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The Development and Use of New Hydrogenation Catalysts[1]

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Abstract—Advantages and drawbacks of commercial catalysts for gas-phase hydrogenation are considered. The use of modified catalysts, including nickel catalysts modified with heteropoly compounds, is promising. Data on the selective reduction of carbonyl compounds and hydrogenation of aromatic hydrocarbons over these catalysts are presented. Palladium films are shown to be the best catalysts for the selective reduction of acetylene compounds to olefins.

MAIN HYDROGENATION PROCESSES

The history of commercial hydrogenation began with the Sabatier's discovery of a nickel hydrogenation catalyst in 1897 [1, 2]. Since then, catalysts containing Group VI–VIII metals have appeared, including platinum catalysts both supported and those in the composition of complex oxide systems, as well as skeleton metal catalysts. Ipatieff's studies on the catalytic hydrogenation under pressure have led to the development of processes that were further commercialized.

Hydrogenation catalysis fills a small place in industrial organic synthesis. Nevertheless, the hydrogenation of fats, the hydrogenation of 2-ethylhexenal and other aldehydes and acids to alcohols, the hydrogenation of benzene to cyclohexane, the hydrogenation of cyclododecatriene to cyclododecane in the production of thermally stable plasticizers, etc., are large-scale industrial processes. The use of hydrogenation catalysts in the pharmaceutical industry and in syntheses of bioactive substances is extending. Supported metals (Ni, Pt, Pd, Rh, and Ru), as well as the copper–chromium and nickel–chromium catalysts prepared by coprecipitation, are among the most active, selective, and stable catalysts, which are used more frequently than others.

Let us consider trends in the use of hydrogenation catalysts in the light of toughening requirements to target product quality, using benzene hydrogenation to cyclohexane as a sample process [3, 4]. It is known that high-purity cyclohexane (>99.88%) is used to produce adipic acid, caprolactam, caprolactam fibers, and nylon-6 according to various technologies. In the United States, the industrial capacity was 1.363 million m^3/year, and the demand was 1.514 million m^3 in 1992 [5].

From the beginning of the 20th century, nickel catalysts (Raney nickel, nickel catalysts supported by impregnation, and supported platinum catalysts) were used in benzene hydrogenation. Side processes (cracking with the formation of *n*-hexane, isomerization to methylcyclopentane, and cracking to light hydrocarbons [3]) occurred in early industrial processes at elevated temperatures and pressures.

To obtain high-purity cyclohexane, a two-stage technological flowchart was developed with a supported Ni catalyst (30–45% Ni/Al_2O_3) used at the first stage and a supported Pt catalyst (0.2–1.0% Pt/Al_2O_3) at the second stage. The purity of cyclohexane reached 99.57–99.88% in this process [6].

At the same time, coprecipitated nickel–chromium catalysts have been developed in the Soviet Union, which enabled the production of high-purity cyclohexane by multiple-stage technology in tubular reactors sensitive to overheating [7, 8].

In the 1990s, the Canadian National Institute of Materials and Chemical Studies proposed to hydrogenate benzene for the storage and safe transportation of hydrogen in the composition of cyclohexane to such countries as Japan where hydrogen should be split off from cyclohexane and used as clean fuel for power stations. It is believed that the electric power thus obtained will cost 30 cents per kilowatt-hour [9].

Large-capacity processes for the hydrotreating of oil fractions were initially desulfurization, hydrodenitrification, and in part hydrogenation. Special hydrogenation catalysts were used, which were prepared by impregnation or coprecipitation and which were stable against catalytic poisons, S-, N-, and O-containing impurities in naphtha. These were Al–Co–Mo–O, Ni–Mo–O, Ni–W–S, and $Pd(S)/Al_2O_3$. Now, the hydrogenation of aromatic and unsaturated hydrocarbons in naphtha is developing rapidly as a separate branch of oil refining and petrochemistry. So-called hydrotreating, that is the removal of aromatic and unsaturated hydrocarbons, is especially urgent for the hydrotreating of the feedstock for jet and diesel fuels (the concentration of olefins in the jet fuel should be at most 0.5–1.0% and aromatic compounds should be at most 10%).

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The high concentrations of aromatic (especially bicyclic) hydrocarbons in jet fuels leads to air pollution, soot and a carbon deposition on the walls of flue tubes of combustion chambers, and burnup of the tube walls. The concentration of aromatics in the environmentally clean diesel fuels should be at most 20%. To enhance the stability of jet fuels, special additives are now used in Russia, but they work better in combination with hydrofining. The two-stage process for the hydrotreating of hydrocarbons is commonly used. At the first stage, the N- and S-containing compounds are removed using Al–Co–Mo catalysts, and at the second stage, expensive Pt or Pd catalysts are used for finer purification.

Along with the hydrotreating of oil fractions, large-capacity processes are developed for the hydrotreating of pyrolytic gases, catalytic cracking, coke manufacturing, and the hydrodealkylation of a benzene–toluene–xylene fraction (BTX fraction), which includes alkyne, diene, and alkene admixtures. Due to the selective hydrogenation of admixtures, high-purity hydrocarbons (ethylene, propylene, etc.) are obtained from the above gaseous fractions used in the synthesis of plasticizers and polymers. Platinum and palladium hydrogenation catalysts are usually used for these purposes.

Table 1 lists the main industrial hydrogenation processes developed worldwide and traditional Russian catalysts, feedstock, and marketable products produced at plants in Russian in 1990 and later.

As can be seen, along with benzene hydrogenation to high-purity cyclohexane for the production of adipic acid, the Ni–Cr catalysts are also widely used in Russia for the hydrogenation of carbonyl compounds. For this purpose, the Ni/kieselguhr and Pd-containing catalysts are also used.

The manufacture of 2-ethylhexanol from 2-ethylhexanal over the above catalysts is the most important of these commercial processes. Dioctyl phthalate, a plasticizer for polyvinyl chloride, is obtained from this high-purity alcohol containing no admixtures of aldehydes and ketones [10]. When any hydrogenation catalysts, for example copper-containing catalysts, are used for this process, the Ni- or Pd-containing catalysts are necessary to achieve complete hydrogenation to 2-ethylhexanol. Ludvig [11] noted that a process suitable for 2-ethylhexanal hydrogenation is also suitable for the hydrogenation of other saturated aldehydes under the same conditions.

Worldwide alcohol production in 1992 was as follows (in millions of tons per year): *n*-butanol, 1.7; isopropyl alcohol, 0.4; 2-ethylhexanol, 2.4; and higher alcohols, 1.2. The production of C_7 aldehydes and alcohols grows in parallel with the production of polymers, especially polyvinyl chloride. The above technologies have also been commercialized in Russia. The fact that they are

Table 1. The main commercial catalysts for hydrogenation

Process	Feed	Catalysts	Marketable product	Plant (conventional domestic catalysts)
Benzene hydrogenation (gas-phase)	BTX fractions: petroleum, catalyzates of reforming, products of pyrolysis and coking	Ni/support, Ni–Cr, Pt/support, Pd/support	High-purity cyclohexane	PO Azot: Cherkassy, Kemerovo, Grodno, Shchekino (Ni–Cr), Kazan PO Orgsintez (Ni–Cr)
Hydrogenation of aldehydes and ketones (*n*-butyric aldehyde, 2-ethylhexanal, C_3–C_{10} aldehydes)	Products of oxo synthesis based on olefins from pyrolysis gases	Cu–ZnO, Cu–Cr_2O_3, Cu–Ni/support, Ni/support Ni–TiO_2/Al_2O_3 MoS_2/carbon NiS/WS_2 Re_2S_7/Al_2O_3 Pd, Ru/support	Alcohols, ➢ C_7 Low alcohols (*n*-butanol, isobutanol)	PO Angarsk-nefteorgsintez (Ni/kieselguhr); PO Salavat-nefteorgsintez (Pd/C, Ni–Cr, Pd/support); PO Orsk-nefteorgsintez (Ni–TiO_2/Cr_2O_3); PO Azot, Nevinnomyssk (Ni–Cr)
Hydrogenation of unsaturated hydrocarbons	Pyrolysis gases: ethane–ethylene fraction, propane–propylene fraction		Ethylene (ethane), Propylene (propane)	Moscow NPZ (Pd/C, Pd/support); Ufa plant of synthetic alcohol; Lisichansk NPZ (Pd/C, Pd/Al_2O_3); Kremenchug NPZ (Pt/Al_2O_3); Shevchenko plant of plastics ($Pd(S)/Al_2O_3$);
	Gases of catalytic cracking, C_3–C_4	Pd/support Pt/support		
	Coking gases	Pd/support Pt/support		
Hydrogenation of CO	Exhaust gases of power stations and chemical industries	Ni–Cr	CH_4	A number of plants (Ni–Cr, Ni/Al_2O_3, Pt/Al_2O_3) Omsk plant of synthetic rubber; PO Sintez-kauchuk, Tolyatti

out of service now is due the collapse of Russian plants and the absence of efficient catalysts for gas-phase hydrogenation.

Low alcohols are used to produce solvents and higher alcohols that are starting materials in surfactant manufacture. To enhance the process selectivity, it is necessary to choose appropriate catalysts. For example, a copper catalyst is selective in the synthesis of *n*-butyraldehyde from croton aldehyde rather than a nickel catalyst, which is excessively active.

Conventional nickel catalysts (Ni–Cr, Ni/kieselguhr, and others) are not selective enough for the hydrogenation of carbonyl compounds. For example, Ni, unlike Cu, catalyzes both hydrogenation and CO elimination from saturated aldehydes:

$$R^1CHR^2CHR^3CHO \longrightarrow R^1CR^2{=}CHR^3 + CO + H_2.$$

When a nickel catalyst is highly active, further olefin hydrogenation to alkane involves much heat, which can lead to an undesirable increase in temperature.

In this connection, the importance of finding a new, less active Ni catalyst with a higher selectivity in the hydrogenation of aldehydes compared to conventional catalysts is urgent. With this purpose, the Ni/SiO_2 and Ni–TiO_2/Al_2O_3 catalysts have been developed. Specially treated SiO_2 was used, which together with the TiO_2 additive, lowers nickel activity in this process. The modified nickel catalysts described below can be considered the best among highly selective catalysts for aldehyde hydrogenation.

Noble metal catalysts enable the selective hydrotreating of pyrolysis gases and other industrial gases to remove unsaturated compounds, especially in ethane–ethylene and propane–propylene fractions are purified from acetylene and its derivatives. A lower cost due to a decrease in the concentration of precious metals in catalysts is as important as activity and selectivity. Recently, domestic catalysts of the GIPKH-108 (2% Pd on carbon) and MA-15 (0.5% Pd(S)/Al_2O_3) types were used for the refinement of the ethane–ethylene fraction. The shortcomings of the GIPKH-108 catalyst are (i) low selectivity in acetylene hydrogenation to ethylene, (ii) low space velocities to achieve maximal conversions, and (iii) a high concentration of Pd. More selective imported catalysts, for example those produced by Südchemie, are now used at Russian plants.

PREPARATION OF NICKEL CATALYSTS

Nickel catalysts are the most abundant in gas-phase and liquid-phase hydrogenation. Catalysts based on noble metals (Pt, Pd, Rh, and Ru) are usually more active and less sensitive to poisons but they are more expensive and used less.

As was mentioned above, our industry gave most attention to nickel–chromium catalysts. They were prepared by coprecipitation from the solutions of Ni and Cr nitrates with a sodium carbonate solution, filtration, washing, calcination, pelleting, and activation by H_2. The concentrations of Ni and Cr are 48–63% and 37–52%, respectively. Other methods for the preparation of Ni–Cr catalysts were also proposed. The disadvantages of these methods are multiple stages, cumbersome equipment, and large amounts of wastewater. The catalysts prepared by these alternative methods were insufficiently active, their specific surface areas were at most 25–30 m^2/g, and thermal stability was lower than 250–280°C [2]. The heating of Ni–Cr catalysts at 350°C decreased the active surface area to 11–18 m^2/g [12].

To overcome the above drawbacks, a waste-free method for the preparation of Ni–Cr catalysts was proposed in the 1980s [8]. The method includes mixing $Ni(NO_3)_2$ and $(NH_4)_2Cr_2O_7$ solutions followed by drying and calcinating salts by sputtering to a heated inert packing in a fluidized-bed mode at 310–340°C, pelleting, and reduction. A multiple-stage synthesis of Ni–Cr, as Al–Ni–Co, Al–Ni–Mo, and Al–Ni–W catalysts for hydrotreating [13, 14] creates technological difficulties. The catalysts prepared are insufficiently active and require a great amount of an active component. Despite the high concentration of Ni in the Ni–Cr catalysts, its active surface area in all the samples is low and the thermal stability is at most 250–280°C [7, 8], imposing technological limitations. Nevertheless, the Ni–Cr catalysts, sometimes imported, are still used in our industry.

The development of new hydrogenation catalysts and improvement of old catalysts intensified considerably in the 1990s. In 1991, 380 new hydrogenation catalysts were developed, whereas the total number of catalysts for petrochemistry and oil refining was 1040. The number of catalysts for cracking, known as a large-capacity process, was only 214; the number of catalysts for hydrocracking was 107, and that for reforming was 113. The number of the catalysts for hydrogenation in 1991 was 54 greater than in 1989, whereas the number of the catalysts for cracking decreased and that for hydrocracking and other oil refining changed slightly [15].

Many studies have concerned the development of supported Ni catalysts, both impregnated and coprecipitated: Ni/Al_2O_3, Ni/SiO_2, Ni/C, and others. The effects of preparation conditions, pH of the solution, concentrations of salts, amount of supported metal, preparation temperature, and the porosity of support, etc., have been studied (see the review [2]).

A large research group from various European countries headed by Coenen has developed the Euro-Ni-1 catalyst (25% Ni/SiO_2) [16]. The catalyst is prepared by homogeneous precipitation in which a portion of nickel forms hydrosilicate on the support surface. The specific surface area of the active metal achieves 113–182 m^2/g. The fact that the catalyst was barely reducible, especially compared to the supported nickel hydroxide, points to strong interaction between Ni and SiO_2 during preparation. A temperature of 500–600°C was required for the complete reduction of the Euro-Ni-1 catalyst. The two-stage method for the preparation of supported Ni catalysts (the introduction of Ni into the support lattice followed by Ni deposition onto the surface) enhances its stability and activity, but a significant fraction of the metal appears in the bound form.

The common drawbacks of Ni catalysts for gas-phase hydrogenation prepared by the above methods are

(1) A high concentration of Ni in commercial catalysts (up to 50% in Ni–Cr);

(2) Low thermal stability (<300°C);

(3) Necessity for expensive oxide additives (from 15 to 40% MoO_3, WO_3, V_2O_5, etc.) if Ni is present in small amounts (4–10%);

(4) Necessity for special supports with complicated structures in some cases;

(5) Technologically complicated preparation methods;

(6) Transfer of Ni to the framework due to local overheating when its concentration is lower than 5%, and the transformation of Ni to Ni^{2+}; and

(7) Insufficient activity and selectivity in some cases.

In connection with this, great attention is given to the design of new catalysts for hydrogenation. It has been found that the preparation method and the nature of supports affect significantly the activity, selectivity, and stability of supported catalysts, but the use of promoters and modifying agents is most efficient.

The decomposition of organometallic compounds is a novel method for the preparation of modified Ni catalysts. The metal–metal bonds are formed on the surface between the cations of a modifying agent and metals of an organometallic compound:

$$\blacksquare\text{–}(O)_xE^{x+} + M(\pi\text{-}C_4H_7)_2 \longrightarrow \blacksquare\text{–}(O)_xE^{x+}M^0 + 2C_4H_8,$$

where $M(\pi\text{-}C_4H_7)_2$ is the organometallic compound, M is a Group VIII metal, and E is the modifying Group IV–VIII element (Mo, W, Re, Sn, etc.) [17]. Sometimes, the nickel dispersion close to an atomic state is reached in the nickel catalysts.

The highly dispersed nickel catalyst was also prepared by modifying support with an organolithium compound from a methanol solution [18]:

$$\blacksquare\text{–OH} + CH_3Li \longrightarrow \blacksquare\text{–OLi} \xrightarrow{NiCl_2} \blacksquare\text{–O–Ni}.$$

However, such modified catalysts are not used in industry. A common drawback of modification by organometallic compounds is a complicated synthesis as well as fire and explosion hazards.

The so-called CVD (chemical vapor deposition) highly active catalysts were prepared by the deposition of metal acetylacetonates onto the surface of supports followed by their decomposition [19].

Active film catalysts of the metal–oxide type on supports, the analogs of cermet films, in which metal particles are uniformly distributed on the surface of ceramics, have also been developed [20]. The salts of active metals (Pt or Pd) were precipitated together with the salts of higher carboxylic acids (Al resinates, stearates, etc.) from an organic solvent, forming an oxide film on the surface that binds a metal, for example, $Pd/Al_2O_3/Al_2O_3$.

NICKEL CATALYSTS MODIFIED BY HETEROPOLY COMPOUNDS

Several recent papers [21–25] provided convincing evidence for the participation of W-containing heteropoly compounds (HPCs) in the hydrogen transfer and catalytic reactions of hydrogenation and isomerization. For example, alkene hydrogenation [22] and skeletal isomerization of *n*-pentane [23] were studied on $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ in the presence of hydrogen. The addition of Pt or Pd to this HPC enhances significantly its hydrogenating properties. Hydrogen is possibly consumed by both the surface and bulk of HPC. Ng *et al.* [21] reported data suggesting that unsaturated compounds adsorbed on the HPC surface could readily be titrated with hydrogen consumed in its bulk.

The use of the Co– and Ni–HPC systems as hydrogenation catalysts was also documented. HPCs with anions of the overall formula $[H_mA_xB_yO_z]^{n-}$, where A = Ni or Co, B = Mo, W, V, were used as modifying agents or an active phase [25, 26]. The Co–Mo, Ni–W, or Ni–Mo catalysts on supports are formed upon their decomposition; however, HPCs can also serve as the modifying agents for Ni-containing catalysts.

To prepare the hydrogenation catalysts of this type and to modify the known Co–Mo, Co–W, and Ni–W ones, nickel heteropoly salts with the anions of the $[NiM_6O_{24}H_6]^{4-}$ type (M = Mo or W) were synthesized [27]. The active phase was formed upon their decomposition. Earlier, salts and acids of this type were largely used as catalysts for oxidation, hydration, dehydration, and other processes.

Supported catalysts prepared by the impregnation of a support with the Ni–Mo and Ni–W heteropoly salts were tested in hydrodesulfurization and hydrogenation [28]. They turned out less active than commercial Ni–Mo and Ni–W catalysts. This fact is due to a lower concentration of Ni, which cannot be increased because HPC is used as a usual active phase in this case.

In the 1980s, one of the authors of this work developed novel nickel catalysts on various supports (activated carbon, Al_2O_3, and SiO_2) in which HPCs of the W series with various compositions served as modifying agents [2, 29–39]. The modified nickel catalysts were prepared by the impregnation of a support with the solutions of heteropoly salt and nickel nitrate, drying, and reduction with hydrogen at 400°C.

The degree of reduction of the modified catalysts reaches high values, although reduction conditions (400°C and 6 h) are milder than, for example, those for the reduction of Euro–Ni-1. In some cases, the degree of reduction of the modified catalysts with a low nickel concentration (for example, 2% Ni) is 100%. This value is not reachable for the nonmodified Ni/Al_2O_3 catalysts, since a fraction of nickel enters into the framework of the support to form the $NiAl_2O_4$ spinel.

When the modified Ni catalysts on supports are prepared, an active phase is formed in which the Ni particles are uniformly distributed over the HPC surface. As electron microscopic patterns show, Ni particles are distributed nonuniformly in the absence of HPCs and the particle size reaches 10 nm. Unlike this, particle sizes in the 4% Ni-HPC/C or Ni-HPC/Al_2O_3 catalysts are 3–7 nm. The maximal degree of reduction depends on the nature of a modifying agent, HPC concentration, and Ni/HPC ratio.

The modified catalysts can be used in the industrial hydrogenation of the following compounds:

– Aromatic mono- and bicyclic compounds, for example, in the synthesis of high-purity (99.99%) cyclohexane in the caprolactam production from benzene, for the two-stage hydrotreating of hydrocarbon feedstock, for the production of environmentally safe high-octane and high-cetane fuels including aviation and new-generation jet fuels for supersonic aircraft (cyclododecane preparation), and high-quality solvents containing no benzene and alkyl-substituted aromatic hydrocarbons and sulfur admixtures;

– Carbonyl compounds (aldehydes and ketones), for example, in the production of 2-ethylhexanol, butanols, water-free isopropyl alcohol, methyl hexyl carbinol from methyl hexyl ketone, and for the hydrotreating of alcohols from admixtures of aldehydes and ketones;

– Unsaturated linear and cyclic C_4–C_{12} hydrocarbons in the processes of the complete hydrogenation of unsaturated hydrocarbons in the raffinates of catalytic reforming, in the hydrogenation of olefin admixtures in butanol, in methanol production, and in other processes of the hydrostabilization of synthetic gasoline and hydrotreating of solvents in the absence of sulfur admixtures; and

– Carbon monoxide during methanation with the minimum formation of CO_2 at elevated temperatures.

It is noteworthy that the proposed modified Ni catalysts in the above hydrogenation processes have a high activity, high selectivity (up to 99%), and thermal stability. The modifying agents differ in composition and allow the control of the activity and functions of the catalysts. For example, samples that are poorly active in the hydrogenation of aromatic hydrocarbons are efficient catalysts for the hydrogenation of carbonyl compounds.

Table 2. A comparison of nickel catalysts in hydrogenation of unsaturated and aromatic hydrocarbons

Catalyst	Productivity, g (g cat)$^{-1}$ h^{-1}
Ni–Cr (50% Ni)	0.32 (based on aromatic hydrocarbons)
Ni–HPC/Al_2O_3 (4% Ni)	0.36 (— // —)
	0.93 (based on olefins)

Comparison of the catalytic activity of modified Ni catalysts with that of conventional Ni–Cr catalysts shows that the modified catalysts can be several times more active and sometimes their activity is comparable or exceeds that of Pd-containing catalysts.

Thus, the capacity of the modified 4% Ni catalyst in benzene hydrogenation to cyclohexane is 0.36 g (g cat)$^{-1}$ h^{-1}, whereas the capacity of the Ni–Cr catalyst is 0.32 g (g cat)$^{-1}$ h^{-1}. The capacity of the modified catalyst (0.93 g (g cat)$^{-1}$ h^{-1}) in the hydrogenation of olefins (octene and nonene) is much higher than that of the Ni–Cr catalyst (see Table 2).

The enhanced activity of modified Ni catalysts lets us think of the possible replacement of expensive Pt- and Pd-containing catalysts in the hydrostabilization or hydrotreating of hydrocarbon feedstock to remove unsaturated compounds. The activity of modified catalysts in the hydrogenation of aromatic and carbonyl compounds is also comparable to that of noble metals.

Calculations showed that the net cost of the modified Ni catalysts is comparable with that of the Ni–Cr catalysts and is an order of magnitude lower than that of noble metal catalysts, which are widely used now in the above hydrogenation processes. The loads of modified catalysts are usually 20–30 vol % lower than that of the Ni–Cr catalyst.

Along with the improved technological parameters, modified catalysts have the following advantages:

– Thermal stability up to 400–450°C (vs. 250–280°C for Ni–Cr catalysts);

– The nickel active surface reaches 300 m^2/g (vs. 25–30 m^2/g for Ni–Cr); and

– Sulfur capacity exceeds the corresponding characteristics for the Ni–Cr catalysts.

Due to the above features, the modified nickel catalysts are expected to have longer service lives. They could replace conventional industrial hydrogenation catalysts, including those containing noble metals. The modified nickel catalysts represent new-generation catalysts prepared by a new technology, which allows flexible control of the composition, activity, and selectivity, depending on the requirements of a technological process. The tests of a large number of modified Ni catalysts in various scientific groups and industrial plants showed that they have improved performance characteristics, controllable activity and selectivity, and, hence, can be adjusted to the process.

Flexible control of the activity of modified Ni catalysts allows one to arrange the catalysts in layers inside the reactor to make heat evolution uniform. In benzene hydrogenation to cyclohexane, this results in process optimization and a stable temperature regime close to isothermic.

HYDROGENATION OF CARBONYL COMPOUNDS OVER MODIFIED NICKEL CATALYSTS

We studied the gas-phase acetone hydrogenation in an alcohol solution and without a solvent in a flow setup at an atmospheric pressure in the presence of different Ni- and Pd-containing catalysts [36]. This study showed that modified Ni catalysts are better and could replace conventional catalysts.

In the first series of experiments performed by A.M. Proskurnin at the State Institute of Nitrogen Industry (Moscow), runs were carried out at 64–137°C at contact times of 0.02–1.16 h (based on the initial mixture). The catalyst loading was 1 g, and hydrogen flow rate was ~ 10 l/h. The rate constants for hydrogenation (*k*) and the relative activity (*A*) were used as parameters.

Table 3 presents the *k* and *A* values for the modified Ni catalysts and a Ni–Cr catalyst in acetone hydrogenation.

According to these data, the maximal activity in acetone hydrogenation at an atmospheric pressure was reached over the modified Ni catalyst MDC-14. The hydrogenating activity was lower in the case of MDC-2, Ni–Cr, and MDC-7 catalysts. All of the modified Ni catalysts were much more active than the Ni–Cr catalyst.

In another series of experiments performed by N.I. Kartashev at the Institute of Physical Chemistry in Moscow the activity and selectivity in acetone hydrogenation were studied in a pulse flow setup at an atmospheric pressure and an H_2 flow rate of 10–30 ml/min; the catalyst loading was 1.5–2.0 g. For comparison, a nickel catalyst without a modifying agent (3% Ni/Al_2O_3) and a palladium film catalyst (PFC) (0.2% Pd/Al_2O_3) were tested. Table 4 shows the findings on acetone hydrogenation at 120–300°C and a flow rate of the initial mixture of 15 ml/min.

It follows from the above data that the modified Ni catalysts with the low metal concentration (4%) were most active at low temperatures (100–140°C). In the absence of modifying agents, the nickel catalyst with a metal concentration of 3 wt % is inactive in this reaction even at 200°C. The acetone conversion at ~300°C is close to 60–67% over all the catalysts, including PFC and excluding MDC-2(1)-1. This sample is the most selective toward alcohols at 100–200°C.

Figure 1a presents acetone conversions vs. temperature in a 10% ethanol solution that models carbonyl admixtures in crude alcohol during hydrogenation over the MDC and the PFC. It follows from this figure that modified nickel catalysts are more efficient in hydrotreating from acetone admixtures than the palladium catalyst over the whole range of low temperatures (120–150°C). Figure 1b shows the yield of isopropyl alcohol formed upon the hydrogenation of a 10% acetone solution over the modified Ni catalyst and Pd film catalyst as a function of temperature. At an atmospheric pressure, the highest yield of alcohol can be obtained over the modified nickel catalysts at lower temperatures than over the palladium catalyst.

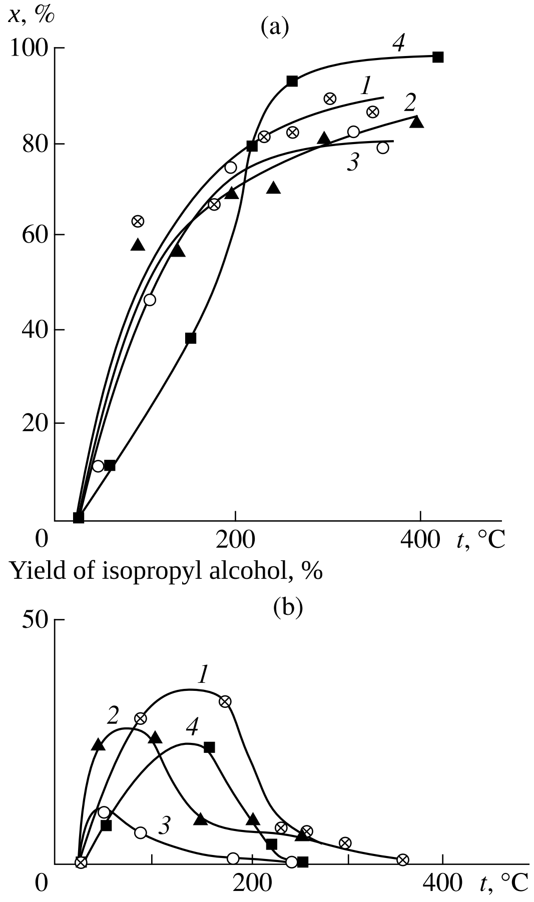

Fig. 1. (a) The conversion (*x*) of acetone in hydrogenation of a 10% mixture of acetone with ethanol and (b) the yield of isopropyl alcohol at the H_2 flow rate of 30 ml/min over catalysts: (*1–3*) Ni catalysts modified by HPC; (*4*) 0.2% Pd/Al_2O_3.

Thus, the model reaction of acetone hydrogenation shows expedience of using the modified nickel catalysts for selective hydrogenation of aldehydes and ketones, including the alcohol syntheses or hydrotreating to remove admixtures of carbonyl compounds.

Table 3. Acetone hydrogenation over Ni-containing catalysts. 120°C, 0.1 MPa

Catalyst	*T*, °C	*A*, rel. u.	k_t
Ni–Cr	110–120	6–17	3–8
MDC-2	135	92–320	25, 30
MDC-7 (Pd)	106–120	60–125	9
MDC-14	75–77	258–523	38, 06

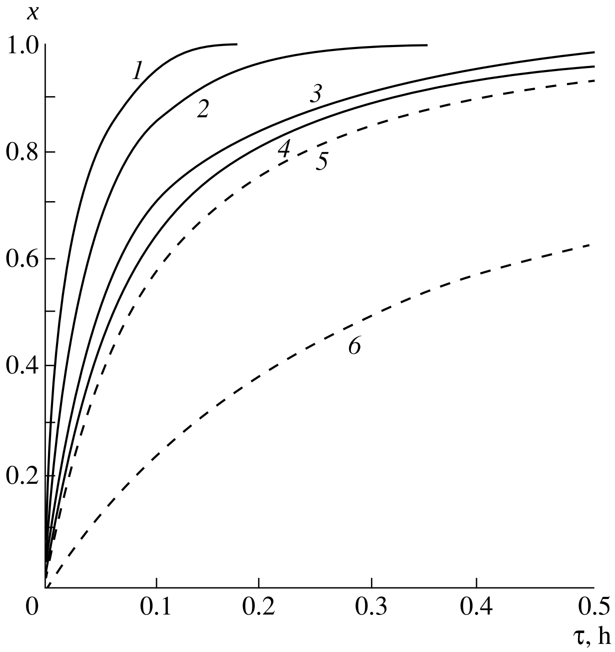

Fig. 2. Benzene conversion (*x*) vs. inverse space velocity of hydrocarbon feed at 160°C and a pressure 1 MPa for various catalysts: (*1*–*3*) 12% HPC; (*1*) 4% Ni, (*2*) 3% Ni, (*3*) 2% Ni, (*4*) 3% of a modifying agent and 4% Ni, (*5*) Ni–Cr, and (*6*) Ni–Cr/Al_2O_3.

HYDROGENATION OF AROMATIC HYDROCARBONS OVER MODIFIED NICKEL CATALYSTS

Figure 2 presents kinetic curves for benzene hydrogenation over the modified nickel catalysts and commercial Ni–Cr and Ni–Cr/Al_2O_3 catalysts, which are used for benzene hydrogenation to cyclohexane. Experiments were carried out by A. M. Proskurnin using a flow setup at an elevated pressure.

Data show that the modified catalysts are active in benzene hydrogenation. Although the nickel concentration is 10 to 20 times lower than that in the commercial Ni–Cr catalysts, the selectivity over the modified catalysts approaches 100%. Side reactions (isomerization and hydrocracking) are virtually absent.

Figure 2 shows that the catalytic activity can be controlled by the concentrations of Ni and a modifying agent. The activity of the modified Ni catalysts per 1 g Ni is 7–18 times higher than that of the Ni–Cr catalysts. When the Ni/HPC ratio is changed, the specific surface area of Ni, its dispersion, and the degree of reduction also change. Table 5 compares these values for the modified Ni catalysts and a series of known Ni catalysts.

Figure 3 shows similar data for toluene hydrogenation. It is seen that the use of a modifying agent results in a significant decrease in the reaction temperature compared to the Ni–Cr catalyst. This allows one to optimize the process and cut down energy consumption.

Another advantage of modified catalysts over the Ni–Cr catalysts is the possibility for reaching a regime that is close to isothermal. Previously, Proskurnin calculated heat evolved in benzene hydrogenation over a series of catalysts in a tubular reactor. When the tubular reactor is charged by two layers of the modified Ni catalysts containing 2% Ni at the inlet and 4% Ni at the outlet, the reaction system becomes more isothermal than in the case of the Ni–Cr catalyst; this is seen from the temperature profiles (Fig. 4). This enables process optimization.

Expensive Pt and Pd catalysts are commonly used at the second stage of hydrotreating in the production of aviation and jet fuels both in Russia and abroad. These catalysts require the desulfurization of feedstock to 0.001% S. The degree of the hydrogenation of aromatic hydrocarbons over the platinum catalyst AP-64 is only 90% at 250–350°C, a pressure of 2–4 MPa, and a space

Table 4. Activity and selectivity of Ni- and Pd-containing catalysts in acetone hydrogenation

Catalyst	*T*, °C	Conversion, %	Reaction products		
			alcohols (Σ)	isopropyl alcohol	propane
PFC (Pd)	140	13.6	11.8	11.8	1.8
	200	51.4	25.9	10.7	25.5
	280	67.8	6.1	6.1	61.7
3% Ni/Al_2O_3	200	0.5	–	–	0.5
	300	60.4	3.1	–	51.8
Ni-MDC-2(1)-1	100	10.1	10.1	10.1	–
	200	20.5	20.5	20.5	–
	300	28.7	21.1	21.1	7.6
Ni-MDC-2(5)-1	100	13.5	13.5	13.5	–
	120	26.3	16.9	16.9	9.4
	300	64.4	30.3	30.3	33.6

velocity of 1.5–5 h^{-1}. Hydrocracking is a side reaction on the Pd–zeolite catalysts, which are widely used abroad. The use of commercial nickel catalysts (Ni–Cr, Ni on kieselguhr, etc.) for complete hydrogenation at the second stage requires elevated pressures (up to 8–10 MPa) and a low sulfur concentration.

Nickel catalysts modified by HPCs proposed by us can be used at the second stage in a two-stage hydrotreating process. They are economically efficient, exhibit high activity and enhanced resistance to sulfur, and have other advantages in the hydrogenation of aromatic and unsaturated compounds. As follows from our data [39], both samples of the modified nickel catalysts were more active than the commercial Ni–Cr catalyst at 0.5 MPa and 160°C, although the concentration of metal was an order of magnitude lower. The temperature of the hydrogenation of monocyclic aromatic compounds can be decreased to 80°C if the lowered conversion of benzene or toluene is needed, which is comparable to that achievable over the Ni–Cr catalyst (50%). At 160–200°C and 1.0 MPa, one can reach 100% benzene conversion over the modified Ni catalysts at τ = 0.5–0.6 h. The complete benzene conversion is not reached over the Ni–Cr catalyst under these conditions.

In tetralin hydrogenation over modified Ni catalysts, complete conversion with 100% selectivity is reached at 200–260°C, a pressure of 1 MPa, and τ = 4.5–5 h. These data show that the modified nickel catalysts can provide deep dearomatization of mixtures of mono- and bicyclic aromatic hydrocarbons at lower pressures than the commercial Ni, Pt, and Pd catalysts. Hence, they can be used at the second stage of hydrotreating in the production of environmentally clean high-quality aviation fuels with a concentration of aromatic hydrocarbons below 10%.

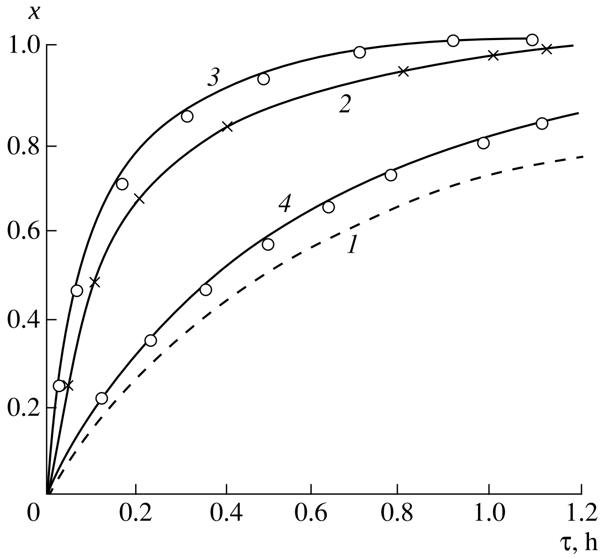

Fig. 3. Toluene hydrogenation over Ni-containing catalysts (160°C, 0.5 MPa): (*1*) Ni–Cr, (*2*) 4% Ni + 12% Mod/Al_2O_3 (at 160°C), (*3*) 4% Ni + 3% Mod/Al_2O_3, (*4*) 4% Ni + 12% Mod/Al_2O_3 (at 80°C).

The modified Ni catalysts are highly active in the hydrogenation of unsaturated hydrocarbons (octene, nonene, and decene) [39]. The complete hydrogenation of octene is reached at 90–110°C, a pressure of 0.5 MPa at τ = 0.5 h and at 70°C at τ = 1 h. When nonene and decene are hydrogenated over the modified 4% Ni catalyst, 100% selectivity is reached at 110–120°C, 0.5 MPa, and τ = 0.4 h.

More active modified nickel catalysts have also been developed, which are capable of selectively hydrogenating unsaturated hydrocarbons, except for aromatic hydrocarbons, to hydrocarbon mixtures.

The performance of modified nickel catalysts can be flexibly controlled by the nature and a composition of a modifying HPC.

Table 5. A comparison of nickel catalysts modified by heteropoly acids with known catalysts for benzene hydrogenation

Catalyst	Ni, %	S_{Ni}, m^2/g	α, %, Extent of reduction	α_{H_2}, %	d_{Ni} (H_2), nm	d_{Ni} (magn.)*, nm
Euro–Ni-1 (Ni/SiO_2)	25–52	113–181	–	–	6–8	–
Ni/SiO_2 (Al_2O_3)	2–20	–	–	–	12–35	–
Ni–Cr (ind.)	48–63	25–27	–	–	–	–
Ni/Al_2O_3 (Exxon)	8.8	197	–	–	3.4	–
Ni-MDC-1/Al_2O_3	4	220	70	27	2.6	3.4
Ni-MDC-2/Al_2O_3	4	39	67	16	14	–
Ni-MDC-3/Al_2O_3	4	334	87	32.5	1.7	2.3
Ni-MDC-4/Al_2O_3	4	56	27	6	10	4.4

* The data of [3, 36].

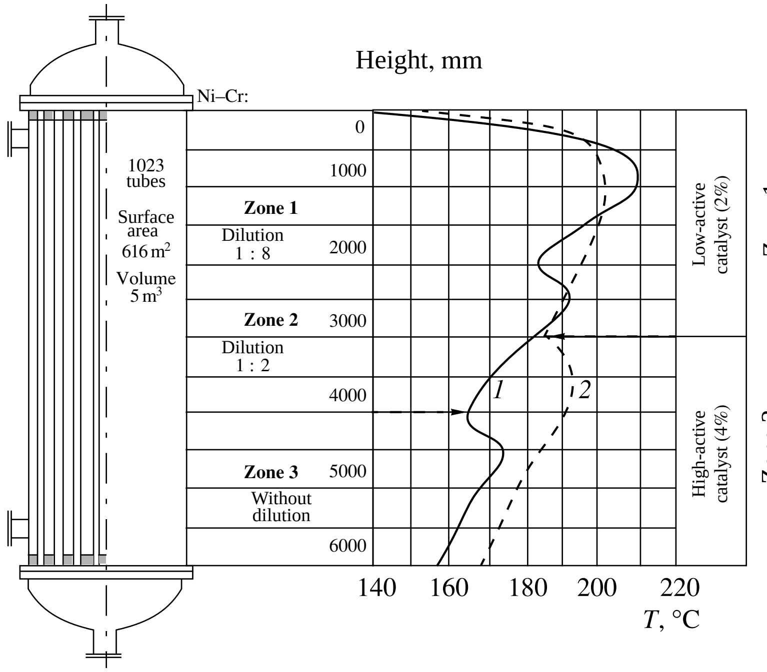

Fig. 4. A scheme of heat evolution during benzene hydrogenation in a tubular reactor: (*1*) over Ni–Cr catalyst and (*2*) over the modified Ni catalyst loaded layer-by-layer: 2% Ni at the inlet and 4% Ni at the outlet of the reactor.

EFFICIENT PALLADIUM CATALYSTS OF A NEW TYPE FOR HYDROGENATION

The main industrial method for ethylene manufacture is hydrocarbon pyrolysis (ethane–ethylene fraction, propane–propylene fraction, and butane fraction). It is necessary to remove acetylene (0.4–2.2%) from the ethane–ethylene fraction of pyrolysis gases produced at ethylene plants. The removal of acetylene hydrocarbons is often necessary in other processes. The operation conditions are the following: 0.1–2.6 MPa; 60–100°C; and space velocity, 2500–12000 h^{-1}.

Now the ethane–ethylene and propane–propylene fractions are purified from acetylene by selective hydrogenation over catalysts containing supported noble metals (Pt, Pd, and Rh). The metal concentration is varied from 0.5 to 2%.

The selectivity of C_2H_2 hydrogenation to ethylene over conventional supported Pd catalysts is lowered because of the side reactions of complete C_2H_2 hydrogenation to C_2H_6 and oligomerization of C_2 products to C_4, and C_6 hydrocarbons and other oligomers. During hydrotreating, Pd catalysts are rapidly covered by polymer deposits and thus rapidly deactivated. Frequent regeneration of the catalysts is required.

To remove such drawbacks, Procatalyse, the French Petroleum Institute, and other companies in Europe and the United States develop and produce improved bimetallic catalysts, such as Pd–Au/Al_2O_3. In Russia, the GIPKh-108 (Pd/C) catalyst and MA-15, a sulfided Pd(S)/Al_2O_3 catalyst, were used for selective hydrotreating to remove acetylene, and this resulted in a higher selectivity compared to conventional Pd catalysts.

These catalysts have some drawbacks. For example, it is impossible to prepare bimetallic catalysts with a Pd concentration $<3\%$ by a common impregnation method. The procedures for their preparation including organometallics or the vapor deposition of two metals on a support (by one or two successive stages) are quite complicated and cannot be used in industry. GIPKh-108 requires low space velocities (1000 h^{-1}) due to the low activity and high temperatures (up to 165°C), although the concentration of a hydrogenating component in the catalyst is high. The reaction temperature over MA-15 is lower, but side reactions producing oligomers (so-called “green oil”) occur.

The stability and possible regeneration of the above Pd catalysts are often unsatisfactory. For example, the catalyst Pd(S)/Al_2O_3 for the selective hydrogenation of alkynes loses sulfide sulfur during both the hydrogenation of an ethane–ethylene fraction and the regeneration of the catalyst. The surface area of the catalysts decreases from 208 to 20 m^2/g in 900 h. The regeneration of Pd/C is also impossible.

New catalysts for the selective hydrogenation of acetylene hydrocarbons are based on a thin-layer oxide film (Al_2O_3) with a low palladium concentration (0.05–0.3%) deposited on a support (Al_2O_3, SiO_2, etc.). The patented film catalysts (Pd/Al_2O_3/Al_2O_3) can be prepared on various supports by a special procedure [18]. Metal particles are formed on the surface of the γ-Al_2O_3 granule with the additive of a thermally stable aluminum oxide at a Pd/Al_2O_3 ratio of 1 in the oxide layer whose thickness is at least 100 nm. The palladium particles are uniformly distributed over the oxide layer. The average diameter of Pd particles is 5 nm. The catalysts are thermally stable and can subjected to oxidative regeneration.

The activity and selectivity of the palladium film catalysts were tested at the Institute of Organic Chemistry (Moscow) in the Laboratory headed by Professor S.L. Kiperman in a flow-circulation setup at an atmospheric pressure using the model mixture of 0.7% C_2H_2, 1.4% H_2, 72.9% C_2H_4, and 25% He at 30°C and a space velocity of 4500–1500 h^{-1}. Table 6 presents the findings for the film catalyst PFC-1, as well as for commercial catalysts $Pd(S)/Al_2O_3$ and ICI.

It is obvious from the above data that the new palladium film catalysts are more active and selective than $Pd(S)/Al_2O_3$ even when the Pd concentration in the film is five times lower. Moreover, according to additional data obtained by Z.T. Beisembaeva using a pilot plant with a real hydrocarbon feedstock (ethane–ethylene fraction from the ethylene setup of the Shevchenko plant for polymeric materials), the catalysts with a Pd concentration of ~0.5% are less selective than PFC-1 containing 0.1% Pd.

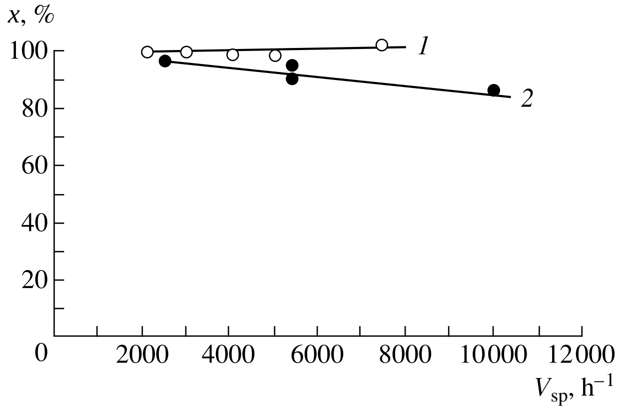

Fig. 5. The effect of the space velocity on the conversion of C_2H_2 in ethane–ethylene fraction over (*1*) PFC-1 and (*2*) MA-15.

Figure 5 compares the degree of acetylene hydrogenation in the real ethane–ethylene fraction over the PFC-1 and $Pd(S)/Al_2O_3$. It is seen that despite the essentially lower Pd concentration, the new palladium film catalyst exhibits better performance in the hydrotreating of the ethane–ethylene fraction than the domestic commercial catalyst MA-15. Table 6 shows

Table 6. Activity and selectivity of various palladium catalysts in acetylene hydrogenation (0.1 MPa; a mixture of C_2H_2, 0.7%, C_2H_4, 72.9%, H_2, 1.4%, He, 25%)

Catalyst	Pd, wt.%	*T*, °C	Space velocity, h^{-1}	Activity, mol (g cat)$^{-1}$ h^{-1}	Selectivity, %			
					C_2H_4	C_2H_6	C_4	C_6
PFC-1	0.1	60	3900	0.90	0.74	0.08	0.09	0.07
		60	4900	1.17	0.79	0.08	0.07	0.06
		30	2550	0.58	0.77	0.07	0.08	0.08
$Pd(S)/Al_2O_3$	0.55	60	3500	0.80	0.69	0.18	0.10	0.03
|C|	0.05	60	2000	0.45	0.81	0.06	0.06	0.07

Table 7. The effect of regeneration on the activity and selectivity of palladium catalysts (0.01 MPa, H_2/C_2H_2 = 2)

Catalyst	*T*, °C	Space velocity, h^{-1}	Activity, mol (g cat)$^{-1}$ h^{-1}	Selectivity, %			
				C_2H_4	C_2H_6	C_4	C_6
Before regeneration							
PFC-1	60	3400	0.86	0.60	0.23	0.15	0.02
$Pd(S)/Al_2O_3$	60	3500	0.80	0.67	0.20	0.10	0.03
	40	3900	0.89	0.76	0.11	0.08	0.05
After regeneration							
PFC-1	60	4900	1.17	0.79	0.08	0.07	0.06
$Pd(S)/Al_2O_3$	40	3900	0.32	0.51	0.28	0.17	0.04

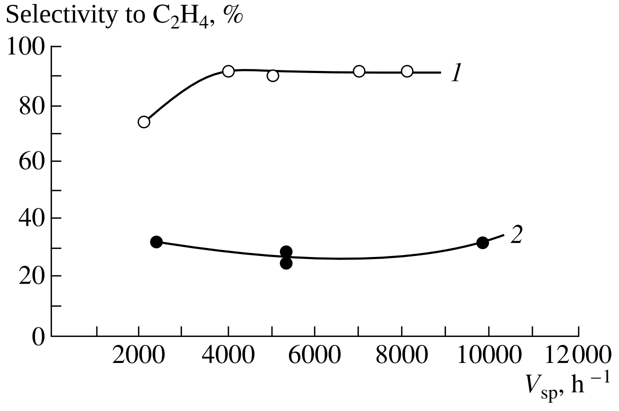

Fig. 6. The selectivity of acetylene hydrogenation over (*1*) PFC-1 and (*2*) MA-15. 80°C, 2.6 MPa, $H_2/C_2H_2 = 2$.

that PFC-1 with a low palladium concentration is more active at 60°C than the ICI catalyst. The ICI catalyst is completely inactive at 30°C, whereas PFC-1 is highly active and selective.

It is interesting that, after oxidative regeneration, the PFC-1 catalyst was also active and selective at 55–60°C, unlike Pd(S)/Al_2O_3. Table 7 compares the results of testing the PFC-1 and Pd(S)/Al_2O_3 catalysts after oxidative regeneration at 500°C. The results point to the enhanced thermal stability of the PFC-type catalysts and the possibility for prolonging their service life compared to Pd(S)/Al_2O_3.

Figure 5 shows that PFC-1, unlike MA-15, is stable over a wide range of feed space velocities and efficiently removes acetylene. It is substantially more selective in hydrogenation to ethylene than Pd(S)/Al_2O_3 (MA-15), and the selectivity is stable at high space velocities of feed (4000–10000 h^{-1}), reaching 90% (Fig. 6) under the chosen conditions for hydrogenation.

Thus, the palladium film catalysts for acetylene selective hydrogenation differ from previously known catalysts and have the following useful properties:

—They have higher activity. This allows one to use low reaction temperatures (down to 30°C) and a low H_2/C_2H_2 ratio of 2 (see Table 7), in comparison to the ratio $H_2/C_2H_2 = 3–4$ required by Pd(S)/Al_2O_3 containing 0.5% Pd.

—The selectivity to C_2H_4 is higher due to a decreased yield of “green oil” at low temperatures (Fig. 6).

—It is possible to increase the feed space velocities to 4500–15000 h^{-1} without increasing the H_2/C_2H_2 ratio to ~4, which is typical of the MA-15 catalyst. The activity remains constant in this case (Fig. 5).

—They have higher thermal stability (above 450°C).

—High-temperature oxidative regeneration is possible, which results in enhanced activity (Table 4).

—The Pd concentration in the oxide layer on the surface of Al_2O_3 is low (0.05–0.30%), and palladium distribution can be controlled.

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