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Formation, Nature of Activity, and Hydrogenation Catalysis by Nickel Bis(Acetylacetonate)–Lithium Tetrahydroaluminate Systems

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Abstract—A new approach to synthesis of nickel catalysts under the action of lithium tetrahydroaluminate was proposed which allows preparation of high-performance nanosized catalytic systems with well-reproducible properties. The major stages of formation and the nature of catalytically active species and inhibitors formed in the $\text{Ni}(\text{acac})_2\text{--LiAlH}_4$ system were determined. The catalytic properties of the nickel nanoclusters were studied in relation to the nature and concentration of the proton-containing compounds. Factors responsible for the promoting action exhibited by these compounds were analyzed.

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Ziegler-type catalytic systems comprised of transition metal complexes and organic (or hydride) compounds of I–III Group nontransition metals rank among the major commercial hydrogenation (in particular, polymer hydrogenation) catalysts. They have been the subject of investigation for 40 years. One of the central tasks in catalysis is to elucidate the formation mechanism, composition, and structure of catalytically active species, as well as the factors responsible for their deactivation, in order to control the synthesis and optimize the application of these systems for hydrogenation catalysis. Relevant studies showed that, depending on the composition of Ziegler-type catalytic systems, it is possible to prepare truly homogeneous and microheterogeneous (nanosized) catalysts (for details on the nature and properties, see [1]). The nanosized nature of the catalytically active species was established for Ziegler-type systems based on iron, cobalt, nickel, and palladium acetylacetonates as combined with aluminum organic derivatives [2–5]. It was shown that the function of organometal compounds in Ziegler-type systems is not limited to reduction of transition metal compounds: Organoaluminum compounds and their transformation products [e.g., $\text{AlR}_2(\text{acac})$] contribute to stabilization of metal nanoclusters [3–5]. Excessive AlR_3 compounds are catalytic poisons [5, 6].

A special place among hydrogenation catalysts is occupied by systems in which the function of reducing agent is accomplished by more readily accessible complex hydrides, in particular, LiAlH_4 and NaBH_4 and their derivatives [7–16]. The nature of nickel boride catalysts is well understood [11], while data on hydrogenation catalysts formed under the action of LiAlH_4 and on their properties are disconnected and frequently contradictory [7, 8, 12–16]. For example, Matyushin et al. [13, 14] studied hydrogenation of polycyclic arenes over a nickel catalyst prepared by the reaction of nickel bis(acetylacetonate) with LiAlH_4 . That study showed that the activity of the catalyst is determined not only by the LiAlH_4 to $\text{Ni}(\text{acac})_2$ ratio but also by the aggregation state of lithium tetrahydroaluminate introduced into the system in the catalyst formation stage. Those researchers succeeded in preparation of a catalyst with a satisfactorily reproducible activity only in the case when powdered LiAlH_4 was added to a solution of $\text{Ni}(\text{acac})_2$ in a mixed benzene : tetrahydrofuran = 5 : 1 solution, but did not analyze the nature of the catalyst. At the same time, Takegami et al. [7] found that, surprisingly, the catalytic properties of $\text{MX}_n\text{--LiAlH}_4$ catalytic system were significantly affected by even insignificant change in its

composition.

Ambiguous data were also obtained in experiments utilizing not only lithium tetrahydroaluminate but also its alkoxy hydride derivatives as reducing agents. Schuldts et al. [15] also noted that the activity and stability of the catalyst synthesized by the reaction of CoBr_2 and $\text{Li}[\text{AlH}(\text{O}-\text{tert-Bu})_3]$ solutions in tetrahydrofuran is largely determined by its preparation procedure. Surprisingly, out of naphthalene, anthracene, and phenanthrene substrates tested in that study under identical conditions, only anthracene exhibited significant conversions in hydrogenation with the above-mentioned catalytic system. By contrast, the conversions of the two remaining aromatic hydrocarbons did not exceed several per cent even after a prolonged period. The factors responsible for such different types of behavior displayed by the catalyst in hydrogenation of naphthalene, anthracene, and phenanthrene were not analyzed. Based on the amount of hydrogen evolved in the reaction between the CoBr_2 - $\text{Li}[\text{AlH}(\text{O}-\text{tert-Bu})_3]$ system components, it was concluded [15] that CoBr_2 is reduced to Co(I) , and the active complex comprises unchanged reducing agent, $\text{Li}[\text{AlH}(\text{O}-\text{tert-Bu})_3]$.

At the same time, studies of the hydrogenating properties of the catalytic systems based on $\text{Pd}(\text{acac})_2$ showed that the catalytically active species are nanosized in nature and that, upon incomplete hydrolysis and alcoholysis of LiAlH_4 [16] and AlEt_3 [5, 6] prior to their use in reduction of Pd(II) compounds, the activity of the palladium catalysts sharply increased, and the inhibitory action of the excess of these compounds in the catalyst preparation stage was diminished.

Here, we studied the interaction between the components of the $\text{Ni}(\text{acac})_2$ - LiAlH_4 catalytic system in solution by various chemical and physical methods and elucidated conditions conducive to formation of nickel catalysts exhibiting reproducible properties in hydrogenation reactions.

EXPERIMENTAL

The solvents (benzene, THF), substrates (styrene, phenylacetylene, nitrobenzene, naphthalene), and reagents (ethanol, *n*-propanol, *tert*-butanol, *iso*-butanol, *n*-pentanol) were purified by standard procedures used for manipulations with organometal substances [17]. For more exhaustive drying, benzene was additionally distilled from LiAlH_4 on a distillation column and

stored under argon in sealed ampules over 4A molecular sieves. Tetrahydrofuran, after removal of peroxides, was distilled successively from sodium, LiAlH_4 , and benzophenone ketyl and stored under argon in sealed ampules. The water concentration was estimated by the Fischer method [18] at 1.1×10^{-3} and 6×10^{-3} M for benzene and THF, respectively.

Nickel bis(acetylacetonate) was synthesized by the procedure described in [19].

Lithium tetrahydroaluminate (LiAlH_4 , commercial) was used without preliminary recrystallization. A weighed portion of LiAlH_4 was dissolved in THF, and the resulting solution was filtered in an inert atmosphere through a glass filter. The LiAlH_4 concentration was estimated from the amount of hydrogen evolved in hydrolysis at 95–98% of the theoretical value. The ^{27}Al NMR spectrum (δ , ppm, solvent THF): 98 quintet ($^1J_{\text{Al-H}}$ 173 Hz).

The interaction between nickel bis(acetylacetonate) and LiAlH_4 at different reactant ratios was studied under dry deoxygenated argon in a thermostated vessel whose design presumes preliminary evacuation and filling with argon. The reaction products for the components of the $\text{Ni}(\text{acac})_2$ - LiAlH_4 system were analyzed spectroscopically (^{27}Al NMR, IR, UV, and ESR) and volumetrically.

For quantitative analysis of the molecular hydrogen evolved during interaction of the catalytic system components we used a special thermostated vessel provided with an internal "pocket" for the second component. For example, into a preliminarily evacuated argon-filled thermostated vessel connected to the volumetric system, a solution of 0.02534 g (1×10^{-3} mol) $\text{Ni}(\text{acac})_2$ in 12 ml of benzene was poured, and an aliquot of a LiAlH_4 solution in THF, into the internal "pocket" of the vessel. The vessel was plugged with a Teflon stopper, and the LiAlH_4 and $\text{Ni}(\text{acac})_2$ solutions were mixed together under vigorous shaking. The resulting hydrogen was analyzed volumetrically, and the solution, by UV spectroscopy. The $\text{Ni}(\text{acac})_2$ conversion was calculated by the iteration method using the Bouguer–Lambert–Beer equation. In calculation of the distribution of acetylacetonate ligands among Ni, Li, and Al, based on the optical-spectroscopic data, we took into account the fact that the resulting $\text{Li}(\text{acac})$ is virtually insoluble in benzene and used the following molar absorption coefficients: $\text{Ni}(\text{acac})_2$ $\epsilon_{300} = 15\,100$ and $\epsilon_{288} = 11\,800$; $\text{Al}(\text{acac})_3$ $\epsilon_{300} = 33\,460$ and $\epsilon_{288} = 43\,600$.

The UV spectra were recorded on a Specord UV-VIS spectrometer at 280–430 nm in an all-soldered cell.

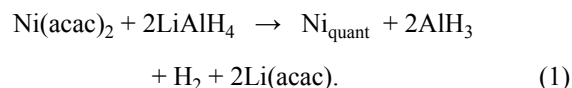
The IR spectra of the solutions were measured on a Specord 75-IR spectrometer (solvent benzene–THF) in a 0.2-mm-thick KRS cell preliminary blown through with argon. The NMR spectra were recorded on a VXR-500S Varian pulse spectrometer. The chemical shifts of the ^{27}Al signals were measured relative to 0.1 $\text{MAl}(\text{NO}_3)_3$ solution (external standard); to prevent hydrolysis, the analyzed solution was poured into a preliminarily evacuated argon-filled quartz ampule 5 mm in diameter, which was further sealed. The transmission electron microscopic examinations were carried out with the use of a Philips EM-410 microscope.

The experiments on hydrogenation of unsaturated compounds were carried out in a duck-shaped thermostated vessel at 35°C and hydrogen pressure of 1 gauge atm (0.20265 MPa) under vigorous stirring, which precluded transition of the reaction to the diffusion region. A weighed portion of $\text{Ni}(\text{acac})_2$ (from 1×10^{-5} to 2×10^{-4} mol) and benzene (10 ml) were successively charged in a hydrogen stream into the preliminarily evacuated hydrogen-filled thermostated duck-shaped vessel, and the resulting mixture was stirred until complete dissolution. Next, the substrate and a solution of LiAlH_4 in THF were poured to the resulting light-green solution. The vessel was plugged with a Teflon stopper supplied with a rubber gasket (for taking samples), whereupon excess hydrogen pressure (1 gauge atm) was produced, and hydrogenation was carried out. We monitored the reaction by volumetric and gas-liquid chromatographic methods. If no catalytic activity was observed after the first 20 min of the process, the catalyst was activated by introduction of proton-containing compounds (alcohols, water, phenol, acetic acid). The styrene hydrogenation products, aromatic compounds, phenylacetylene, and nitrobenzene were analyzed on a KhROM-5 chromatograph with a flame-ionization detector (carrier gas nitrogen; 3.6 m \times 3 mm packed column; Carbowax-20M phase). The heating program was as follows: 50°C (4 min), 100°C (12 min), 140°C (4 min).

Despite partial or quantitative reduction of nickel bis(acetylacetonate), the $\text{Ni}(\text{acac})_2$ – LiAlH_4 catalytic system resulted from interaction of the solutions of these components in benzene and THF, respectively [$\text{LiAlH}_4/\text{Ni}(\text{acac})_2 = 1$ –20], was catalytically inactive in hydrogenation of aromatic compounds (benzene,

naphthalene), as well as of double and triple bonds in unsaturated compounds (1-hexene, styrene, phenylacetylene, tolan) and of nitro and carbonyl groups (nitrobenzene, benzaldehyde). Upon replacement of the solutions of lithium tetrahydroaluminate in THF by its alkoxy hydride derivatives [$\text{LiAlH}_{4-x}(\text{OR})_x$, where $x = 1, 2, 3$; R = *n*-Bu, *tert*-Bu], the situation remained unchanged, by contrast to palladium catalysts [20]. The catalytic inertness in hydrogenation processes, exhibited by the nickel-based systems prepared under the action of LiAlH_4 solutions in THF, was rather a surprising result, because the available published data prove the contrary [7, 8, 12].

Addition of the LiAlH_4 solution in THF to the $\text{Ni}(\text{acac})_2$ solution in benzene led to a change in the color of the solution from green to dark brown and to evolution of hydrogen. Volumetric analysis of hydrogen formation in time for the $\text{Ni}(\text{acac})_2$ – LiAlH_4 system revealed two stages: first, rapid stage which was complete within 1–2 min, and the second stage which proceeded at a nearly three orders of magnitude lower rate. Hydrogen formation in the second stage was observed for at least 6 h. Notably, the hydrogen yield even in the first stage significantly exceeds 1 mol [$\text{Ni}(\text{acac})_2$ mol] $^{-1}$ as estimated from the stoichiometric equation describing the most frequently observed case of reduction of transition-metal compounds with lithium tetrahydroaluminate [21]:



The amount of hydrogen evolved was ≥ 8 mol per Ni mol at $\text{LiAlH}_4/\text{Ni}(\text{acac})_2 \geq 6$ (Fig. 1).

The optical-spectroscopic examination showed that the conversion of $\text{Ni}(\text{acac})_2$ to $\text{Ni}(0)$ depends on the $\text{LiAlH}_4/\text{Ni}(\text{acac})_2$ molar ratio. Quantitative analysis of the UV spectra for the $\text{Ni}(\text{acac})_2$ – LiAlH_4 reaction system, taken after 5 min of the reaction, with the aim to elucidate the distribution of acetylacetonate ligands among Ni, Li, and Al, showed that $\text{Ni}(\text{acac})_2$ was converted quantitatively at the molar ratio $\text{LiAlH}_4/\text{Ni}(\text{acac})_2 > 5$ (Fig. 2). At lower reactant ratios, there was unchanged nickel bis(acetylacetonate) remaining in the reaction system. At $\text{LiAlH}_4/\text{Ni}(\text{acac})_2 = 2$, $\text{Ni}(\text{acac})_2$ was converted by 40–45%, with ~85% acetylacetonate groups bound to lithium ion as $\text{Li}(\text{acac})$, and 14%, to aluminum. At $\text{LiAlH}_4/\text{Ni}(\text{acac})_2 = 5$, there was 96–98% acetylacetonate ligands bound to lithium, and only

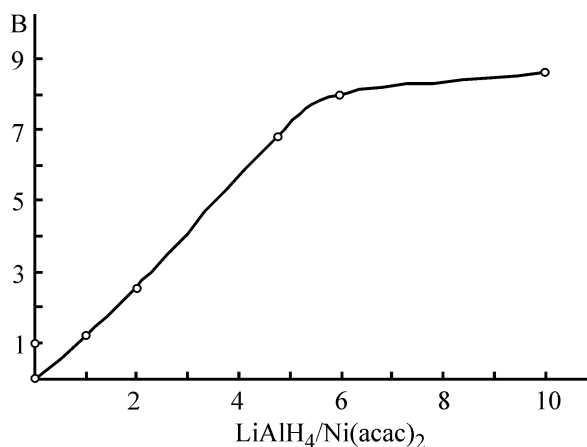


Fig. 1. Yield of molecular hydrogen Y , mol $[\text{Ni}(\text{acac})_2 \text{ mol}]^{-1}$, vs. reactant ratio in the $\text{Ni}(\text{acac})_2$ – LiAlH_4 system. Solvent benzene:THF = 6 : 1, $c_{\text{Ni}} = 0.01 \text{ M}$, solution volume 12 ml; the same for Fig. 2.

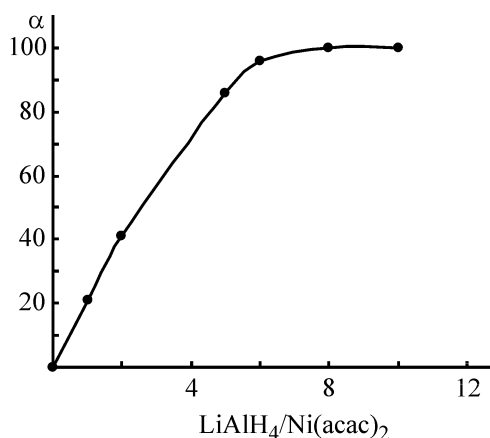


Fig. 2. Conversion of $\text{Ni}(\text{acac})_2$ α , % vs. reactant ratio in the $\text{Ni}(\text{acac})_2$ – LiAlH_4 system.

2–4%, to aluminum, and at $\text{LiAlH}_4/\text{Ni}(\text{acac})_2 = 8$ –10 all the acetylacetonate groups passed from nickel to lithium.

Nonquantitative conversion of $\text{Ni}(\text{acac})_2$ under the action of lithium tetrahydroaluminate at $\text{LiAlH}_4/\text{Ni}(\text{acac})_2 = 2$ in accordance with the stoichiometric equation (1) proved to be rather a surprising result. It should be noted that $\text{Pd}(\text{acac})_2$ was exhaustively converted in reaction with LiAlH_4 even at $\text{LiAlH}_4/\text{Pd} = 1$ [16]. The reason is that palladium bis(acetylacetonate) was also reduced by Al, AlH_3 , the redox transformation products of LiAlH_4 , which appeared in the reaction system.

The information on conversion of LiAlH_4 and on the products of its transformation in the reaction with

$\text{Ni}(\text{acac})_2$ was derived from the ^{27}Al NMR and IR spectroscopic data.

The ^{27}Al NMR spectrum of lithium tetrahydroaluminate contains a resonance signal at 98 ppm represented by a quintet characterized by the spin-spin coupling constant $^1J_{\text{Al-H}}$ 173 Hz and halfwidth $\Delta\nu_{1/2}$ (^{27}Al) of 47 Hz (Fig. 3a). A multiplet structure of the spectrum is due to scalar spin-spin coupling of equivalent protons with the aluminum isotope and suggests that the

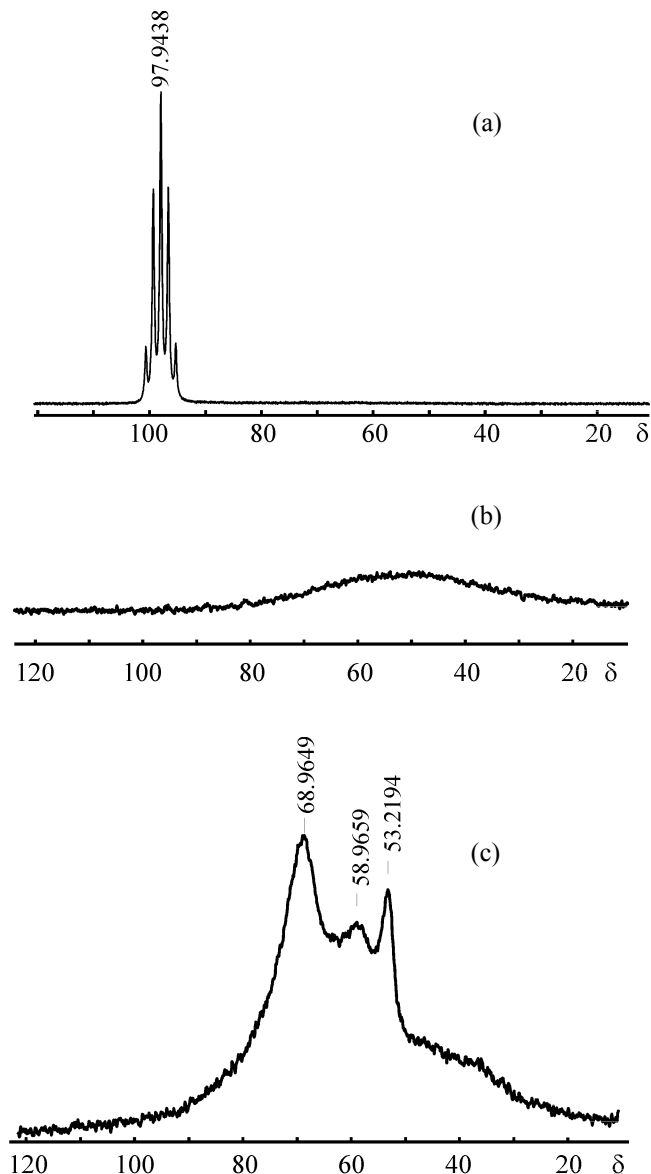


Fig. 3. ^{27}Al NMR spectra of (a) solution of LiAlH_4 in THF and (b, c) $\text{Ni}(\text{acac})_2$ – 6LiAlH_4 system (b) before and (c) after activation with *tert*-BuOH. Solvent benzene : THF = 5 : 1, $c_{\text{Ni}} = 0.03 \text{ M}$, $[\text{tert-BuOH}]/[\text{LiAlH}_4] = 4$. (δ) Chemical shift, ppm.

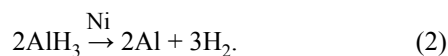
AlH_4^- anion preserves its tetrahedral configuration in a THF solution [22, 23]. At the same time, there were no resonance signals from AlH_4^- and its transformation products in the ^{27}Al NMR spectrum of the $\text{Ni}(\text{acac})_2$ – LiAlH_4 reaction system at the molar ratio of reactants $\text{LiAlH}_4/\text{Ni}(\text{acac})_2 \leq 10$ (Fig. 3b). A resonance signal from AlH_4^- at 98 ppm was recorded in the ^{27}Al NMR spectrum at $\text{LiAlH}_4/\text{Ni} \geq 20$ solely.

The NMR data for the $\text{Ni}(\text{acac})_2$ – LiAlH_4 system agree with the IR spectroscopic findings. The IR spectra suggests a decrease in intensity at $\text{LiAlH}_4/\text{Ni}(\text{acac})_2 = 2$ for the absorption bands associated with $\nu(\text{C}=\text{O}) + \nu(\text{C}=\text{C})$ (1585 and 1510 cm^{-1}) stretching vibrations in O,O-chelated acetylacetonate ligand in $\text{Ni}(\text{acac})_2$, as well as with stretching $\nu(\text{Al}-\text{H}) = 1690 \text{ cm}^{-1}$ and bending $\delta(\text{Al}-\text{H}) = 765 \text{ cm}^{-1}$ vibrations of LiAlH_4 [24]. Upon completion of the reaction the $\text{Ni}(\text{acac})_2$ concentration in the $\text{Ni}(\text{acac})_2$ – LiAlH_4 reaction system [$\text{LiAlH}_4/\text{Ni}(\text{acac})_2 = 2$] was close to 50%. It should be noted that the IR spectra did not contain absorption bands from tetrahydroaluminate anion [$\nu(\text{Al}-\text{H}) = 1690 \text{ cm}^{-1}$, $\delta(\text{Al}-\text{H}) = 765 \text{ cm}^{-1}$] and from alane which has a characteristic broad absorption band at 1600–1800 cm^{-1} , peaked at 1750 cm^{-1} [25]. According to the IR spectroscopic data, $\text{Ni}(\text{acac})_2$ is quantitatively converted at $\text{LiAlH}_4/\text{Ni}(\text{acac})_2 = 6$.

An ESR spectroscopic study of the $\text{Ni}(\text{acac})_2$ – LiAlH_4 system [$\text{LiAlH}_4/\text{Ni}(\text{acac})_2 = 5, 10, 20$] revealed formation of ferromagnetic nickel clusters ($g = 2.2$, $\Delta H = 600 \text{ Oe}$).

Thus, our experiments revealed incomplete reduction of $\text{Ni}(\text{acac})_2$ at $\text{LiAlH}_4/\text{Ni}(\text{acac})_2 < 6$, formation of up to 8.5 mol (Ni mol) $^{-1}$ hydrogen, and lack of free LiAlH_4 at $\text{LiAlH}_4/\text{Ni}(\text{acac})_2 < 20$. Combined, these findings suggest that LiAlH_4 participates not only in a redox process involving $\text{Ni}(\text{acac})_2$.

As known, highly dispersed powders of transition metals catalyze decomposition of alane into components under mild conditions [16, 21]:

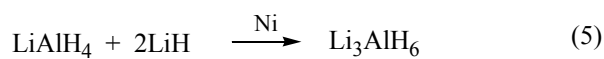
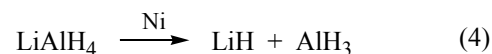


However, the total amount of molecular hydrogen in the $\text{Ni}(\text{acac})_2$ – LiAlH_4 system, formed by reactions (1) and (2), cannot exceed 4 mol [$\text{Ni}(\text{acac})_2 \text{ mol}$] $^{-1}$ even if alane is exhaustively decomposed into elements:



These data suggest that the $\text{Ni}(0)$ clusters catalyze decomposition of not only alane but of lithium tetrahydroaluminate as well.

At the present time, the LiAlH_4 decomposition products still remain to be identified, but Li_3AlH_6 is commonly recognized as one of the stable products of thermal decomposition of LiAlH_4 [26]. A presumption that lithium tetrahydroaluminate is decomposed under the action of $\text{Ni}(0)$ via formation of Li_3AlH_6 leads to conclusion that this process, along with Li_3AlH_6 , should additionally yield alane:



whose catalytic decomposition results in additional hydrogen evolution. Low conversion of $\text{Ni}(\text{acac})_2$ at the stoichiometric reactant ratio may be associated specifically with catalytic decomposition of LiAlH_4 by reaction (6), catalyzed by nickel clusters resulted from $\text{Ni}(\text{acac})_2$ reduction.

At the same time, the above-discussed facts do not disclose reasons for catalytic inertness of nickel systems. As mentioned above, the ESR data suggest that the reaction of $\text{Ni}(\text{acac})_2$ with LiAlH_4 at various reactant ratios yields ferromagnetic nickel particles. A transmission electron microscopic examination showed that, at $\text{LiAlH}_4/\text{Ni}(\text{acac})_2 = 10$, the nanoparticles measured ca. 2 nm in size. The stability of the resulting disperse systems varies with the molar ratio of the reactants. The disperse phase particles formed in the $\text{Ni}(\text{acac})_2$ – LiAlH_4 system at $\text{LiAlH}_4/\text{Ni}(\text{acac})_2 = 1$ – 2 precipitated already after 1 h, by contrast to $\text{LiAlH}_4/\text{Ni}(\text{acac})_2 = 10, 20$, in which case the particles remained stable for several weeks. The ESR spectroscopic and electron microscopic data suggest formation of reduced nickel nanoparticles, but their isolation from the dispersion medium proved to be problematic. They were essentially reversible colloids; transition to dissolved state after complete removal of the solvent in a vacuum was achieved under the action of not only THF, benzene, and diethyl ether but of hexane as well. Precipitation from $\text{Ni}(\text{acac})_2$ – 10LiAlH_4 was observed only after contact with air and formation, according to

the XPA data, of nickel oxide.

As known, there exist electrostatic, steric, and electrosteric stabilizers of metal nanoparticles; mere solvents (in our case, benzene, THF) are unable of metal nanocluster stabilization [27]. The ability of complex hydrides to form bridging bonds with the surface atoms of transition metals [28] suggests that tetrahydroaluminate anions can contribute to stabilization of nickel nanoparticles. Also, formation of Ni–AlH_x ($x = 0, 1, 2$) groups on the surface of the nickel nanoparticles (in catalytic decomposition of alane) cannot be ruled out. Hence, catalytic inertness of the nickel catalysts formed under the action of LiAlH₄ can be associated with poisoning of the active surface nickel sites by aluminum, surface aluminum hydride (Ni–AlH_x), and LiAlH₄. These compounds form fairly strong bonds, thereby blocking active sites of the catalyst. The lack of a resonance signal from both free and coordinated LiAlH₄ in the ²⁷Al NMR spectrum of the Ni(acac)₂–LiAlH₄ [LiAlH₄/Ni(acac)₂ < 20] reaction system does not contradict the above presumption: This fact may be due to broadening of the resonance signal owing to formation of a dispersed system and low concentration of stabilizers.

Considering the above-said, we proposed the following strategy for synthesis of high-performance nickel catalysts. First, Ni(acac)₂ is to be reduced with LiAlH₄ excess in the presence of a substrate in order to prepare highly dispersed systems, and this is to be followed by introduction of a proton-donating compound to chemically bind LiAlH₄ and its transformation products. Our experiments showed that, indeed, the introduction of proton-donating compounds (water,

alcohols, acids, and phenol) upon reduction of Ni(acac)₂ with LiAlH₄ excess caused appearance of a catalytic activity within a brief (1–2 min) period. The catalytic activity level depends on the nature and concentration of proton-donating compounds (see table). Among the compounds that we tested, the strongest promoting effect was exhibited by *n*-butanol. Weaker promoting powers of *tert*- and *iso*-butanol are evidently due to their lower reactivities. In fact, adding *n*-butanol to the Ni(acac)₂–10LiAlH₄ catalytic system activated by *tert*-butanol, caused its catalytic activity in styrene hydrogenation to increase sixfold.

It should be noted that acetic acid, when tested as promoter, caused a 400-fold deceleration of the reaction even when in a twofold excess. The reason is that acetic acid reacts not only with catalytic poisons but also with nickel and converts it to the oxidized state. A promoting effect is exhibited by water as well. In the presence of equimolar amounts of water with respect to the initial LiAlH₄ the catalytic activity of nickel-based systems in styrene hydrogenation reached 70 styrene mol (mol Ni)⁻¹ min⁻¹. These results allow understanding the contradictions in the published data to be associated with the experimental integrity, i.e., the presence of various uncontrollable amounts of water in the reaction system.

The catalytic activity of Ni(acac)₂–LiAlH₄ systems depends not only on the nature and concentration of the promoter but also on the LiAlH₄/Ni(acac)₂ ratio and Ni(0) concentration (Fig. 4). The occurrence of a maximum in the dependence of the catalyst activity on the Ni(acac)₂ concentration is consistent with the

Influence of the nature of the proton-containing compound on the catalytic activity of the Ni(acac)₂–20 LiAlH₄ system in styrene hydrogenation $c_{\text{Ni}} = 3.85$ mM, [substrate]/[Ni] = 174, solvent benzene : THF = 10 : 2, solvent volume 12 ml, $T = 35^\circ\text{C}$, $P_{\text{H}_2} = 1$ atm

ROH	Catalytic activity, substrate mol (Ni mol) ⁻¹ min ⁻¹ , at indicated [ROH]/[LiAlH ₄], mol mol ⁻¹				
	1	2	4	8	11
H ₂ O	69	94	94	76	–
C ₂ H ₅ OH	47	123	130	164	–
<i>n</i> -C ₄ H ₉ OH	100	151	220	131	131
<i>tert</i> -C ₄ H ₉ OH	35	38	50	45	49
<i>iso</i> -C ₄ H ₉ OH	41	90	90	49	49
<i>n</i> -C ₅ H ₁₁ OH	82	192	123	123	130
C ₆ H ₅ OH	–	–	–	–	37
CH ₃ COOH	82	0.2	0.6	0	0

nanosized nature of the catalytically active species. A dramatic decline in activity with increasing $\text{Ni}(\text{acac})_2$ concentration is explained by aggregation of the catalyst particles and decrease in the proportion of the active surface sites. Enhancement of the catalytic activity with increasing LiAlH_4 concentration is due to formation of a more highly dispersed nickel catalyst.

Introduction of promoters, e.g., alcohols, into the $\text{Ni}(\text{acac})_2$ - LiAlH_4 reaction system was accompanied by an additional fast (within 0.5–1 min) evolution of molecular hydrogen which may result from alcoholysis of LiAlH_4 , Li_3AlH_6 , and/or surface compounds of the $\text{Ni}-\text{AlH}_x$ type. For example, adding a fourfold excess of *n*-butanol to the $\text{Ni}(\text{acac})_2$ - LiAlH_4 system caused evolution of additional 2, 3, and 20 ml of hydrogen at $\text{LiAlH}_4/\text{Ni}(\text{acac})_2$ of 2, 6, and 10, respectively. Formation of hydrogen was also observed upon introduction of other proton-containing promoters into the catalytic system.

According to the NMR spectroscopic data that we obtained, introduction of *tert*-butanol into $\text{Ni}(\text{acac})_2$ - LiAlH_4 ($\text{LiAlH}_4/\text{Ni} = 6$) catalytic system leads to appearance in the ^{27}Al spectra of three poorly resolved signals in a weak field with chemical shifts at 53, 59, and 69 ppm (Fig. 3c). The resonance shift at 53 ppm is characteristic for $\text{LiAl}(\text{tert-BuO})_4$ ($\delta = 52$ ppm [29]), and that near 69 ppm can be most probably assigned to $\text{LiAlH}(\text{tert-BuO})_3$ [29]. The lack of hyperfine structure is not surprising, since it is known that, if one of the ligands in the AlH_4^- anion differs in nature from the other ones, the multiplet structure in the ^{27}Al spectrum is not manifested [23]. A shift of this signal by 9 ppm to stronger fields can be associated with distortion of the tetrahedral structure [30] owing to interaction with nickel clusters. The assignment of the third signal ($\delta = 59$ ppm) still remains problematic.

The use of *n*-butanol as promoter for the $\text{Ni}(\text{acac})_2$ - LiAlH_4 system leads to appearance in the reaction system of $\text{LiAl}(\text{n-BuO})_4$, as follows from the ^{27}Al NMR spectroscopic data.

Our data suggests that alcoholysis of lithium tetrahydroaluminate adsorbed on the nickel clusters belongs to factors responsible for the promoting action by alcohols (or other proton-containing compounds).

This presumption was additionally validated by our kinetic experiments. When 1 or even 0.5 mol LiAlH_4 $[\text{Ni}(\text{acac})_2 \text{ mol}]^{-1}$ is introduced into the catalytic system during styrene hydrogenation, the catalytic activity dramatically decreases from 70 (substrate mol) $(\text{Ni mol})^{-1} \text{ min}^{-1}$

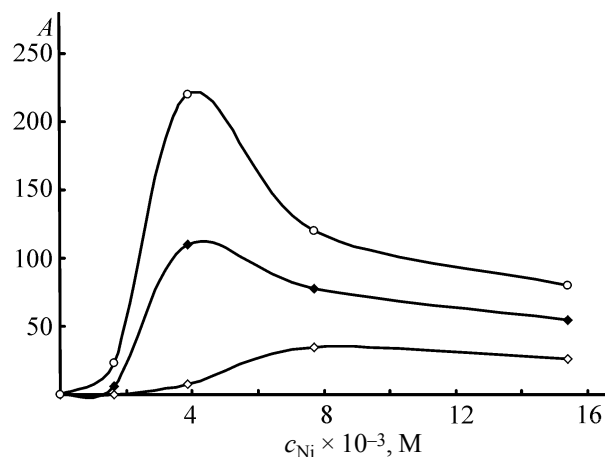


Fig. 4. Catalytic activity A , styrene mol $(\text{Ni mol})^{-1} \text{ min}^{-1}$, of the $\text{Ni}(\text{acac})_2$ - LiAlH_4 system activated with *n*-butanol in styrene hydrogenation vs. catalyst concentration c_{Ni} , M, at the $[\text{LiAlH}_4]/[\text{Ni}(\text{acac})_2]$ ratio of (1) 5, (2) 10, and (3) 20. $v_{\text{styrene}} = 8.7 \times 10^{-3} \text{ M}$, $V_{\text{C}_4\text{H}_9\text{OH}} = 1 \text{ ml}$, $T = 35^\circ\text{C}$, $P_{\text{H}_2} = 1 \text{ atm}$.

to zero. Reactivation of the nickel catalyst with *n*-BuOH allowed the catalytic activity not only to regain its initial value but even to double. These data validate the poisoning action of lithium tetrahydroaluminate but do not completely rule out the inhibitory action of its catalytic decomposition products.

Thus, the $\text{Ni}(\text{acac})_2$ - LiAlH_4 system examined by us is distinguished from similar palladium catalysts described in literature [16, 20] by the ability of the resulting nickel nanoparticles to catalyze decomposition of not only alane but also of lithium tetrahydroaluminate. The function of LiAlH_4 is not limited to reduction of the nickel precursor: The tetrahydroaluminate anions are adsorbed on the surface and act as stabilizers of nickel nanoparticles. Moreover, tetrahydroaluminate anions and, probably, the catalytic decomposition products of LiAlH_4 , occupy vacant surface sites and act as catalytic poisons. The latter undergo chemical transformations via reaction with proton-donating compounds, which leads to nickel catalysts exhibiting high performance characteristics in hydrogenation of alkenes. The strategy that we proposed allows preparation of nanosized nickel catalysts of alkene hydrogenation with well-reproducible properties, which are considerably superior in the activity not only to similar systems based on iron triad [8] but also palladium catalysts [16, 20].

CONCLUSIONS

(1) It was found that the $\text{Ni}(\text{acac})_2$ - LiAlH_4 system

in a mixed benzene–tetrahydrofuran solvent does not exhibit catalytic activity in hydrogenation of alkenes and alkynes, as well as of nitro- and carbonyl-containing and aromatic compounds.

(2) A synthesis strategy was proposed which is based on reduction of Ni(acac)₂ with LiAlH₄ excess, followed by introduction into the system of a proton-donating promoter with a view to chemical conversion of LiAlH₄ and its catalytic decomposition products.

(3) The catalytic properties of the nickel systems were studied in relation to the nature and concentration of proton-containing compounds (alcohols, acids, water), among which the strongest promoting action was exhibited by *n*-butanol.

(4) The prepared nicked catalysts are considerably superior in the activity displayed in hydrogenation of alkenes not only to similar systems based on iron triad but also to palladium catalysts.

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