which is explained by the stronger bonding of $MoO_3$ with $\eta$-$Al_2O_3$ and easier subsequent sulfidisation.[246]

Ammonium molybdate $(NH_4)_2MoO_4$ is a precursor of $MoO_3$. In acidic media, polymolybdates are formed

$$7MoO_4^{2-} + 8H^+ \rightleftharpoons Mo_7O_{24}^{6-} + 4H_2O.$$

At high levels of ammonium molybdate, further condensation takes place

$$Mo_7O_{24}^{6-} + MoO_4^{2-} + 2H^+ \rightleftharpoons [H_2Mo_8O_{28}]^{6-}.$$

At pH > 7, polymolybdates dissociate to recover $MoO_4^{2-}$. These acid-base processes involve the surface of $Al_2O_3$, which is amphoteric in its chemical nature

$$AlOH + 2H^+ \rightleftharpoons AlOH_2^+, \quad AlOH \rightleftharpoons AlO^- + H^+.$$

In order to form polymolybdates in the preparation of catalysts by the impregnation procedure, it is necessary that the pH be kept below the isoelectric point of a given support (3–6 for $Al_2O_3$ and below 2 for $SiO_2$). After impregnation, the catalyst is dried at 250–300 °C and calcined in air at 500–550 °C; the dispersity of $MoO_3$ changes insignificantly. The use of various physical methods (Raman and IR spectroscopy, EXAFS, and others) showed that at typical $MoO_3$ concentrations (10%–12%) the initial molybdates form Al–O–Mo bonds with $Al_2O_3$ and represent two-monolayer-thick islets containing seven molybdenum atoms.[244]

Supports may be impregnated with HPC solutions, *e.g.*, with nickel or cobalt heteropolymolybdates.[247] In this case, however, because of the strong interaction of HPC with the OH groups of $Al_2O_3$ the precursor does not penetrate into the pores, and a 'crusty', rather than regular distribution, of the active component over the support takes place. Thioheteroanions are also used for the preparation of such catalysts.[248]

Another method for the preparation of the Mo–Al–O catalysts is the mechanical mixing of $MoO_3$ and $Al_2O_3$ at 400–500 °C in the presence of water. The system thus formed possesses virtually the same catalytic properties as an $MoO_3$/$Al_2O_3$ contact obtained by impregnation.[244]

A very large specific surface (174–184 $m^2\ g^{-1}$) is characteristic of a catalyst prepared by precipitation of $MoO_3$ on $SiO_2$ in a solution of nitric acid with a mixture of urea and thioacetamide and with subsequent drying at 120 °C and sulfidisation at 400 °C.[249]

The second component ('promoter') is introduced by impregnating the support with cobalt or nickel nitrates; the sequence of impregnation steps may be different. It is assumed[244] that impregnation of the support first with molybdenum and then with cobalt salts favours higher activity. There is an opposite viewpoint however, according to which it is more advantageous to impregnate the support first with cobalt salts or to bring about simultaneous impregnation with Co- and Mo-containing compounds. When $Co^{2+}$ or $Ni^{2+}$ are introduced by ion exchange, it is recommended to do it at low pH after deposition of molybdenum.

A two-stage method for the preparation of a catalyst includes impregnation of γ-$Al_2O_3$ in the fluidised bed with $(NH_4)_2Mo_7O_{24}$ solution at constant pH = 7, calcination in air at 500 °C, then impregnation with nickel or cobalt nitrates until the pores are filled, and further calcination at 500 °C.[250]

Active hydrogenation catalysts are prepared using thiosalts, *e.g.*, by impregnating a support with a mixture of $(NH_4)_2MoS_4$ and $Ni(NO_3)_2$ or $Co(NO_3)_2$ and subsequent heating in a mixture of $H_2S$ and $H_2$ at 400 °C.[251]

Unsupported Co–Mo–S catalysts are obtained by treating $MoO_3$ and $Co_3O_4$ powders with a hot solution of $(NH_4)_2S$ or by mixing solutions of $Co(NO_3)_2$ and $(NH_4)_2Mo_7O_{24}$ followed by addition of $(NH_4)_2S$, drying and calcination. In the latter case, the catalyst contains larger quantity of labile sulfur and is characterised by a higher dispersity of the $Co_9S_8$ phase and activity, though it is deactivated more rapidly.[252, 253]

Lewis *et al.*[254] assume that the catalyst activity depends on the acidity of the support. This is rationalised by the presence of surface OH groups capable of interaction with molybdenum and cobalt salts.

Catalysts are calcined at 400–600 °C, at which temperature the salts are completely decomposed but undesired solid-phase reactions have not yet occurred. According to results obtained by different physical methods,[244] an amorphous $MoO_3$ phase and anions of the $(Mo_7O_{24})^{6-}$ type appear on the surface of $Al_2O_3$ after calcination of Mo–Al catalysts.

Calcination of mixed catalysts leads to the formation of polymolybdates, $MoO_3$, $CoMoO_4$ or $NiMoO_4$, $Co_3O_4$, or NiO, $Al_2(MoO_4)_3$, $Ni(Al_xMoO_{4+1.5x})$ ($x = 0.1-1.0$) and Co or Ni aluminates.[244, 255–258] At low calcination temperatures, the cobalt is mostly in the octahedral coordination. It is with the content of this Co form that the catalyst activity after its sulfidisation correlates. At higher temperatures, intercalation into the $Al_2O_3$ lattice results in the formation of tetrahedral cobalt, which undergoes sulfidisation with more difficulty. Therefore, calcination at temperatures above 600 °C is not reasonable.

Upon calcination, the nickel acquires octahedral coordination and interacts more strongly than cobalt with the $Al_2O_3$ lattice. Chukin *et al.*[259] believe that the formation of nickel or cobalt molybdates or polymolybdates, which can be removed by extraction with water, is beneficial for the subsequent sulfidisation or formation of a mixed NiMo or CoMo phase. The introduction of $NiMoO_4$ prepared beforehand into the Ni–Mo–Al matrix makes it possible to enhance the catalyst activity.

The content of the active component depends on the specific surface of the support. Usually, from 8 mass % to 15 mass % of molybdenum can be deposited on $Al_2O_3$, which corresponds to a specific $Al_2O_3$ surface of $\sim 250\ m^2\ g^{-1}$. The Co : Mo ratio varies from 0.1 to 1.0. The ratio of molybdenum to cobalt or molybdenum to nickel depends on the sequence of impregnation steps and is equal to 2 in the best catalysts.

Active catalysts may be produced by decomposition of cobalt and molybdenum carbonyls on supports.[260, 261]

The maximum effect of promotion of CoMo/γ-$Al_2O_3$ catalyst with $WO_3$ is attained at $W:(W + Mo) = 0.25$. Impregnation of the support first with a tungsten salt solution and then with a cobalt salt solution yields more active catalysts than those resulting from the reverse impregnation order. According to the results of EPR and XPES studies, tungsten favours the alteration of the molybdenum coordination from octahedral to tetrahedral and facilitates its reduction.[262]

## 2. Sulfidisation of oxides

Sulfidisation of Mo/$Al_2O_3$ catalysts at low temperatures leads to the substitution of the oxygen atoms by sulfur

$$Mo^{6+}-O + H_2S \longrightarrow Mo^{6+}-S + H_2O$$

and formation of the bridging bonds Al–O–Mo–SH or Al—O—Mo(S)(S) (Ref. 263).

Each of the species thus formed contains seven Mo atoms. Prolonged sulfidisation at 300 °C leads to the reduction of $Mo^{6+}$ to $Mo^{4+}$ and formation, as follows from electron microscopy data,[244 264, 265] of planar hexagonal $MoS_2$ particles below 3 nm in size that are retained on the surface by the Mo–O–Al bonds and mostly situated normally to the $Al_2O_3$ surface. Sulfur-containing Co–Ni heteropolycompounds are formed in the incomplete sulfidisation.[266]

At the optimum sulfidisation temperature (400 °C), the Mo–O–Al bonds are cleaved, and the distribution of the $MoS_2$ particles occurs parallel to the support surface; they are enlarged, the ratio of the basal to lateral planes of particles remaining constant. However, there is no oriented growth (epitaxy) of the $MoS_2$ particles on $Al_2O_3$: they are linked to each other by physical forces. The smaller the mean sizes of $MoS_2$ and $WS_2$ particles the more active the catalyst in the hydrodesulfurisation processes.[257] Higher catalyst activity appears to be reached with the incomplete sulfidisation of $MoO_3$.[267] Complete transformation of the oxygen-containing surface phase into $MoS_2$ occurs only at 970 °C,

though at such a high temperature the $MoS_2$ phase is sintered.[268, 269]

Apparently the nature of the support does not strongly affect the final form of molybdenum and tungsten oxides and sulfides. In most cases, Mo/C proves to be more active than $Mo/Al_2O_3$.[270] Isolated molybdenum ions or highly dispersed $MoO_3$ particles were detected on a molybdenum catalyst deposited on activated carbon. These species are sulfidised more rapidly on carbon than on $Al_2O_3$: at 400 °C the sulfidisation is already completed. After the sulfidisation, $MoS_2$ forms plates on $Al_2O_3$ and three-dimensional particles on carbon. This is explained by a stronger interaction of its oxide precursor with the $Al_2O_3$ surface than with carbon. The catalytic activity of $MoS_2$ is higher on carbon than on alumina.[271, 272]

Pratt *et al.*[273] observed a somewhat different orientation of $MoS_2$ particles on supports: plates were found on $Al_2O_3$ and $SiO_2$ oriented normally to their surface, while on $TiO_2$ and $ZrO_2$, particles were coplanar. The latter displayed higher catalytic activity.

Treatment of a $MoO_3-SiO_2$ system with a $H_2S + H_2$ mixture at room temperature leads to the formation of $MoO_xS_y$. At 150 °C $MoS_3$ particles appear, while at 250–270 °C the $MoS_2$ phase is formed.[274] Electron microscopy data showed that in a $Co-Mo-S/Al_2O_3$ system, $MoS_2$ particles are formed, and their size is increased from 1 to 1.5 nm at the sulfidisation temperature.[275] These particles are linked to form chains. At high cobalt content, the $Co_9S_8$ phase is formed.[276] In Ni–Mo–S and Ni–W–S catalysts, the phase NiS was also observed along with mixed phases.[277]

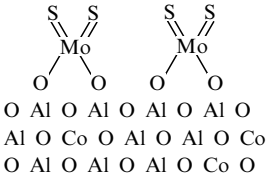
According to NMR and EXAFS data, the major active phase of a molybdenum sulfide catalyst consists of $MoS_2$ plates with Mo coordination number 4 or 5 and with the Co atoms at their edges.[244] The formation of a continuous $MoS_2$ phase, *e.g.*, after long operation of the catalyst, leads to its deactivation. Analogous phases formed on $SiO_2$ or carbon are less strongly bound to these supports than to $Al_2O_3$.

To model sulfide hydrotreating catalysts, several layers of sulfur were applied onto the Mo(110) plane with subsequent spraying of Zn or Co.[272] Zinc and cobalt were found to accelerate the sulfidisation of molybdenum. The hydrodesulfurisation activity of catalysts was observed to correlate with the ease of molybdenum sulfidisation. The Mo atoms become coordinatively unsaturated in the presence of zinc or cobalt.

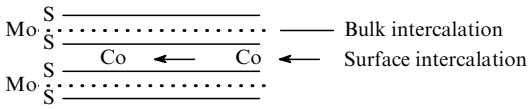
## 3. The role of different phases in sulfide catalysts

To elucidate the role of different phases in the active surface formation, the following models of sulfide catalysts may be considered.[5]

1. A structural model of a $Co-Mo/Al_2O_3$ catalyst implies the formation of a molybdenum monolayer on the surface of alumina.[278] According to this model, molybdenum is bound to the $Al_2O_3$ surface through the OH groups, whereas $Co^{2+}$ ions replace $Al^{3+}$ ions in the surface layer. Due to its large size, the $S^{2-}$ ion replaces two $O^{2-}$ ions.




2. In the initial version of the intercalation model the cobalt (nickel) ions were supposed to intercalate between the layers of the $MoS_2$ ($WS_2$) structure.[279] Later, it was found that intercalation inside the lattice is impossible, and the model has been modified. Now it is assumed that Co ions are intercalated near the sulfide surface:




The promoter atoms interact with $MoS_2$.[280]

$$Co^0 + 2Mo^{4+} \longrightarrow 2Mo^{3+} + Co^{2+}.$$

3. According to the model of contact synergism,[257, 281] hydrogen is activated on the $Co_9S_8$ or NiS phases, while the compound subject to hydrogenation is activated, on the $MoS_2$ phase. Hydrogen spillover takes place between these phases. A later modification of the model assumes hydrogen spillover between the $CoS_2$ and CoMoS phases.[282]

In recent times, the prevalent view is that the sulfide phases $Co_9S_8$ and NiS apparently play no special role in the hydrotreating processes.[5, 283–296] The application of different physical methods (EXAFS, NMR, XPD, and others) revealed a kind of a 'Co–Mo–S phase' in which the Co atoms are localised on lateral facets or edges of $MoS_2$ microplates. According to EXAFS data, the coordination number of Co is 4 or 5. The catalyst $MoS_2/Al_2O_3$ undergoes no deactivation after its sulfidisation. It is the distribution of Co atoms at the edges of the $MoS_2$ particles that determines the optimum ratio between Co and Mo. At high Co contents all its atoms cannot be placed at the edges of the $MoS_2$ particles.

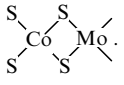
Mössbauer spectroscopy showed[245] that the sulfidisation of $CoMo/Al_2O_3$ and CoMo/C leads to the formation of the same particles as in the $Co/Al_2O_3$ and Co/C systems, respectively. This casts doubts on the concept of the 'Co–Mo–S phase' and makes one suspect that the $MoS_2$ phase is merely a diluent. However, it is believed that the systems CoMoS/C and $CoMoS/Al_2O_3$ differ. The Co/C catalyst is only three times less active than CoMoS/C, whereas $Co/Al_2O_3$ and $CoMoS/Al_2O_3$ exhibit much larger differences.

According to Chianelli *et al.*,[245] in the Co–Mo–S system the Co atoms are situated at the edges of the $MoS_2$ crystallites. The $Co_9S_8$ phase is also present; however, its function is reduced not to hydrogen spillover, but rather to the role of an additional support for the Co–Mo–S phase.

By analogy with the 'Co–Mo–S phase', the 'Ni–Mo–S phase' is also supposed to exist.[255, 256] The nickel-modified sulfide ($MoS_2$) adsorbs three times as much hydrogen as the pure $MoS_2$.[297] The excess phase $Ni_3S_2$ can be removed from the Ni–Mo catalyst by dissolution, and this does not affect its catalytic activity.[298]

Ekman *et al.*[299] synthesised catalysts based on the so-called Chevrel phases ($M_xMo_6Z_8$, where Z = S, Se or Te and M is a transition metal). In these phases, the transition metal cations may be localised not at the edges but inside the sulfide phase. Such systems differ from the usual mixed sulfide catalysts.

The results of $^{59}Co$ NMR suggested[287, 300] that the high activity of a Co–Mo–S system is associated with the presence of Co atoms with perturbed tetrahedral environments. In this system, octahedral cobalt is also present but the catalytic activity correlates only with the concentration of the tetrahedral cobalt. The active centre is assumed to have the following structure:




Electron exchange stabilises the structure $Co_{tetr}-S-Co_{oct}-S-Mo-S$.

The appearance of the $NiWO_4$ phase in the Ni–W–Al catalysts upon calcination of an $NiO + WO_3$ mixture decreases the efficiency of subsequent reduction and sulfidisation. This results in the formation of an unordered $WS_2$ phase and of $Ni^{2+}$ and $Ni^{3+}$ ions rather than an NiS phase.[301, 302] The higher activity of an Ni–W/C catalyst than that of $Ni-W/Al_2O_3$ is supposed[303]

to be due to the fact that the active nickel in the former is linked to six sulfur atoms. The major advantage of the use of carbon as the support apparently lies in the fact that, in contrast to $Al_2O_3$, it has no acidic properties and does not undergo coking.[304]

The role of cobalt (nickel) in a mixed catalyst may be dual. Presumably, cobalt (or nickel) favours the reduction of $MoO_3$[305] or $WO_3$.[306] According to the opposite viewpoint,[307] $Ni^{3+}$ incorporated into the $MoO_3$ layer decreases its susceptibility to reduction. It is also believed[268, 285, 299, 308, 309] that cobalt stabilises the dispersed $MoS_2$ microparticles preventing them from sintering. Some investigators[283, 286, 300, 301] presume that Co does not increase the $MoS_2$ dispersity, but participates instead in the hydrogen activation. There are also reports[310–312] that cobalt accelerates the sulfidisation of $MoO_3$ and suppresses deactivation of catalysts after sulfidisation.[287, 313]

In the $CoMoS/Al_2O_3$ system, sulfur is hydrogenated at a lower temperature than in the $CoS/Al_2O_3$ or $MoS_2/Al_2O_3$ systems. The ease of sulfur hydrogenation correlates with the catalytic activity.[314] A higher rate of sulfur hydrogenation within $MoS_2$ was also observed when Co, Ni or Fe were deposited on a $MoS_2$ plate.[315]

The presence of Ni in a Ni–Mo hydrodesulfurisation catalyst promotes the reduction of $MoO_3$ to $MoO_2$ and partly to Mo.[308] Thus, nickel can act as a catalyst for $MoO_3$ reduction. Cobalt also accelerates the reduction of Mo(VI) to Mo(IV) and even to Mo(III).[316, 317] In this case, some vacancies appear in the sulfide layer.

## 4. The hydrodesufurisation mechanism

The most popular hydrodesulfurisation mechanism includes the formation of anion vacancies in the sulfide layer and their subsequent filling with sulfur from a sulfur-containing compound, *e.g.*, thiophene.[244, 278, 318, 319] The thiophene molecules are adsorbed normal to the surface. The vacancies may either be initially present in the $MoS_2$ phase, most probably at the edges of the microplates, or be formed in the course of sulfide reduction with hydrogen

$$2Mo^{4+} + S^{2-} + H_2 \rightleftharpoons 2Mo^{3+} + \square_s + H_2S,$$

$$Mo^{4+} + S^{2-} + H_2 \rightleftharpoons Mo^{2+} + \square_s + H_2S.$$

Low-valent forms of molybdenum were in fact revealed by IR spectroscopy and EPR. The use of these techniques also provided evidence of S–H group formation under catalysis conditions, while XPES revealed low-valent sulfur in the form of $S^-$ or $(S-S)^{2-}$.[316, 320, 321] The disulfide groups, possibly localised at the $MoS_2$ edges, may take part in the hydrogen activation.

$$S_2^{2-} + H_2 \longrightarrow 2SH^-.$$

Hydrogen forms in sulfide catalysts were studied by IR spectroscopy and neutron diffraction.[322] No bands corresponding to vibrations of the Co–H and Mo–H bonds were found after the adsorption of $H_2$ in the systems $CoMo_{1.3}S_{1.6}$, $MoS_2$ and $Co_9S_8$, but S–H vibrations bands were observed. This led to the conclusion that in the course of $H_2$ adsorption processes of the type

$$Mo-S + H_2 \longrightarrow H-Mo-S-H$$

do not occur, giving way to the reaction

$$2Mo-S + H_2 \longrightarrow 2Mo-S-H$$

or

$$Mo-S-S-Mo + H_2 \longrightarrow 2Mo-S-H.$$

The Co (Ni) atoms may be directly involved in the formation of active centres or neighbours with the vacancy at the peripheral molybdenum atom. The number of cobalt atoms in the catalyst was observed to correlate with the number of peripheral molybdenum atoms. According to EXAFS,[323, 324] the vacancies are formed near the cobalt atoms. This was confirmed in particular by experiments on the adsorption of selenophene (a thiophene analogue).[325] The vacancies available in the $Co_xMo_{1-x}S_{2\pm\delta}$ phase are involved in the following reactions:

$$Mo^{4+} + Co^{2+} + \square + S^{2-} + HSR \longrightarrow$$

$$\longrightarrow Mo^{3+} + Co^{3+} + SH^- + SR^-,$$

$$Mo^{3+} + Co^{3+} + SH^- + SR^- + H_2 \longrightarrow$$

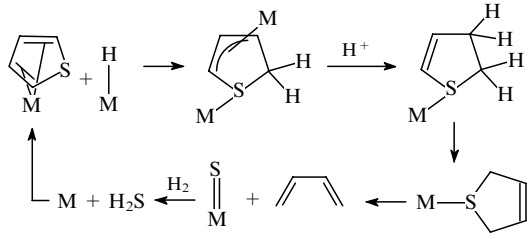
$$\longrightarrow Mo^{3+} + Co^{3+} + 2SH^- + HR,$$

$$Mo^{3+} + Co^{3+} + 2SH^- \longrightarrow Mo^{4+} + Co^{2+} + \square + S^{2-} + H_2S.$$

According to the results of TPR,[326] sulfur is more weakly bound in the Co–Mo–S system than in $Co_9S_8$ or $MoS_2$: the $H_2S$ peak is observed at a lower temperature. However, an investigation of the isotope exchange of labelled hydrogen sulfide $H_2{}^{35}S$ with the $NiS/Al_2O_3$, $MoS_2/Al_2O_3$, and $NiMoS/Al_2O_3$ catalysts unexpectedly showed that the exchange rate on $NiMoS/Al_2O_3$ was lower than on $MoS_2/Al_2O_3$, which in turn was lower than on $NiS/Al_2O_3$.[327] This surprising finding was explained by the participation of sulfur atoms bound to both molybdenum and nickel in the reaction. The results reported by Topsøe *et al.*[326] may also be explained by the associative mechanism of this reaction without participation of vacancies.

Experiments with $^{35}S$ showed that the loss of sulfur from the catalyst as a result of its interaction with hydrogen can be compensated for at the expense of thiophene sulfur.[318] The quantity of mobile sulfur and the catalytic activity increase in the presence of promoters (Co, Ni).

According to Markel *et al.*,[328, 329] dihydrothiophene is formed as an intermediate in the reaction of thiophene hydrodesulfurisation




The idea of an associative mechanism underlying the hydrogenolysis of thiophene without participation of the sulfide layer vacancies was also put forward by Startsev,[323] who assumed that thiophene is adsorbed on the Co(Ni)–Mo–S catalyst in the coordination sphere of cobalt, while dissociative adsorption of $H_2$ takes place at the terminal sulfur atoms flanking the electroneutral macromolecule $MoS_2$. This viewpoint stands in need of more conclusive evidence.

Different opinions exist as to the nature of the active centres in the hydrogenation of various organic compounds. According to the most popular concepts, the role of the active centres in the hydrodesulfurisation is played by the molybdenum or cobalt atoms on the lateral facets of $MoS_2$.[5] The activity of hydrodesulfurisation catalysts was found to be proportional to the number of centres on the lateral facets of $MoS_2$ determined by the EXAFS method *in situ*.[326] There is a relationship between the activity of catalysts and the concentration of $Mo^{5+}$ in them (according to EPR data).[330] The activity of $WS_2$ in the hydrogenation of benzene correlates with the concentration of $\square_S$ vacancies on the lateral sulfide facets measured by EPR.[275]

The mechanism of thiophene hydrodesulfurisation on the $Co-Mo/Al_2O_3$ catalyst was investigated using the TPD and TPR techniques and D–H isotope exchange.[331–335] The TPR and TPD spectra of thiophene, dihydrothiophene, and butanethiol were found to be very similar on $Mo/Al_2O_3$ and $Co-Mo/Al_2O_3$, but somewhat shifted towards lower temperatures on the Co-containing catalyst. At the same time, the shape of the spectra on $Co/Al_2O_3$ was completely different and most of the products formed in the first two systems under TPR conditions were not

produced in the latter case, whereas hydrogen was desorbed at a lower temperature. These results confirm the traditional viewpoint, according to which thiophene is adsorbed on the anionic vacancies of $MoS_2$, while hydrogen is activated on cobalt. We cannot say whether the Co and Mo centres are situated in different phases or in different crystallographic positions of the same phase, though they do not appear to be spatially separated. In any event, no results have been reported to disprove this viewpoint.

Desorption of thiophene at low temperatures characteristic of all catalysts is most likely to occur from the weakly bound π-adsorbed state. The high-temperature desorption of thiophene characteristic of $Mo/Al_2O_3$ and $Co/Al_2O_3$ catalysts seems to be related to the dehydrogenated forms. In such cases, strong retention of molecules by the surface is ensured by both the bonding of the sulfur atom and the σ-bonds (possibly several) of carbon atoms in the ring. When there is a surface hydrogen shortage the limiting stage of the thiophene desorption may be the interaction of such surface complexes with the hydrogen atoms.

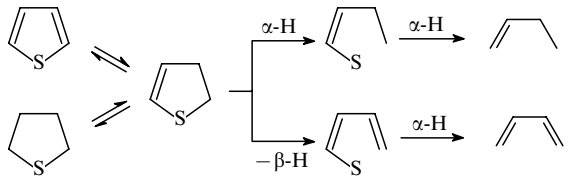
To bring about desulfurisation, it is necessary to activate the adsorbed molecule of the S-containing compound. This first requires the formation of sufficiently strong bonding of the sulfur atom with the surface and, second, surrounding of the reacting sulfur-containing molecule with hydrogen atoms situated in the immediate proximity. Under TPR conditions, such a complex may be formed with the participation of migrating hydrogen according to the mechanism of reverse spillover from the support.

The coincidence of kinetic parameters for the formation of $C_4$ hydrocarbons from thiophene and tetrahydrothiophene indicates that the hydrodesulfurisation of these compounds on Mo and Co–Mo catalysts proceeds *via* the same intermediates, probably dihydrothiophenes.

Markedly easier desulfurisation of thiols than of thiophene and tetrahydrothiophene may suggest that the cleavage of the second C–S bond in the surface intermediates is not the limiting stage of the entire hydrodesulfurisation process.

In contrast with the desulfurisation of tetrahydrothiophene and thiophene, butadiene is absent from the products of butanethiol desulfuration, which indicates that the surface butanethiolate cannot be an intermediate compound in the hydrodesulfurisation of thiophene and tetrahydrothiophene, at least under low hydrogen pressure in the gaseous phase.

Rozanov *et al.*[334] proposed the following generalised scheme for the desulfurisation mechanism:




According to this scheme, thiophene and tetrahydrothiophene can be interconverted *via* dihydrothiophene as the intermediate compound. Depending on the hydrogen pressure and the reaction temperature, equilibrium may be shifted towards thiophene or tetrahydrothiophene. Butene may be formed from the intermediate dihydrothiophene as a result of two-stage hydrogenolysis of α-C with concomitant cleavage of the C–S bond, while butadiene may result from β-elimination in the first stage and α-hydrogenolysis in the second stage. Presumably, hydrogenation–dehydrogenation reactions occur on one type of centres, while hydrodesulfurisation occurs on another type of centre. The limiting stage of the whole process is the cleavage of the C–S bond.

This conclusion was drawn from studies on the hydrodesulfurisation of thiophene on $Rh_2S_3$, Co/C, and Mo/C catalysts.[336] It can be mentioned that the limiting stage of the reaction on Co–Mo/C is hydrogenation, which determines the low selectivity of formation of hydrogenation products in this case.

Some investigators believe that hydrodesulfurisation and hydrogenation take place on the same active centres,[337] while others think that these centres are different.[338] Hydrogenation of propylene requires molybdenum(IV), and hydrogenolysis of propane occurs on the more reduced Mo forms, up to its metallic state. On different supports, one may observe different orientations of $MoS_2$ and Co–Mo–S particles.[339] When these particles are deposited on $Al_2O_3$, their activity in the hydrogenation is higher and that in the hydrocracking is lower than in their deposition on $Al_2O_3 \cdot SiO_2$, $MgO \cdot SiO_2$ or MgO. The molybdenum- and cobalt-containing phases have no synergistic effect in the hydrodesulfurisation of thiophene, but they do manifest this effect in the hydrogenation of butenes and butadiene.[318] In contrast to Co–Mo–S, the Ni–W–S system accelerates hydrogenation of biphenyl more strongly than hydrodesulfurisation of dibenzothiophene.[340] According to Topsøe *et al.*,[5] the stronger deactivating effect of $H_2S$ on Co–Mo–S catalysts in the hydrogenation of aromatic compounds than in the hydrogenation of alkenes is indicative of the difference between the active centres in these reactions.

In conclusion, it is noteworthy that the reactions of hydrogenation and hydrodesulfurisation on Co(Ni)–Mo(W) catalysts are the best studied catalytic processes, judging from the number of publications devoted to them. Nonetheless, the mechanism of these reactions has not been totally elucidated and remains the subject of numerous discussions. This also holds for the preparation of hydrotreating catalysts. Studies in which the reaction mechanism was investigated by physical methods *in situ* are virtually absent. Without an adequate understanding of the mechanism of the process, it is impossible to develop scientific grounds for the preparation of catalysts. To this end it is necessary to elucidate what component of the catalysts activates hydrogen and what component activates an organic compound, and how to distribute these components most effectively on supports.

## IX. Conclusion

The aim of this review was to consider hydrogenation catalysts, including modified supported Ni catalysts, carbides, sulfides, and others that have been most actively studied in recent years.

Investigation into the mechanism of action of hydrogenation catalysts by physicochemical methods made it possible to reveal some of their common features. It was found that hydrogen and compounds subject to hydrogenation are, as a rule, activated on different active centres: the former, on metallic (or reduced) centres, the latter, on oxidised centres which are often formed by ions of the basal metal intercalated into supports or modifiers. Hydrogen transport between centres may be brought about by the spillover mechanism. Therefore, the role of support or modifier is often played by systems capable of accumulating hydrogen. The secondary structure of the support and catalyst (specific surface, dispersity, porosity) has a significant effect on the supply of hydrogen to the compound under hydrogenation, as well as on the thermostability and selectivity of catalytic systems.

Co-precipitated metal–oxide catalysts, complex oxides, skeletal catalysts, and hydrides of intermetallides, which are also actively studied nowadays, remained almost totally outside the scope of this review.

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