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Hydrogenating Activity and Adsorption Capacity of Supported Nickel Catalysts Modified by Heteropoly Compounds

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Abstract—The catalytic activity, adsorption capacity, and pore structure of low-percentage nickel catalysts supported on γ-Al_2O_3 or activated carbon and modified by tungsten heteropoly compounds are studied. The activity, selectivity, and thermal stability of the catalysts in the vapor-phase hydrogenation of olefins and aromatic hydrocarbons are higher than those for conventional nickel catalysts. The concentration of nickel in the catalysts is 10–15 times lower than that in commercial catalysts. However, the modified catalysts have higher specific surface areas of metal, higher dispersion, a uniform distribution of metal particles, and a pore-radius distribution other than in the support. The study of water adsorption and desorption showed that the heteropoly compound modifying the γ-Al_2O_3 support covers the support surface completely, and supported nickel interacts with the active surface of the modifying agent rather than with Al_2O_3. A hydrogenation mechanism is proposed, which involves H_2 dissociation on Ni particles and the subsequent diffusion of hydrogen atoms via a spillover mechanism to the adsorbed organic compound with the participation of the OH groups of the modifying agent.

INTRODUCTION

Although nickel catalysts are active and inexpensive, they have some shortcomings, which are clearly seen in vapor-phase hydrogenation processes: (1) commercial Ni–Cr catalysts have very high nickel concentrations (up to 50 wt %), (2) they have low thermal stability (lower than 280–300°C), (3) when the nickel concentration is low (4–10%), expensive oxides should be added in large amounts (from 15 to 40% of MoO_3, WO_3, Nb_2O_5, or others), (4) to enhance the catalytic activity, one should use specially synthesized supports (zeolites, aluminophosphates, Al_2O_3 and SiO_2 of a special structure, etc.), and (5) catalyst preparation is technologically complicated. A search for new active, selective, thermally stable, and inexpensive catalysts for hydrogenation is urgent now due to the development of new technologies and toughening requirements for diesel fuels. These requirements imply fuel hydrofining to remove as much aromatic and unsaturated compounds as possible [1].

Among the nickel catalysts for vapor-phase hydrogenation, the low-percentage of (up to 10% Ni) supported catalysts modified by MoO_3, WO_3, Cr_2O_3, and zeolites have become more frequently used [2, 3]. Physical methods (differential thermal analysis, thermogravimetry, ESR, and ferromagnetic resonance) have been used to show that specific nickel active sites are formed on their surfaces. These sites have properties different from those of nickel in the Ni–Cr and bulk Ni catalysts. For example, in the Ni/Al_2O_3 catalyst for thiophene hydrogenolysis modified by MoO_3 and a zeolite, thermally stable molybdenum compounds with zeolite are formed [4]. This favors a more uniform distribution of nickel active sites and results in the formation of a more dispersed metal phase upon the reduction of nickel molybdates.

The decomposition of organometallic compounds of Group IV–VII elements (Mo, W, Re, and Sn) on a support together with the salts of Group VIII metals also allows the preparation of highly dispersed, thermally stable, and highly active hydrogenation catalysts [5]. The most probable reason for the enhancement of thermal stability is the interaction of an active component (Ni and Co) with other ions and the formation of the metal–metal bond with the participation of a modifying agent.

Further development of procedures for the preparation of supported nickel catalysts is associated with the use of heteropoly compounds (HPCs) for their synthesis [3, 6]. Nickel salts with anions of the $[H_6XY_6O_{24}]^{4-}$ type, where X = Co or Ni and Y = Mo or W, are decomposed on the support surface and produce an active phase [6]. Until recently, these and other HPCs were used in catalysis mainly in oxidation, hydration, dehydration, and other reactions [7–11]. Testing nickel catalysts prepared from Mo- or W-containing HPCs on a support in the hydrodesulfurization and hydrogenation processes showed that these catalysts are less active than commercial Co–Mo, Ni–Mo, and Ni–W catalysts. This is due to a low Ni concentration and catalyst poisoning by sulfur compounds under the reaction conditions [6].

In the 1980s, one of the authors of this work proposed new low-percentage nickel catalysts on supports (activated carbon, Al_2O_3, and SiO_2) in which various tungsten HPCs were used as modifying agents [12–20]. In these catalysts, Ni interacts with a support only through a modifying agent and, as a result, the metal acquired different properties. These catalysts were tested in many gas-phase and vapor-phase reactions such as the hydrogenation of aromatic (mono- and bicyclic) compounds, olefins, ketones, CO, and carbons; toluene hydrodemethylation; the hydrocracking of gasoline fractions, dehydrogenation of cycloalkanes, and dehydroaromatization of *n*-paraffins. In most cases, they exhibited high and controllable activity and selectivity. The above catalysts have the following characteristics: a low concentration of metal (2–6% Ni) and modifying agents (<15% or <7% based on W) on the surface of a support and the high surface area of Ni, high dispersion, thermal stability, and the practically feasible preparation procedure.

In this work we studied the hydrogenating activity and adsorption capacity of Ni catalysts modified by HPCs.

EXPERIMENTAL

Nickel catalysts modified by tungsten heteropoly compounds (HPCs) with the overall formula $M_n[SiWO_m]$, where $n = 4$, $m = 40$ at M = Li, K, and Cs and $n = 2$, $m = 39$ at M = Ni, were prepared by the successive impregnation of the support (γ-Al_2O_3 or activated carbon) by HPCs (3–12%) and Ni nitrate (4–6% Ni) followed by drying, thermal treatment in air at 400–500°C, and reduction with hydrogen at 300–400°C. The modifying heteropoly compounds (HPC-1, HPC-2, HPC-3, HPC-4, and HPC-5) had slightly different compositions and structures.

The hydrogenation of hydrocarbons (benzene, toluene, olefins C_8–C_{10}, and their mixtures with saturated hydrocarbons as models of motor fuels) was studied in the vapor phase using a setup at the State Institute of Nitrogen Industry and Products of Organic Synthesis with a flow reactor under a pressure of 0.5–1.5 MPa at 80–260°C and a space velocity of the liquid hydrocarbon of 0.2–10.0 h^{-1} and electrolytic hydrogen from 30 to 300 h^{-1}. The amount of the catalyst was 5–25 g. Starting hydrocarbons (benzene, toluene, olefins C_8–C_{10}, and their mixtures with paraffins) were analyzed on a Tsvet-100 gas–liquid chromatograph with a flame-ionization detector using programmed heating. Experimental data were treated by the procedure developed for vapor-phase hydrogenation in a fixed-bed reactor [21]. The rate constants k were estimated from the experimental dependence of the starting hydrocarbon conversion on a contact time $\tau = 1/u$ at a constant temperature and a constant pressure and were calculated according to the empirical equation

$$w = \frac{x}{1/u} = kP^n C_H^{(1-x)}(1-0.9x), \qquad (1)$$

where w is the hydrogenation rate, x is the conversion of the starting hydrocarbon (in molar fractions), k is the rate constant, P is the overall pressure, C_H is the hydrogen concentration, and u is the space velocity. Empirical Eq. (1) has been verified for many catalytic vapor-phase hydrogenation reactions [21]. In our work, the curves for the reaction rate vs. contact time were linearized in the coordinates of Eq. (1) at $n = 0.15$.

The adsorption properties of the support (γ-Al_2O_3), modifying agents HPC-1, HPC-2, and others, and the nickel catalysts were estimated from their water adsorption capacities (AC_{H_2O}) similarly to the procedure used in [19], as well as from water thermal desorption during heating from 20 to 600°C.

The measurements of AC_{H_2O} and water thermal desorption were performed by thermogravimetry (TG) on a Q-500 analyzer. The water thermal desorption was also studied by the differential thermal analysis (DTA) on a Dupont analyzer in air at a heating rate of 5–10°C/min. To estimate the AC_{H_2O} values, starting samples were dried at 120°C until a constant weight and stored in a hydrostat at P_{H_2O} = 17.5–20.0 torr also to a constant weight. Then, water thermal desorption was carried out until reaching a plateau on the TG curve. The AC_{H_2O} values were calculated according to the procedure described in [19].

The adsorption properties of carbon supports with various specific surface areas (G-6-1 and G-6-2) and modified Ni catalysts on their basis were studied by chromatography using *n*-hexane adsorption at 200°C according to a procedure proposed in [22] for Pd-zeolite catalysts. The specific retention volumes of *n*-hexane on the supports and Ni catalysts were measured in the presence or absence of HPCs. Experiments were carried out in a H_2 flow on the reduced catalysts.

The specific surface area of nickel in the supported modified catalysts (S_{Ni}) was determined by H_2 and O_2 adsorption.[1] The porosity of the catalysts was measured by the low-temperature nitrogen adsorption.[2]

The electron-microscopic study was performed using an EM-30 Phillips microscope at voltages of 80 and 100 kV and a space resolution of 0.2–0.7 nm [17].[3]

RESULTS

As mentioned above, the main features of the new Ni catalysts are the low concentration of a metal and the

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[1] Measurements were carried out at the Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, in the Laboratory headed by Professor A.A. Slinkin.

[2] Measurements were conducted by G. Parsum in the Haldor TopsØe Laboratory (Lyngby, Denmark).

[3] Measurements were carried out at the Institute of Physical Chemistry, Russian Academy of Sciences, in the Laboratory headed by Professor A.E. Chalykh.

Table 1. Specific surface area of Ni in various hydrogenation catalysts

Catalyst	Concentration of Ni, wt %	S_{Ni}, m^2/g	Ref.
Ni–HPC-1/Al_2O_3	4	220	Our data
Ni–HPC-1/Al_2O_3	2	79	″
Ni–HPC-2/Al_2O_3	4	330	″
Ni–HPC-3/Al_2O_3	4	56	″
Ni–HPC-4/Al_2O_3	4	180	″
Commercial Ni–Cr catalyst	48–63	26	[23]
Ni/SiO_2 (Euro-Ni-1)	25–52	180	[24]
Ni/Al_2O_3 (Exsson)	8–10	195	[25]

presence of the tungsten HPC modifying additives. These features determine the high specific surface area of the Ni metal on the support, its high dispersion, and enhanced thermal stability (heating to 400–500°C does not change its properties). The thermal stability was studied by IR spectroscopy [15] and DTA [19].

Table 1 lists the data on the specific surface area of metal in the new Ni catalysts supported on γ-Al_2O_3 with various modifying additives (HPC-1, HPC-2, HPC-3, and HPC-4). The corresponding values for known hydrogenation catalysts are presented for comparison [23–25].

As can be seen from the table, the high metal surface area on Al_2O_3 modified by additives of various HPCs can be obtained even at a low Ni concentration (4 wt %). Moreover, the Ni specific surface area in the samples modified by HPC-1 and HPC-2 can be higher than in the commercial Euro-Ni-1 and Exxon catalysts and 9–12 times higher than in the Ni–Cr catalyst, although the metal concentration in the modified catalysts is an order of magnitude lower. When other modifying agents (HPC-3 or HPC-4) are used or the Ni/HPC ratio changes, the S_{Ni} value approaches the specific surface areas of the known catalysts.

It has been shown earlier by electron microscopy that the Ni particles in the modified nickel catalysts are distributed uniformly [17]. The modified and unmodified low-percentage Ni/C catalysts on the G-6-1 and G-6-2 carbon supports were the focus of this work. The specific surface area of G-6-1 is 37 m^2/g and that of G-6-2 is 675 m^2/g.

As is seen from Fig. 1, the Ni particles in the unmodified catalysts with a size of 20–40 and even 80 nm are distributed nonuniformly. After modification, the distribution of Ni particles becomes uniform (Figs. 2a, 2b) and the particle size decreases to 2.5–7.0 nm (reduction temperature was 300–420°C). These thermally stable metal-containing active sites are formed in the presence of the tungsten HPC on any support (C, Al_2O_3, SiO_2, etc.). The Ni particle size on Al_2O_3 can be smaller, 3–4 nm (Figs. 2c–2e). All these catalysts exhibit high hydrogenating activity [14].

The Ni/Al_2O_3 catalysts modified with different HPCs (HPC-1, HPC-2, HPC-3, HPC-4, and HPC-5) show enhanced thermal stabilities. Their specific surface areas and dispersion of metal do not change upon heating to 450–500°C, whereas the sintering and coarsening of particles in the known supported Ni catalysts are found already at 380–400°C and the commercial Ni–Cr catalyst deactivates at temperatures of ~220°C [3, 17, 19].

Data on the pore structure of the support and modified Ni catalyst upon the formation of the active phase are shown in Fig. 3. As can be seen, the pore structure of the γ-Al_2O_3 support changes after the deposition of HPC-1 and Ni salt. The maximum of the pore distribution at 10 nm is retained, but two new maxima appear, which correspond to radii of <2 and 7 nm.

The adsorption properties of the modified and unmodified catalysts on carbon supports are presented in Table 2. The adsorption retention volume V_a is determined by the adsorption coefficient of the physically adsorbed hydrocarbon [22].

It follows from Table 2 that the surface area of the large-pore G-6-1 carbon support increases from 37 to 53 m^2/g upon the deposition of the HPC-1 heteropoly compound. The HPC-1/G-6-1 system is capable of adsorbing much more HPC than Ni/G-6-1. The deposition of Ni also increases *n*-hexane adsorption (sample 12% Ni/G-6-1). When the active phase deposits on the narrow-pore carbon support G-6-2, the specific surface area decreases, but the *n*-hexane adsorption also increases. Apparently, the Ni/HPC ratio is of crucial importance for the adsorption capacity of the modified Ni catalysts.

The electron diffuse-reflectance spectra provide evidence that the Ni^{2+} ions of two types with a different crystal field, which differ from Ni^{2+} in $NiAl_2O_4$, form on γ-Al_2O_3. The spectra suggest the formation of the Ni^{2+} active sites including HPC and the absence of direct interaction between Ni and Al_2O_3.

The degree of Ni reduction in the modified catalysts achieves high values despite the low metal concentration and mild reduction conditions (400°C, 6 h) compared, for example, to the catalyst Euro-Ni-1 standard (600–630°C, 10–26 h). In some cases, the modified catalysts with a low nickel concentration were reduced completely (2% Ni–HPC-1/Al_2O_3). They were highly active in the hydrogenation of aromatic hydrocarbons [14] unlike unmodified Ni/Al_2O_3 catalysts, in which a fraction of Ni enters the framework of the support, forming the $NiAl_2O_4$ spinel [3].

It has been shown earlier that the hydrogenation of monocyclic aromatic hydrocarbons [12, 16] and olefins [12, 20] can occur over HPC-modified nickel catalysts on carbon supports and Al_2O_3. Hydrogenation conditions for aromatic compounds (benzene and toluene) were rather strict: P = 3–5 MPa and T = 180–300°C

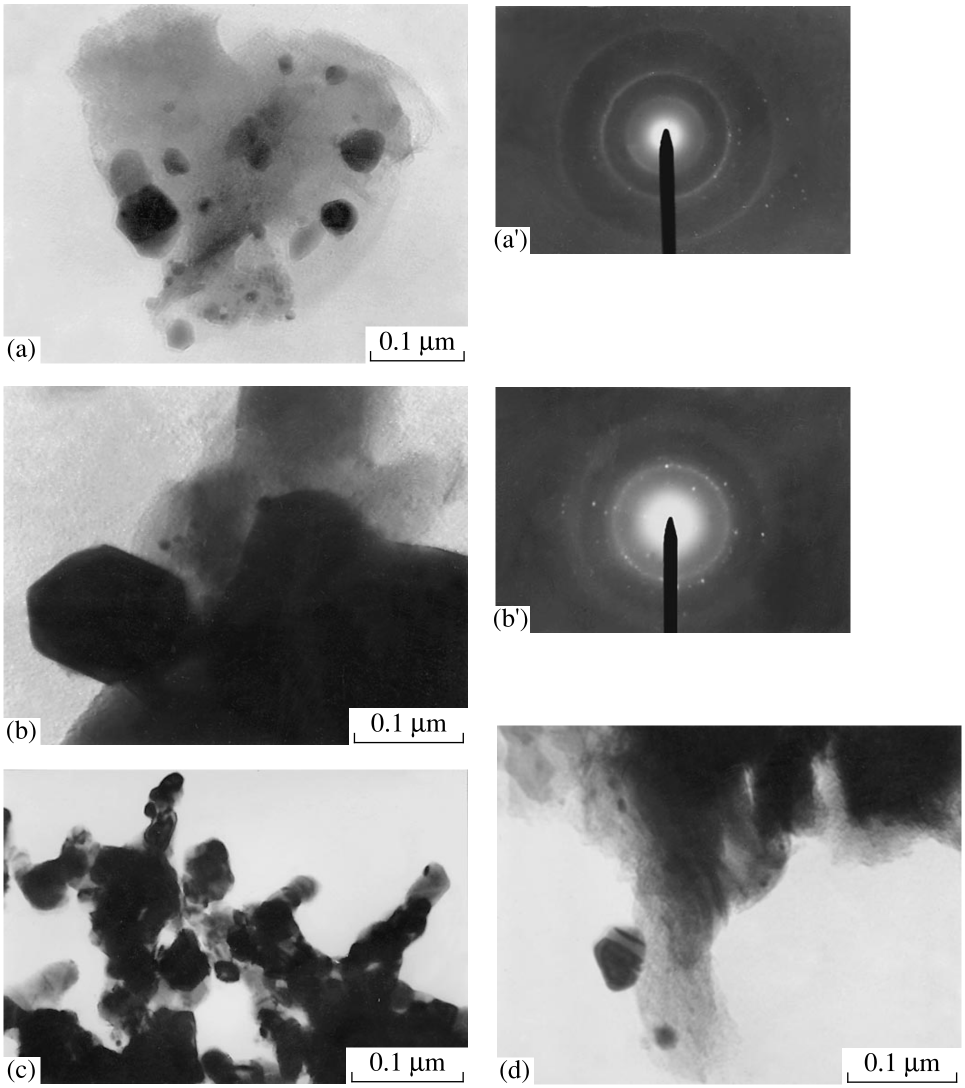


Fig. 1. Micrographs of Ni/C samples reduced at 400°C: (a) 2% Ni on G-6-1; (b) 2% Ni on G-6-1 (another part); (c) 4% Ni on G-6-1; (d) 4% Ni on G-6-2; (a') and (b') are microdiffraction of regions (a) and (b), respectively.

[12, 14, 16]. Figures 4 and 5 show the results of the study of benzene hydrogenation over the modified nickel catalysts at pressures of 0.5, 1.0, and 1.5 MPa.

Figure 4a presents benzene conversion (x) on the 4% Ni–HPC-2/Al_2O_3 catalyst as a function of a contact time ($\tau = 1/u$) at temperatures of 80–200°C. The curves correspond to empirical Eq. (1). It follows from the figure that benzene is completely hydrogenated over this sample under the chosen pressure (1 MPa) only at 120–200°C and $\tau > 0.5$–0.9 h. When the pressure increases to 1.5 MPa, the above curves shift to lower τ values and complete benzene conversion is achieved at $\tau = 0.4$–0.7 h.

As can be seen from Fig. 4b, when the metal concentration increases from 2 to 4% Ni, the catalytic activity increases. The activity of the modified catalyst is higher than that of the commercial Ni–Cr catalyst containing much more Ni.

The curves describing the temperature dependence of the rate constant of benzene hydrogenation over Ni–HPC-2/Al_2O_3 have clearly seen inflection points at 130°C (Fig. 5). This can be due to the fact that at $T > 130$°C, the reaction starts to be controlled by internal diffusion. However, since the complete benzene conversion is achieved only at high temperatures, the kinetics of benzene or toluene hydrogenation over other modified catalysts was studied at temperatures ranging from 140 to 240°C. When a pressure is increased, the hydrogenation rate increases (Fig. 5) and this process is slower in the range from 1.0 to 1.5 MPa than at 0.5–1.0 MPa.

Similar results were obtained for toluene hydrogenation. The activity of Ni/Al_2O_3 catalysts modified with HPCs can be changed by changing the amount of Ni or by changing the amount and nature of the HPC. The commercial Ni–Cr catalyst was markedly less active;

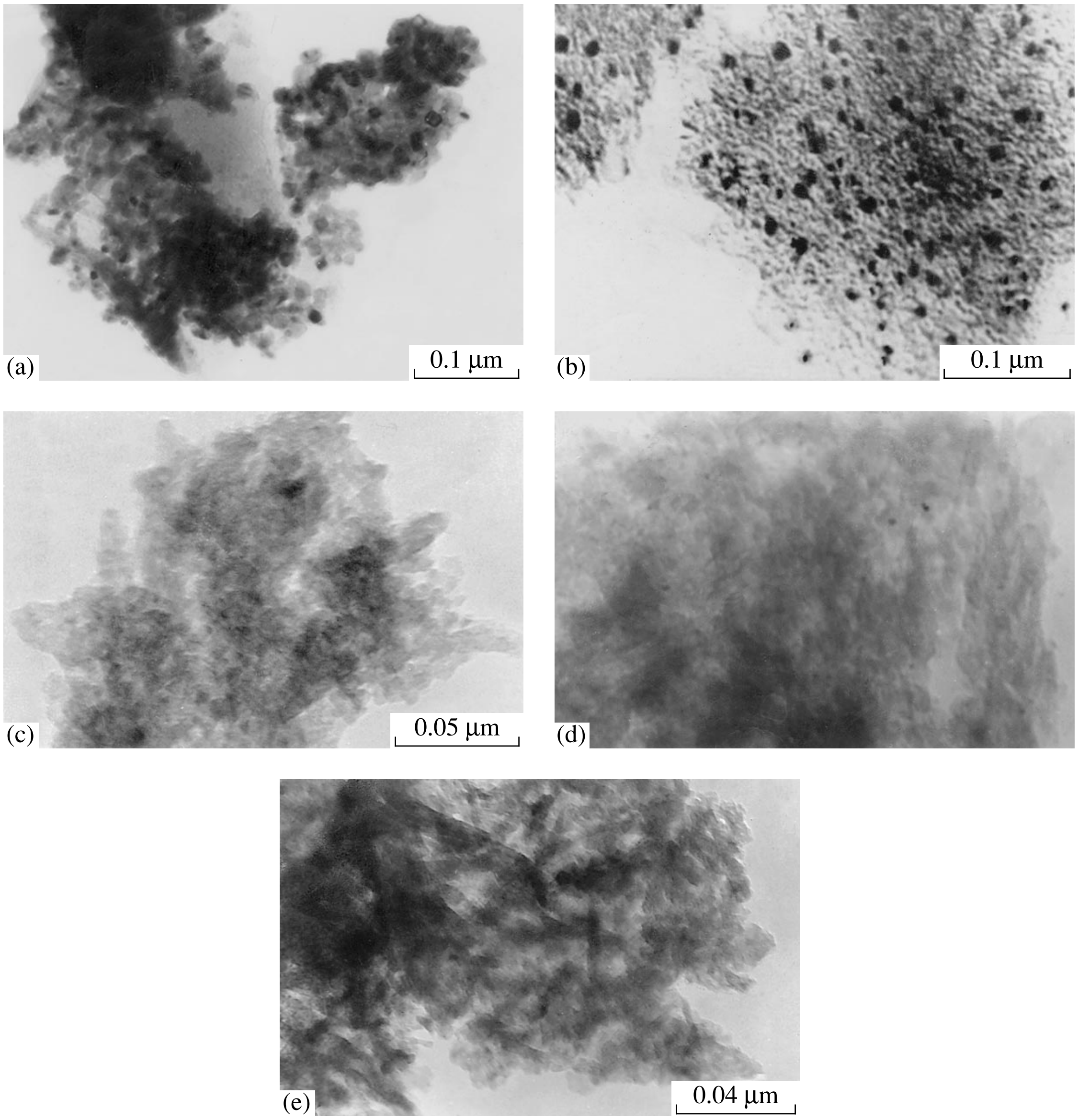


Fig. 2. Micrographs of nickel catalysts modified by HPCs on various supports: (a) 6% Ni–HPC-3 on G-6-2 (reduced at 400 °C); (b) 4% Ni–HPC-1 on G-6-2 (reduced at 300°C); (c) 4% Ni–HPC-1 on Al_2O_3 (after reaction at 400°C); (d) 2% Ni–HPC-1 on Al_2O_3 (reduced at 420°C); (e) 2% Ni–HPC-1 on Al_2O_3 (reduced at 600°C).

its activity at 160°C is comparable to that of Ni–HPC-2/Al_2O_3 at 80°C.

Similar kinetic curves were obtained for the hydrogenation of octene and other olefins. Figure 6a presents the results for the vapor-phase octene hydrogenation (a 50% solution of octene in cyclohexane prepared before was fed to a catalyst) over the modified Ni–HPC-2/Al_2O_3 at a pressure of 0.5 MPa. As is seen from Fig. 6a, the complete olefin conversion is achieved not only at a substantially lower pressure than on commercial catalyst (0.5 MPa) but also at a lower temperature (70–110°C). The hydrogenation kinetics is approximated by Eq. (1). The kinetic curves describing the hydrogenation of nonene, decene, and octene at 110°C (cf. Fig. 6a and 6b) over the same catalyst virtually coincide.

The rate constants of hydrogenation over the modified catalysts calculated according to empirical Eq. (1) are close to or higher than those over the commercial Ni–Cr catalyst, containing 12 times more Ni. The hydrogenation rates for octene, nonene, and decene at 160°C and a pressure of 1 MPa over the 4% Ni–HPC/Al_2O_3 catalyst were 15.6–25.4 h^{-1} ml^{-1}, whereas the rate for decene, for example, over the commercial Ni–Cr catalyst (50% Ni) was 11.5 h^{-1} ml^{-1}. The productivity of the 4% Ni–HPC-2/Al_2O_3 catalyst in benzene hydrogenation was 1.39 l (l Cat)$^{-1}$ h^{-1} and that in octene hydrogenation was 3.57 l (l Cat)$^{-1}$ h^{-1}. The productivity of a commercial Ni–Cr catalyst in decene hydrogenation was 1.25 l (l Cat)$^{-1}$ h^{-1}. The specific catalytic activities of the HPC-modified Ni catalysts per 1 g Ni were 6.5–16.6 times higher than that of the commercial Ni–Cr catalyst. The maximal duration of our experiments was 140 h, and the catalytic activity remained constant.

The adsorption properties of carriers and supported catalysts depend significantly on the amount and nature of hydroxyl groups on their surfaces. It has been shown in [19] that upon the interaction of HPC-1 with Ni on γ-Al_2O_3, the adsorption properties of the active surface with respect to H_2O change. The adsorption properties of a series of modifying agents (HPC-2, HPC-3, HPC-4, and HPC-5), modified nickel catalysts, and model systems with intermediate compositions were studied in this work. When all these samples are heated in the chosen temperature range, only water evolves.

Figure 7 shows changes in the sample weights during the thermolysis of the heteropoly compound (HPC-2), heating the support (γ-Al_2O_3), and the HPC-2/Al_2O_3 system (without Ni). These data allow the determination of the maximal adsorption capacity with respect to water (AC_{H_2O}) for every sample. As is seen from Fig. 7, the adsorption capacity of the support changes upon modifying it with HPC-2. The maximal adsorption capacity for the modifying agent is ~6.5% and the AC_{H_2O} for γ-Al_2O_3 approaches 7%. The AC_{H_2O} value for the modified support in the whole range of measurements is higher than that for Al_2O_3 and HPC-2. Obviously, a new structure whose adsorption properties differ from those of the starting components arises upon the deposition of HPC-2.

As is seen from Fig. 8, when the concentration of heteropoly compound (HPC-2) is increased, the adsorption capacity of the modified Ni catalysts with respect to water decreases to the corresponding values AC_{H_2O} for Al_2O_3 or lower. Hence, it is possible to change purposefully the adsorption capacity of the catalyst, varying the concentration of the modifying agent independently of the HPC nature.

The shape of the temperature-programmed desorption (TPD) curves for water from the modified nickel catalysts depends significantly on the Ni concentration (Fig. 9). The above data show that both weakly adsorbed and strongly chemisorbed water is present in the highly active modified Ni catalysts supported on Al_2O_3. These water species desorb at 50–150 and 200–250°C, respectively. The presence of water desorbing at higher temperatures, 500–600°C and even 700°C, is possible. These high-temperature species are absent from the low-active sample (curve *3*).

Figure 10 presents the TPD curves for the supported Ni catalysts both with (HPC-1 and HPC-2) and without a modifying agent. The high-temperature species of the adsorbed water are present on Ni–HPC/Al_2O_3 and are absent from the less active Ni/Al_2O_3 catalyst. The most active modified nickel catalysts are characterized by a higher adsorption capacity with respect to water (up to 12% or higher) compared to the unmodified Ni/Al_2O_3, in which only water removable in the high-temperature region is present.

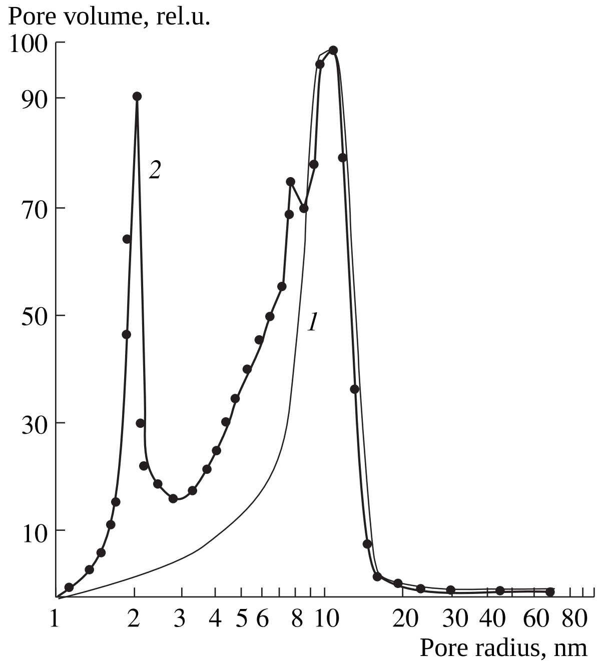


Fig. 3. Pore radius distribution: (*1*) γ-Al_2O_3 after thermal treatment, (*2*) catalyst Ni–HPC-1/Al_2O_3.

DISCUSSION

Our findings show that the low-percentage nickel catalysts modified by tungsten heteropoly compounds are efficient in the vapor-phase hydrogenation of monocyclic aromatic hydrocarbons and olefins and, hence, can be useful for the two-stage hydrotreatment of hydrocarbon feedstock for the production of high-qual-

Table 2. Adsorption of *n*-hexane on carbon supports and modified Ni catalysts (0.1 MPa, 200°C)

Catalyst	S_{sp}, m^2/g	V_a, cm^3/g
Carbon G-6-1	37	7.5
Ni/G-6-1	–	16.4
HPC-1/G-6-1	53	107.0
Carbon G-6-2	670	48.5
Ni–HPC-1/G-6-2 (a)*	540	83.0
Ni–HPC-1/G-6-2 (b)*	505	110.0
Ni–HPC-1/G-6-2 (c)*	425	55.0

* Samples a, b, and c are arranged in the series b > a $\gg$ c according to the concentration of HPC-1.

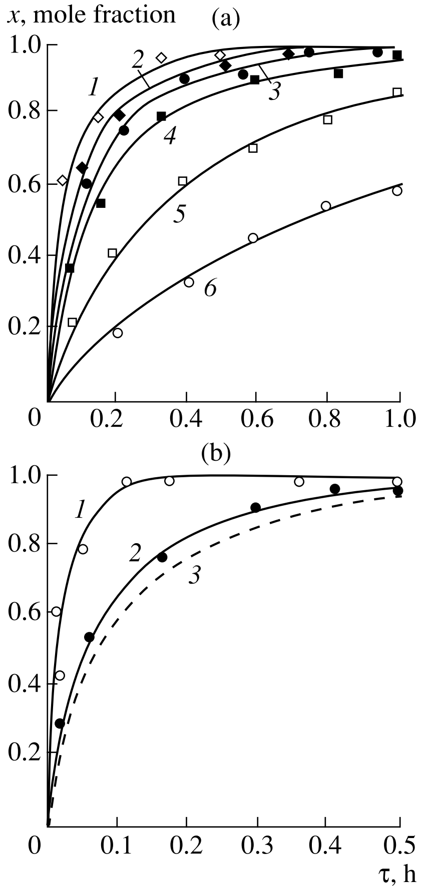


Fig. 4. Benzene conversion vs. contact time on the modified nickel catalysts at 1 MPa: (a) on the catalyst 4% Ni–HPC-2/Al_2O_3 at (*1*) 200, (*2*) 160, (*3*) 130, (*4*) 110, (*5*) 100, and (*6*) 80°C; (b) on the catalysts (*1*) 4% Ni–HPC-1/Al_2O_3, (*2*) 2% Ni–HPC-1/Al_2O_3, and (*3*) Ni–Cr at 160°C.

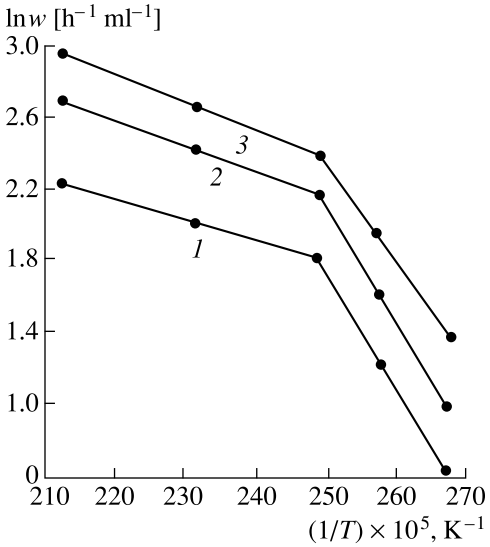


Fig. 5. Temperature dependence of the benzene hydrogenation rates on the Ni–HPC-2/Al_2O_3 catalyst at pressures, MPa: (*1*) 0.5, (*2*) 1.0, and (*3*) 1.5.

ity environmentally clean fuels (gasoline, diesel, and jet fuels). As follows from Fig. 4b, the catalyst containing 2% Ni, γ-Al_2O_3 support, and an HPC as a modifying agent is highly active in benzene hydrogenation and is comparable in its activity with the Ni–Cr catalyst containing 50% Ni. A similar catalyst 2% Ni/Al_2O_3 without an HPC transforms into the $NiAl_2O_4$ spinel almost completely and hence is rapidly deactivated during the reaction [3]. The modified samples can catalyze the hydrogenation of unsaturated and monocyclic aromatic hydrocarbons at lower pressures and temperatures than conventional catalysts. The purposeful synthesis of catalysts depending on the requirements of a process is also possible.

The catalysts obtained are similar in many parameters to expensive noble-metal catalysts. As in the case of the Pt and Pd catalysts, a two-stage process is needed for the hydrotreating of fuels in which the S- and N-containing compounds are removed at the first stage. These processes are abundant in industry [3]. However, the oil refining industry usually uses an Al–Co–Mo catalyst at the first stage. At the second stage, noble metal catalysts or Ni–Mo and Ni–W catalysts with a high Ni concentration containing also up to 20–30% WO_3 are used. The above data show that the Ni–HPC catalysts with a low Ni concentration can be used at the second stage.

As has been shown earlier [3, 14–18], the HPC-modified Ni catalysts are more selective in the hydrogenation of aromatic and unsaturated compounds than noble metal catalysts. Unlike Pt catalysts, the Ni/HPC catalysts samples do not promote hydrocracking and the metathesis of bicyclic hydrocarbons and operate at lower temperatures. For example, the AP-64 platinum–alumina catalyst is used at the second stage of hydrogenation to decrease the concentration of aromatic hydrocarbons to 10% or lower in the feedstock for the production of aviation fuel. However, the complete hydrogenation of aromatic hydrocarbons in real feedstock containing 60–70% aromatics is not achieved even at 250–350°C and a pressure of 2–4 MPa and the yield of stable hydrogenation product is only 87.6% because of the high cracking ability of AP-64. The HPC-modified Ni catalysts are free from these drawbacks.

The hydrogenating ability of Ni can be changed by varying the nature and concentration of the modifying HPC and especially the Ni/HPC ratio. To elucidate the factors that affect the activity and selectivity of the catalysts, we studied their dispersion, adsorption capacity, and other characteristics. As can be seen from Fig. 1, the introduction of HPC strongly affects the metal dispersion even when an inert activated carbon is used as a support.

The adsorption study showed that the most active modified Ni catalysts are characterized by high AC_{H_2O} values (at least 12%), while a fraction of water desorbs at high temperatures. The hydroxyl coverage of the surface of modified Ni catalysts differs markedly from that

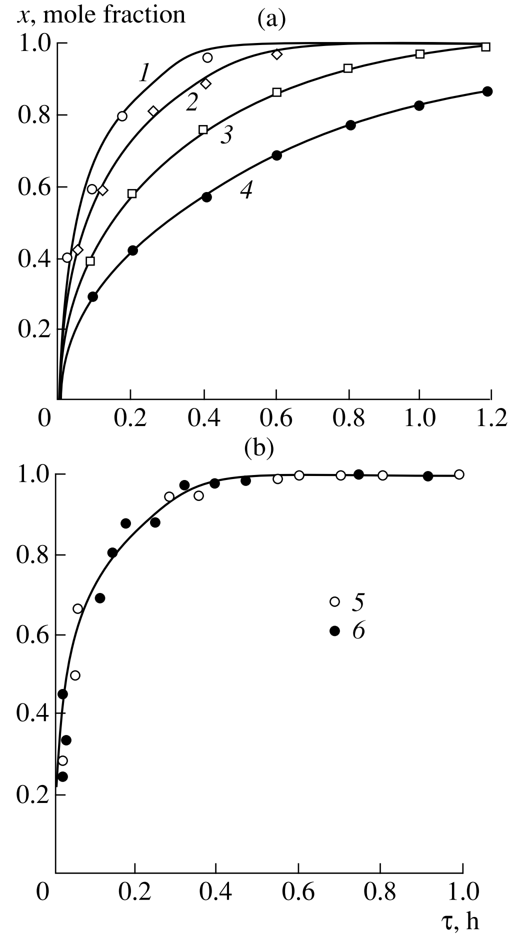


Fig. 6. Conversions of (a) octene and (b) nonene and decene vs. contact time on the Ni–HPC-2/Al_2O_3 catalyst at 0.5 MPa and temperatures, °C: (*1*, *5*, *6*) 110, (*2*) 90, (*3*) 70, and (*4*) 50.

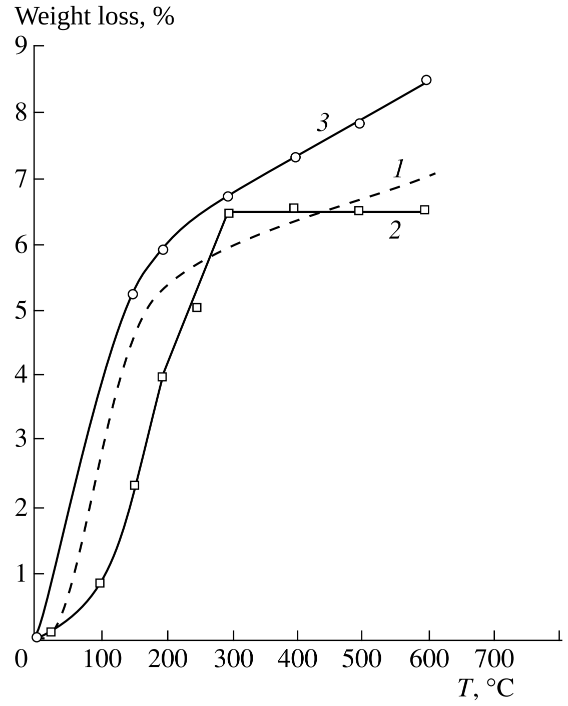
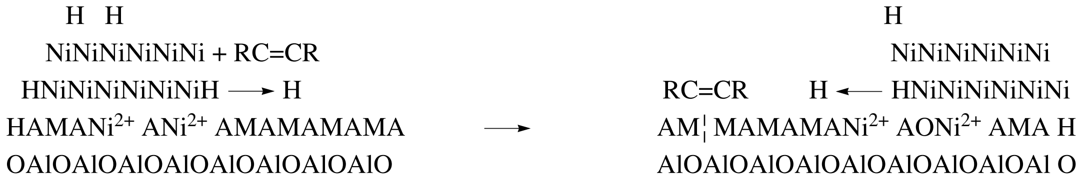


Fig. 7. Changes in the sample weight upon heating: (*1*) Al_2O_3, (*2*) HPC-2, and (*3*) HPC-2/Al_2O_3.

of the HPC, starting support (Fig. 7), and Ni/Al_2O_3 (Fig. 10). The hydroxyl coverage corresponds to the nature of the newly formed active surface with Ni and the modifying agent (HPC). It is nonuniform and crucially affects the formation and state of metal active sites. As mentioned above, Ni does not directly contact Al_2O_3 or C in modified catalysts. The Ni^{2+} ions that manifest themselves in the electron diffuse-reflectance spectra are likely involved in heteropoly compounds rather than in the $NiAl_2O_4$ spinel formed upon the interaction of Ni^{2+} with the support. The defects in the hydroxyl coverage can serve as the centers of nickel crystallization and participate in the adsorption of organic hydrogenation substrates. This is schematically shown below (M is the cation and A is the anion of a modifying agent):



The Ni islands are located above the defect layer of the HPC, which is a modifying agent. The Ni^{2+} of the HPC can participate in Ni crystallization. The Ni islands do not contact directly with the support and are thermally very stable. Hydrogen adsorbs on the Ni surface and diffuses to the MA surface via a spillover mechanism. Organic hydrogenation substrates are mainly adsorbed on the surface of a heteropoly compound MA.

These HPC structures are stable up to 500°C, as was recently exemplified by molybdenum heteropoly compounds [26]. Upon water loss, anionic vacancies (□) arise in the structure of the Keggin anion in HPC instead of oxygen ions that are removed together with water. These vacancies can take part in the heterolytic H_2 dissociation and, hence, in hydrogen spillover:

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

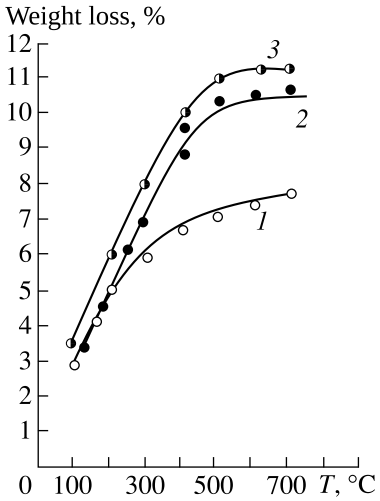


Fig. 8. Changes in the weight upon the heating of samples of 4% Ni–HPC-2/Al_2O_3 catalyst containing HPC-2, %: (*1*) 12, (*2*) 6, and (*3*) 3.

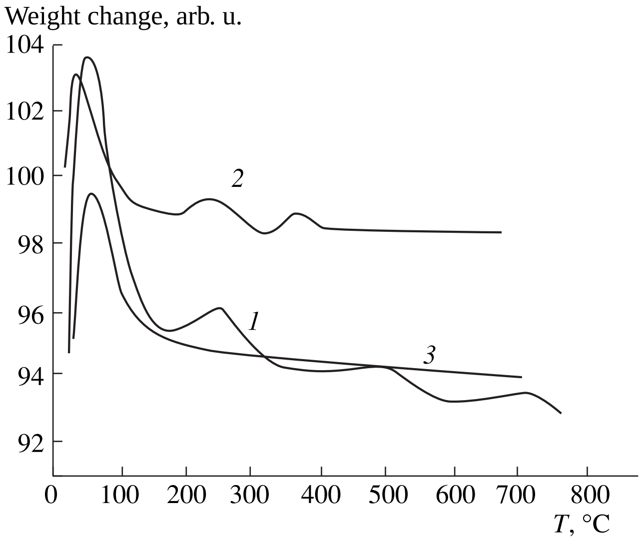


Fig. 9. TPD spectra for water from the modified Ni–HPC-2/Al_2O_3 catalysts with the Ni concentration, %: (*1*) 2, (*2*) 3, and (*3*) 4.

Hydrogen consumed by the HPC can be titrated by an unsaturated compound,

$$H^- + OH^- + C_nH_m \longrightarrow C_nH_{m+2} + O^{2-},$$

which is adsorbed on the heteropoly compound. The concentration of consumed hydrogen in some HPCs can reach 2.7 mol H_2 per mole HPC or up to 1.3×10^{-3} mol H_2 per 1 g HPC.

Similar mechanisms probably operate in the case of tungsten heteropoly compounds. Hydrogen dissociates more readily on the Ni surface than on the HPC. Apparently, Ni accelerates H_2 dissociation and allows hydrogen atoms to reach directly vacancies in the HPC via a spillover mechanism. As has been shown by many authors [27] (see also the review [28]), the presence of hydroxyl groups favors hydrogen spillover. Correspondingly, the degree of reduction of the HPC surface in the presence of Ni should be higher than that in its absence. We believe that the hydrogenated organic compound adsorbs on the surface of the modifying agent (HPC) in this case as well.

The study of the pore structure of new catalysts showed that heteropoly compounds not only operate as chemical modifying agents but also change the micropore structure (see Fig. 3). The deposition of an HPC changes the pore radius distribution, and both large and very narrow pores appear. This can be explained by the fact that HPCs (the Keggin anions) adsorb mainly on the surface of those support pores with average sizes of 3–8 nm and make some of them inaccessible. New maxima at 9–10 nm correspond to the size of the primary catalyst particles. Very narrow pores (1–3 nm) are close in their sizes to those of HPCs, which are microporous sorbents. These pores can be associated with defects in the HPC layer. The formation of micropores with radii of 2–3 nm favors the formation of active sites for the hydrogenation of aromatic hydrocarbons. Readily reducible Ni oxides are deposited in micropores, and then highly dispersed metal particles are formed upon the activation by hydrogen.

We suggest that the functions of the two phases of the modified catalyst—Ni and modifying agent—are different. Nickel activates hydrogen, and the HPC adsorbs an organic molecule. The HPC facilitates hydrogen transfer. In support of this suggestion, there is strong evidence for the participation of W-containing HPCs in hydrogen transfer and catalytic hydrogenation and isomerization [29–32]. The hydrogenation of alkenes was studied in [31], and the skeletal isomerization of *n*-pentane in the presence of hydrogen over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was studied in [32]. When Pt or Pd are added to this HPC, its hydrogenating properties significantly enhance. Hydrogen is likely consumed not only by the surface but also by the HPC bulk.

The ability of molybdenum and tungsten oxides to consume hydrogen during reduction, producing so-called molybdenum and tungsten bronzes, is well known. Metals accelerate the formation of these bronzes. It was shown in [30] that the maximal rate of styrene hydrogenation to ethylbenzene over the Pd/WO_3 catalyst is achieved at the ratio W/Pd = 6. One can suggest that in this case, as in the case of the Ni–HPC catalysts, the metal/modifying agent ratio determines the ability of the system to accumulate hydrogen via a spillover mechanism and this fact mainly governs the catalytic activity.

The high activity and selectivity of the modified hydrogenation catalysts are likely due to their dual functionality. In this regard, the hydrogenation mechanism over the supported modified Ni catalysts is similar to that of hydrodesulfurization over the Co–Mo sulfide

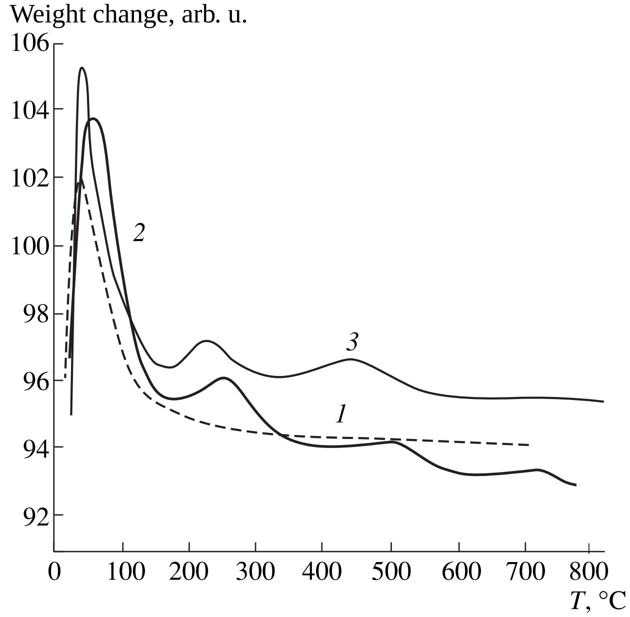


Fig. 10. The TPD spectra for water from various catalysts: (*1*) Ni/Al_2O_3, (*2*) Ni–HPC-2/Al_2O_3, and (*3*) Ni–HPC-1/Al_2O_3.

catalysts in which Co and Mo are known to have different functions [3, 27].

Our findings and the cited papers allow us to assume that the activating effect of the HPC modifying agents on the supported hydrogenation Ni catalysts is due to (1) the formation of new (reduced) surface favoring the adsorption of an unsaturated compound; (2) an increase in the hydrogen adsorption and its activation due to spillover from the metal to HPC; (3) nucleation that provides high Ni dispersion, (4) the formation of a new pore structure favorable for the reaction, (5) the retardation of the interaction of Ni with the support γ-Al_2O_3 leading to the formation of inactive spinel, and (6) an increase in the degree of Ni reduction.

CONCLUSION

Our findings and recent papers [8–16] provide evidence for the possibility of preparing highly dispersed and thermally stable Ni particles on various supports (Al_2O_3, SiO_2, and carbon). The use of such modifying additives as tungsten heteropoly compounds, allows one to obtain new active metal–oxide surface. Nickel is uniformly distributed over the surface and does not interact with the support. High activity is reached at a significant lower nickel concentration than that in unmodified catalysts. The modifying additives allow creating a large hydroxyl coverage containing OH groups removable only at high temperatures. Hydrogen efficiently adsorbs on these catalysts, probably on metal particles. The adsorbed hydrogen exchanges with the modifying agent layer via a spillover mechanism with the participation of the OH groups of the modifying agent. A higher degree of Ni reduction is achieved due to the exchanging hydrogen. The catalytic activity of the system is governed by the Ni/HPC ratio (commonly, the metal/modifying agent ratio). The high selectivity of the hydrogenation of aromatic hydrocarbons is apparently due to the adsorption of the organic compound on the HPC layer.

The results of this and other studies [3, 12–22] show that the catalysts modified with HPC are highly efficient in various vapor-phase hydrogenation reactions including the hydrogenation of olefins, aromatic hydrocarbons, ketones, as well as CO methanation, hydrotreatment, and even dehydrogenation (up to 600°C) and aromatization of *n*-paraffins.

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