ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 8, pp. 1334–1341. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © F.K. Schmidt, Yu.Yu. Titova, L.B. Belykh, V.A. Umanets, S.S. Khutsishvili, 2012, published in Zhurnal Obshchei Khimii, 2012, Vol. 82, No. 8, pp. 1244–1251.

Formation of the Cobalt Hydrogenation Catalysts at the Action of Lithium Aluminum Hydride and Lithium Tri(*tert*-butoxy)aluminohydride and Their Properties

F. K. Schmidt[a], Yu. Yu. Titova[a], L. B. Belykh[b], V. A. Umanets[a], and S. S. Khutsishvili[b]

[a] *Irkutsk State University, ul. Karla Marksa 1, Irkutsk, 664003 Russia*
[b] *Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, Irkutsk, Russia*
e-mail: fkschmidt@chem.isu.ru

Received June 16, 2011

Abstract—The interaction of $Co(acac)_{2(3)}$ with $LiAlH_4$ or $LiAlH(t\text{-}BuO)_3$ was studied using NMR, UV, IR, ESR spectroscopy, electron microscopy, and volumometry. The basic stages of formation of cobalt catalysts for hydrogenation were suggested. The formation of the nanoparticles that are active in the hydrogenation process is shown to occur at a ratio of reagents $5 \leq Red/Co \leq 12$. The nanoparticles are stabilized by an excess of $LiAlH_4$ or $LiAlH(t\text{-}BuO)_3$, as well as by the products of their catalytic decomposition under the action of cobalt in the reduced state. At the ratio $LiAlH_4$ / Co> 12 to obtain the particles active in catalysis their activation by a proton-donor compound is required.

DOI: 10.1134/S1070363212080026

The study of the Ziegler systems based on the transition metal complex compounds combined with the organic hydride compounds of the metals from I–III groups in the hydrogenation catalysis has been carried out since the second half of XX century and is continued now [1–4]. Despite such a long period of study and industrial applications of these systems, in particular, in the process of hydrogenation of polymers [5], some aspects of the formation and nature of the catalytically active species require further research of fundamental nature. This concerns, above all, establishing all the functions of the I–III groups metal compounds in the processes of formation and operation of the Ziegler type catalyst.

To date, experimentally has been shown that the coreagents in the Ziegler type systems are involved in the formation of hydride or an organic derivative of the transition metal, reduction of the transition metal compound, most often to the metal in the zero oxidation state, formation of adducts with the reduced form of the transition metal of the type of acid–base interaction, and stabilization of nanoparticles [6–8]. However, some aspects of this problem have not yet been substantiated experimentally. These include the role of the decomposition reactions of the I–III group metal compounds catalyzed by the transition metals [8, 9].

We have previously shown [10] that in the formation of nickel-based hydrogenation catalysts using lithium aluminum hydride $LiAlH_4$, the function of the latter is not limited to the reduction of the nickel precursor. The tetrahydroaluminate anions adsorbed on the surface act as a stabilizer of the nickel nanoparticles. Besides, the tetrahydroaluminate anions and probably products of catalytic decomposition of $LiAlH_4$ occupying the vacant positions on the surface may act as catalyst poisons. Therefore, the resultant nanoparticles are active in the hydrogenation only when they are activated by a proton-donor compound. In contrast to nickel, the palladium catalysts active in the hydrogenation are formed under the action of $LiAlH_4$ without activation with alcohol or water at a ratio of $LiAlH_4/Pd < 10$ [11].

These results have generated the need to study the cobalt-containing catalytic systems, formed by using $LiAlH_4$ and its alkoxy derivative $LiAlH(t\text{-}BuO)_3$ as the reducing agent, in the hydrogenation processes. Among the catalytic systems of the Ziegler type based on β-diketonates of the metals of first transition series, the cobalt-containing catalysts are distinguished by

Formation of hydrogen in the reaction of $Co(acac)_{2(3)}$ with $LiAlH_4$ or LiAlH(*t*-BuO)$_3$: c_{Co}= 8.3 mM, T = 30°C

Red:Co	(mol H_2)/(g-at Co)				
	Co(acac)$_n$–$LiAlH_4$, n = 2, 3			Co(acac)$_n$–LiAlH(*tert*-BuO)$_3$	
	Co(acac)$_2$[a]	Co(acac)$_2$[b]	Co(acac)$_3$[b]	Co(acac)$_2$[a]	Co(acac)$_3$[a]
2	1.5	1.9	2.2	0.9	0.7
4	2.4	3.2	3.8	1.5	1.4
6	3.2	4.1	5.2	1.8	1.9
8	3.9	4.7	6.3	2.1	2.4
10	4.6	5.1	7	2.3	2.8
16	5.8	5.5	8	2.6	3.4

[a] Mixed solvent: benzene–THF 10:2. [b] Solvent THF.

two features: a high activity in the hydrogenation of alkenes and arenes [3, 7] and a possibility of carrying out the reactions of conjugated hydrogenation of alkenes and arenes in the presence of the systems modified with trialkylphosphines [12]. A research of the cobalt-containing catalytic systems will allow establishing general patterns and characteristics of the catalysts formed at the action of $LiAlH_4$ and its alkoxyhydride derivatives on the cobalt compounds.

The reaction between Co(acac)$_2$ [or Co(acac)$_3$] and $LiAlH_4$ in THF medium at room temperature proceeds with rapid change of the solution color from lilac [or green in the case of Co(acac)$_3$] to brown, and with the release of molecular hydrogen. The analysis of volumetric data suggests the existence of three periods on the kinetic curves: the first period from 0 to 0.5 min, the second from 0.5 to 5 min, and the third, the slowest one, from 5 min to several hours. Given the fact that the formation of cobalt catalysts did not exceed 5 min and the principal amount of hydrogen is evolved in this time interval, we analyze the results of gas release only in the first and second periods.

As can be seen from the data listed in the table, the hydrogen yield at various reactant ratios is much higher than 1 mol of H_2 per 1 mol of Co(acac)$_2$ and 1.5 mol of H_2 per 1 mol of Co(acac)$_3$, as expected according to the stoichiometric equations:

$$Co(acac)_2 + 2LiAlH_4 = Co + 2Li(acac) + 2AlH_3 + H_2, \quad (1)$$

$$2Co(acac)_3 + 6LiAlH_4 = 2Co + 6Li(acac) + 6AlH_3 + 3H_2. \quad (2)$$

In the mixed solvent THF–benzene the hydrogen yield is lower compared to the reaction in THF. These data evidence indirectly that benzene is directly involved in the formation of reduced cobalt particles. The formation of hydrogen in the quantity above equimolar points to the process of decomposition of AlH_3 catalyzed by the transition metal clusters [10, 13]:

$$2AlH_3 \xrightarrow{cat} 2Al + 3H_2. \quad (3)$$

Since the total amount of the released hydrogen is more than 4 mol of H_2 per 1 mol of Co(acac)$_2$ and 6 mol of H_2 per 1 mol of Co(acac)$_3$ (see the table), which could form at the quantitative decomposition of AlH_3 and reduction of $Co(acac)_{2(3)}$, hence, along with the decomposition of aluminum hydride AlH_3 partial decomposition of $LiAlH_4$ occurs.

The hydrogen evolution in amount more than equimolar was also observed in the reaction of cobalt acetylacetonates with LiAlH(*t*-BuO)$_3$ (see the table), but the amount and rate of hydrogen release is about twice lower compared with $LiAlH_4$ in the reaction with Co(acac)$_2$ and 3–5 times less with Co(acac)$_3$. Such a result is quite expectable given the lower reactivity of the aluminum alkoxyhydride derivatives.

According to the volumetric data, the partial order of the reaction with respect to $LiAlH_4$ varies depending on the $LiAlH_4/Co(acac)_{2(3)}$ ratio (Fig. 1). In the range of the ratio $LiAlH_4$/Co(acac)$_2$ = 2–6 the order with respect to $LiAlH_4$ is unity, in the range 6–15, it decreased to 0.3. Similar results were obtained for Co(acac)$_3$: the first order on $LiAlH_4$ in the range of $LiAlH_4$/Co(acac)$_3$ = 2–8, and n = 0.3 in the range of the ratio of reagents 8–15. The reaction order in the mixed solvent (benzene–THF) with both Co(acac)$_2$, and Co(acac)$_3$ in the range of $LiAlH_4$/Co = 6–15 is equal to 0.4 with respect to $LiAlH_4$. The decrease in the reaction order from unity to 0.3 (or 0.4) isprobably due to the heterophase character of the processes of the

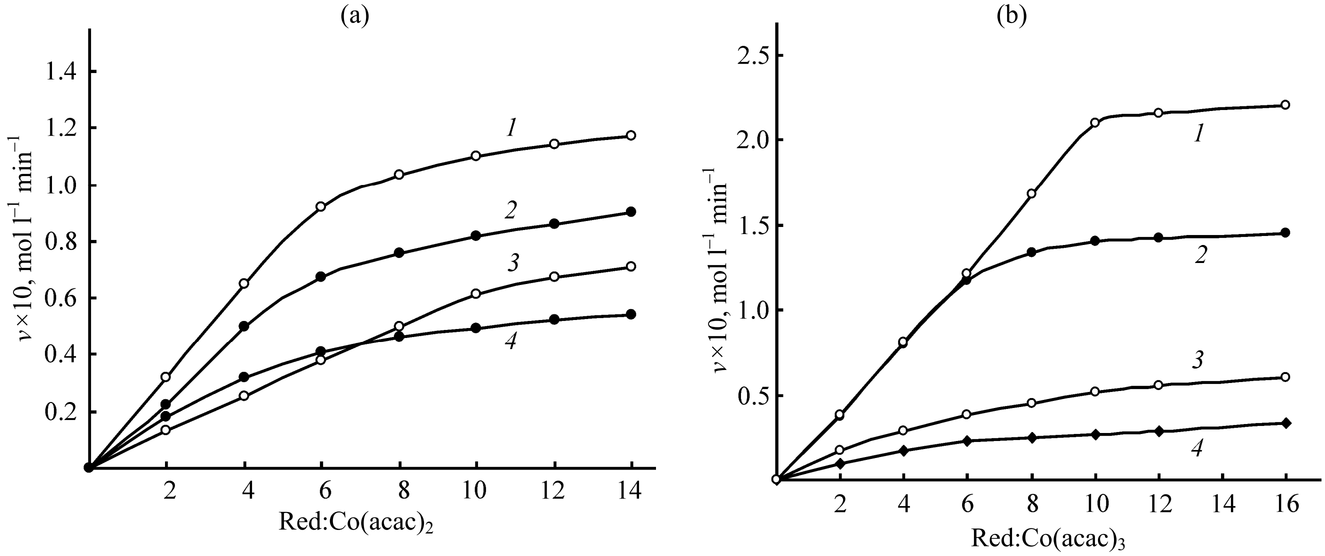

Fig. 1. The dependence of the rate of hydrogen release at the reduction of (a) Co(acac)$_2$ and (b) Co(acac)$_3$ with lithium aluminum hydride (*1*, *2*) and LiAlH(*t*-BuO)$_3$ (*3*, *4*) on the molar ratio of reagents, in THF (light circles) and mixed solvent THF–C$_6$H$_6$ (black circles). c_{Co} = 8.3 mM, T = 30°C.

AlH$_3$ and LiAlH$_4$ decomposition under the action of the reduced form of cobalt. For the system of Co(acac)$_{2(3)}$–LiAl(*t*-BuO)$_3$ there is no clearly expressed areas with a permanent order, the order varies from 1 to 0.5 in the investigated range of the ratio of LiAl(*t*-BuO)$_3$ to Co(acac)$_{2(3)}$ (Fig. 1, curves *3*, *4*).

In parallel with volumometry, we carried out studies of the reaction systems using IR, UV, and NMR spectroscopy. The IR spectra of Co(acac)$_2$–*n*LiAlH$_4$ (n = 2) recorded 10 min after the start of the reaction indicated lower intensity of the absorption bands at 1586 and 1520 cm^{-1} of the mixed stretching vibrations [ν(C=O)+ν(C = C)] of the acac ligands in O,O-chelate form of Co(acac)$_2$ [7] and the appearance of new poorly resolved absorption bands at 1607 and 1515 cm^{-1}, characteristic of stretching [ν(C=O) + ν(C=C)] vibrations of the acac ligand in Li(acac), indicating the transfer of the acac ligands from cobalt to lithium. For n = 4, in the IR spectrum in the region of 1500–1700 cm^{-1} only the absorption bands of acac ligand in Li(acac) were registered. The spectral analysis of reaction mixtures revealed the following pattern: With increasing molar ratio of LiAlH$_4$/Co(acac)$_2$ the Li(acac) concentration in the reaction system decreases. The IR spectroscopy data are consistent with the results of UV spectroscopy. The spectral characteristics of Co(acac)$_2$ (λ_{max} = 288 nm, ε = 288 = 16 200 l mol^{-1} cm^{-1}) and Li(acac) (λ_{max} = 292 nm, ε = 292 = 22 000 l mol^{-1} cm^{-1}) are close, so the quantitative analysis of UV spectra is not possible. However, qualitative analysis of the UV spectra of reaction mixtures of Co(acac)$_2$–*n*LiAlH$_4$ in THF as well as in benzene–THF showed that with the increasing LiAlH$_4$/Co(acac)$_2$ ratio and in the course of time the intensity of the absorption band at 290 nm decreases, in particular, for the Red/Co = 15 it was not observed after 20 min of keeping (Fig. 2, curve *4*). The resulting spectral data indicate the destruction of the π-system of acac ligand that may result from the interaction of the resulting Li(acac) with lithium aluminum hydride:

$$\mathrm{Li(acac) + LiAlH_4} \\ \rightarrow \mathrm{LiO{-}C(CH_3){=}CH{-}CH(CH_3){-}OAlH_3Li}.$$

Similar spectral pattern was obtained at the reduction of Co(acac)$_3$ with lithium aluminum hydride. At replacing the reducing agent by LiAlH(*t*-BuO)$_3$ the acac ligand also is transferred from cobalt to lithium, but the destruction of π-acac ligand in Li(acac) is not practically observed.

The information on the nature of the products of LiAlH$_4$ and LiAlH(*t*-BuO)$_3$ transformation was obtained also from the analysis of ^{27}Al NMR spectra of the reaction systems. According to the ^{27}Al NMR spectroscopy, the resonance signal with the chemical shift 98 ppm, characteristic of the $\mathrm{AlH_4^-}$ anion, was registered in the system Co(acac)$_2$–*n*LiAlH$_4$ at the ratio LiAlH$_4$/Co(acac)$_2$ ≥ 4. Along with the resonance signal

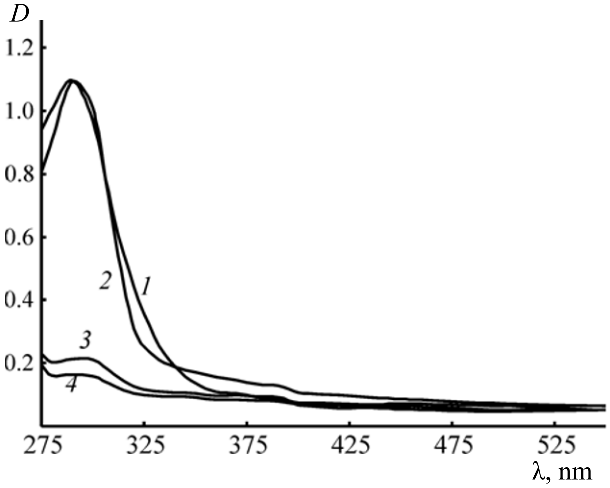

Fig. 2. UV spectra of $Co(acac)_2$ (*1*) and the reaction system of $Co(acac)_2$–$n$$LiAlH_4$ for $n = 2$ (*2*), 6 (*3*), and 15 (*4*). c_{Co} = 8.3 mM, benzene–THF (10:2), $T = 30°C$. Two-fold diluted $Co(acac)_2$ solution (*1*).

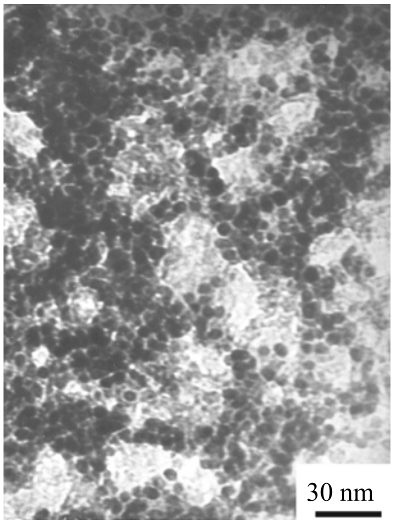

Fig. 3. TEM image of the system of $Co(acac)_2$–10 $LiAlH_4$.

at 98 ppm, in the ^{27}Al NMR spectra the resonance signal of weak intensity with chemical shift 34 ppm, and a broad signal with chemical shift about 70 ppm were observed. The resonance signal at δ 34 ppm, which, according to the scale of chemical shifts, corresponds to pentacoordinted Al, presumably can be assigned to $AlH(acac)_2$. The large width of the resonance signal at δ 70 ppm (~5000 Hz) indicates the presence of aluminum in the form with a high nuclearity, and its position, according to the scale of ^{27}Al chemical shifts, corresponds to the aluminum in a tetrahedral oxygen environment [14]. Most likely, it should be attributed to an associate of the interaction products of Li(acac)with lithium aluminum hydride.

When $LiAlH(t\text{-}BuO)_3$ was used as a reducing agent, the resonance signals with chemical. shifts of 53, 59 and 70 ppm were found in the ^{27}Al NMR spectra. The signals with δ 53 and 59 ppm correspond to $LiAl(t\text{-}BuO)_4$ [15] and $[Al(t\text{-}BuO)_3]_2$, respectively. The $[Al(t\text{-}BuO)_3]_2$ is formed in the redox process between Co $(acac)_{2(3)}$ and $LiAlH(t\text{-}BuO)_3$. The formation of tetra-substituted derivative $LiAl(t\text{-}BuO)_4$ may be the a result of several reactions.

$$2LiAlH(tert\text{-}BuO)_3 \rightleftarrows [AlH(tert\text{-}BuO)_2]_2 + 2Li(tert\text{-}BuO), \quad (4)$$

$$[Al(tert\text{-}BuO)_3]_2 + 2Li(tert\text{-}BuO) \rightarrow 2LiAl(tert\text{-}BuO)_4, \quad (5)$$

$$3AlH(tert\text{-}BuO)_2 \rightleftarrows AlH_3 + 2Al(tert\text{-}BuO)_3. \quad (6)$$

Despite the relative stability of $LiAl(t\text{-}BuO)_4$ and $AlH(t\text{-}BuO)_2$ to disproportionation, these processes will be favored at the decomposition of AlH_3 to the elements catalyzed by the reduced forms of cobalt. The set of reactions (3–6) allows us to understand and explain not only the formation of $LiAl(t\text{-}BuO)_4$ in the reaction system, but also the release of hydrogen in the amount more than equimolar (see the table). The resonance signal from the free $LiAlH(t\text{-}BuO)_3$ was detected in the ^{27}Al NMR spectrum at a molar ratio of $Red/Co(acac)_2 \geq 8$.

Study of the system $Co(acac)_2$–$LiAlH(t\text{-}BuO)_3$ by ESR spectroscopy revealed theappearance of a broad signal of the ferromagnetic resonance in the range of molar ratios Red/Co = 2–16 [3] with the g-factor from 2.22 to 2.47 (ΔH = 860–1520 Gs). This signal is characteristic of associated nanosized cobalt particles in a reduced state like Co(0). In the systems of $Co(acac)_2$–$LiAlH_4$ in the range of molar ratios $LiAlH_4$/Co = 2–16 in the ESR spectrum a low-intensity ESR signal was observed, which so far cannot be attributed to a specific compound. It should be noted that in the systems based on $LiAlH_4$, in contrast to the systems based on $LiAlH(t\text{-}BuO)_3$, the ferromagnetic resonance signal was not observed.

The nanoparticles formed in these systems are likely to be the associates of the heterometallic (Al–Co) compounds appearing at the catalytic decomposition of aluminum hydrides (AlH_3 and $LiAlH_4$) at the action of the complexes containing cobalt in the reduced state [Co(0), Co(I)].

The diameter of the basic particles formed in the

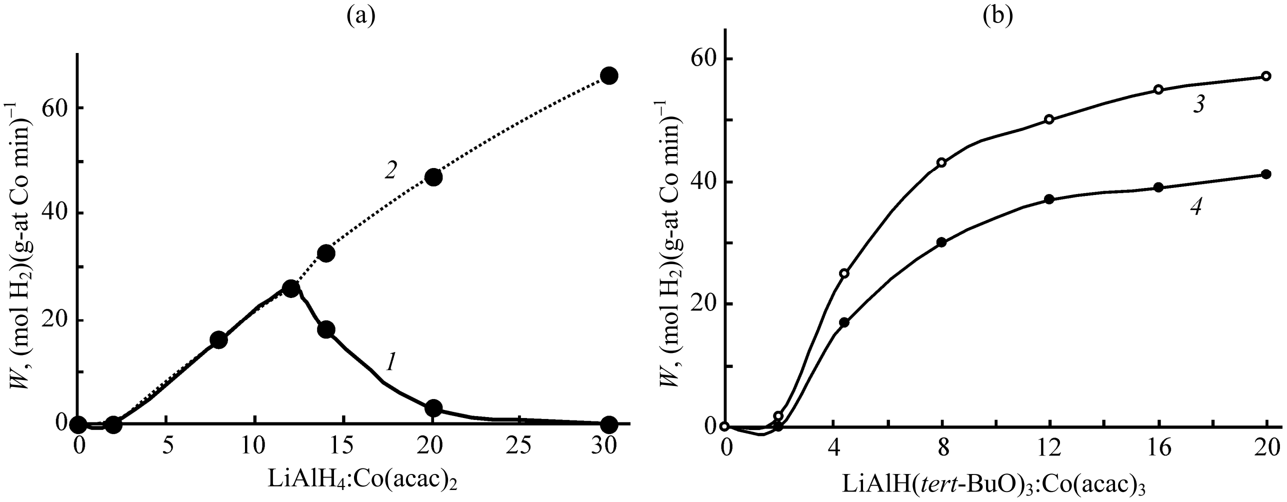

Fig. 4. Dependence of the activity of cobalt catalysts in the hydrogenation of styrene on the Red/Co molar ratio: (a) without adding *n*-BuOH (*1*), after the activation with *n*-BuOH (*2*), c_{Co} = 8.3 mM, (b) at various concentrations of Co(acac)$_3$: c_{Co} = 4.2 mM (*3*), c_{Co} = 12.5 mM (*4*), *T* = 30°C, *P*(H$_2$) = 2 atm.

system Co(acac)$_2$–10 LiAlH$_4$, according to TEM (transmission electron microscopy), is 2–3 nm, they are partially aggregated to form particles with a diameter up to 7–9 nm (Fig. 3). The size of the particles formed at the reduction of Co(II) with LiAlH (*t*-BuO)$_3$ (Red/Co = 10) varies from 1.9 to 5.7 nm.

Thus, at the reduction of cobalt acetylacetonates with LiAlH$_4$ or LiAlH(*t*-BuO)$_3$ the nanoparticles are formed stabilized by the excess of LiAlH$_4$ or LiAlH(*t*-BuO)$_3$ and also by the products of catalytic decomposition of these two reducing agents under the action of cobalt in the reduced state.

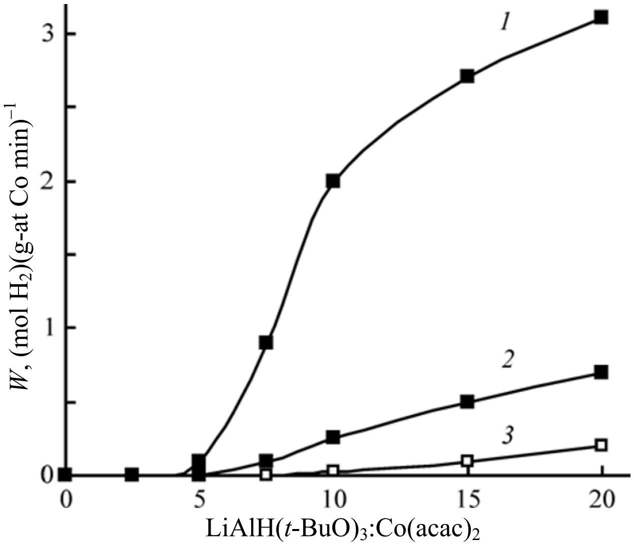

Fig. 5. Dependence of initial rate of anthracene hydrogenation on the Red/Co molar ratio in the presence of a catalytic system Co(acac)$_2$–LiAlH(*t*-BuO)$_3$ formed in the absence of substrate by method *a* (*1*) and in the presence of the substrate by method *b* (*2*, *3*): c_{Co} = 21 mM (*1*), c_{Co} = 8.3 mM (*2*, *3*), *T* = 30°C, *P*(H$_2$) = 2 atm, solvent THF.

Testing the above cobalt-containing systems in the process of hydrogenation of styrene showed that the activity of the nanoparticles formed depends on the nature of the reducing agent, the Red/Co(acac)$_{2(3)}$ ratio, and the sequence of mixing the components. In particular, the Co(acac)$_2$–LiAlH$_4$ system is almost inactive in the hydrogenation at the ratio Red/Co < 5. In the range of 5 ≤ Red/Co ≤ 12 the activity increases, reaching 30 min^{-1} (Fig. 4). With increasing ratio of LiAlH$_4$/Co > 12 a decrease in the catalytic activity occurs and at the Red/Co ≥ 20 the activity almost reaches zero. An extreme form of the dependence was previously found for the Pd(acac)$_2$–*n*LiAlH$_4$ system [11]. The introduction of *n*-butanol to the system of Co(acac)$_2$–LiAlH$_4$ after the formation of the catalyst (*n*-BuOH/LiAlH$_4$ = 1) leads to the appearance and (or) increase in the hydrogenating activity of the system (Fig. 4, curve *2*). Obviously, like the case of nickel catalysts [10], LiAlH$_4$ and its catalytic decomposition products adsorbed on the surface of cobalt nanoparticles poison the catalytically active sites, and introduction of a proton-donor compound can eliminate or diminish their inhibitory effect. In contrast to lithium aluminum hydride, LiAlH(*t*-BuO)$_3$ shows no inhibitory effect on the catalytic properties of the cobalt hydrogenation catalysts (Fig. 5).

By changing the order of mixing the components, that is, by adding the Co(acac)$_2$ in the LiAlH$_4$–styrene solution in THF (or mixed solvent), is possible to increase the activity of the catalytic system by about 30% compared to the catalyst obtained by adding a solution of $LiAlH_4$ to a solution of $Co(acac)_2$. The catalyst performance is better at the Red/Co = 10 without activation with a proton-donor compound, and an improvement of the catalyst in time is observed. At the consecutive hydrogenation of several portions of styrene, the maximum activity was observed at introducing 2nd and 3rd 1-ml portions of styrene. With increasing concentration of Co and $LiAlH_4$ there is a tendency to shift the maximum toward larger amounts of styrene.

Effect of the order of mixing components on the catalyst system can also be seen in the hydrogenation of anthracene. The activity of a $Co(acac)_2$–LiAlH(*t*-BuO)$_3$ system formed in the presence of anthracene in the hydrogenation reaction at 30ºC and hydrogen pressure 2 bar is very low (Fig. 5, curve *3*). The rate of hydrogenation of anthracene increases dramatically (by ~2 orders of magnitude) when anthracene is added to a solution of catalyst 2–5 min after the components have been mixed and the release of the main part of hydrogen has ceased, that is, after the formation of the cobalt nanoclusters. Anthracene is converted into 9,10-dihydro- and 1,2,3,4-tetrahydroanthracene quantitatively. The rate of hydrogenation of anthracene in the presence of the cobalt catalyst prepared in this way (method *a*) depends on the Red/Co molar ratio (Fig. 5, curve *1*) and the concentration of $Co(acac)_2$ (Fig. 5, curves *1*, *2*.) The increase in the Red/Co ratio leads not only to increase in the initial rate, but also to the improvement in the catalyst performance. A formal order with respect to cobalt is equal to 2.2–2.4, which indicates a microheterogeneous (nanoscale) nature of the catalysis.

The study of the system using electron microscopy showed that the average particle size is 3.7 nm prior to the anthracene hydrogenation and 10.9 nm after it. The cobalt nanoclusters aggregation may be one of the causes of deactivation of the examined catalysts.

The results obtained show the occurrence of rather complex processes at the formation of cobalt catalysts under the action of lithium aluminum hydride and its *t*-butoxyhydride derivative, as seen from the catalytic properties of the catalyst. Comparison of the catalytic properties of systems based on $Co(acac)_2$ and $Ni(acac)_2$ obtained at the action of lithium aluminum hydride shows their fundamental difference. Nickel catalyst is formed only after the activation with a proton-donor substance regardless of the catalyst system composition [10], whereas for $Co(acac)_2$ the composition in the range $5 \leq LiAlH_4/Co \leq 12$ not requires an additional proton-donor compound for the formation of a hydrogenation catalyst. At increasing the molar ratio over twelve it becomes necessary to add alcohol for the catalyst activation. It follows from these observations that the decomposition products of lithium aluminum hydride appearing under the influence of cobalt do no block the entire surface of the Co(0) nanoclusters, due may be to a lower degree of decomposition of $LiAlH_4$. The comparison of the yield of hydrogen in the reaction of $LiAlH_4$ with $Co(acac)_2$ and $Ni(acac)_2$ shows that the yield of hydrogen per one mole of the metal is about 1.5–2 smaller for the former. However, we cannot exclude also other possible causes of the observed results. For example, cobalt aluminides are richer in aluminum compared with nickel derivatives at the identical conditions of their production, and probably this decreases the effect of poisoning of the cobalt catalyst compared to nickel one.

EXPERIMENTAL

Solvents [benzene, tetrahydrofuran (THF)], substrates (styrene, anthracene), reagent (*t*-butanol) were purified by the techniques used commonly in the work with organometallic materials [16]. For deeper removing water, benzene was subjected to further distillation over $LiAlH_4$ on a distillation column and stored under argon in sealed ampules over molecular sieves 4A. THF after the removal of peroxides was distilled successively over sodium, $LiAlH_4$, and benzophenone ketyl, and then stored under argon in sealed ampules. Water concentration determined by the method of Fischer [11], was in benzene 1.1×10^{-3} M, in THF 1.6×10^{-3} M.

Anthracene was additionally purified by sublimetion (T = 160–170ºC, 1 mm Hg).

Synthesis of cobalt bis-acetylacetonate and tris-acetylacetonate was carried out in accordance with the procedures described in [17] and [18], respectively.

Lithium aluminum hydride (commercial) was used without prior recrystallization. Weighed portion of $LiAlH_4$ was dissolved in THF, the solution was filtered in an inert atmosphere through a glass frit. The $LiAlH_4$ concentration determined by the volume of hydrogen released at the hydrolysis was about 95–98% of theoretical. ^{27}Al NMR spectrum (THF): δ_{Al} 98 ppm, quintet, $^1J_{AlH} = 173$ Hz.

Synthesis of LiAlH(*t*-BuO)$_3$ was carried out by alcoholysis of LiAlH$_4$ with *t*-butanol in THF at 30°C over 48 h in accordance with [19], the molar ratio [*t*-BuOH]/[LiAlH$_4$] = 3. Monitoring was carried out by ^{27}Al NMR spectroscopy. The ^{27}Al NMR spectrum (THF): δ_{Al} 78 ppm (singlet).

Study of the reaction of Co(II) and Co(III) bis (acetylacetonates) with LiAlH$_4$ [or LiAlH(*t*-BuO)$_3$] at the different ratios of the initial components was carried out in an atmosphere of dry oxygen-free argon in a thermally controlled reactor providing a possibility of preliminary evacuation and filling with argon.

To quantify the amount of the molecular hydrogen produced in the reaction of components of a catalytic system a special vessel was used under temperature control, with an additional section inside where to place the second component. Into the reactor, pre-evacuated, filled with argon, and connected to a volumetric system was placed a solution of 0.0257 g (1×10^{-4} mol) of Co(acac)$_2$ or 0.0356 g (1×10^{-4} mol) of Co(acac)$_3$ in 10 ml of benzene. To the internal section was placed an aliquot of LiAlH$_4$ [or LiAlH(*t*-BuO)$_3$} solution in THF. The vessel was closed with a Teflon stopper, and at vigorous stirring the reducing agent and the Co(acac)$_{2(3)}$ solutions were mixed. The resulting hydrogen was determined volumetrically. The solutions were analyzed using UV, IR, and NMR spectroscopy.

UV spectra were recorded on a SF 2000 spectrometer in the range of 250–430 nm in a fused quartz cell with absorbing layer thickness 0.01 cm. The IR spectra of solutions were taken on a Specord 75 IR spectrometer using a KRS cell of 0.2 mm thickness flushed with argon (solvent benzene–THF). NMR spectra were recorded on a VXR-500S Varian pulse spectrometer. The ^{27}Al chemical shifts were measured relative to external reference: 0.1 M solution of Al(NO$_3$)$_3$. To prevent hydrolysis at recording the ^{27}Al NMR spectra, the liquid sample was placed in a quartz ampule 5 mm in diameter previously evacuated and filled with argon, and sealed. The ESR spectra were recorded on ELEXSYS E580 Bruker spectrometer at room temperature.

The study of samples with transmission electron microscopy was performed on a Philips EM-410 microscope. A drop of the catalyst solution formed in situ was applied to the bearing mesh coated with carbon film and dried under argon. The conditions of registering preclude melting and decomposition of the samples under electron beam.

Experiments on the hydrogenation of styrene were carried out in a hydrogenation vessel of common form with temperature control, at 30°C, hydrogen pressure 2 atm (0.20265 MPa), at vigorous stirring, which ensures that the reaction in the diffusion region occurs in kinetic region. In the pre-filled with hydrogen and evacuated reactor was charged successively under hydrogen weighed sample of Co(acac)$_2$ (2×10^{-4} mol) and benzene (10 ml), and the mixture was stirred till dissolving. To the resulting lilac solution of Co(acac)$_2$ was added substrate (styrene, 1 ml) and LiAlH$_4$ or LiAlH(*t*-BuO)$_3$ solution in THF. The reactor was closed by a Teflon stopper with a rubber gasket (for sampling), hydrogen was added at a pressure of 1 atm, and the stirring was switched on. The course of the hydrogenation reaction was monitored by a decrease of the hydrogen pressure and by GLC on a Chrom-5 chromatograph with a flame ionization detector (FID), carrier gas nitrogen, column length 3.6 m, diameter 3 mm; phase carbowax 20M. Similarly the experiments with Co(acac)$_3$ were carried out.

Hydrogenation of anthracene. *a*. In the pre-filled with hydrogen and evacuated hydrogenation vessel of common form under the hydrogen flow were charged successively a solution of LiAlH(*t*-BuO)$_3$ in THF (1 ml) and a solution of Co(acac)$_2$ (1×10^{-4} to 5×10^{-4} mol) in 23 ml of THF. To the resulting dark brown solution of the catalyst was added anthracene under the hydrogen flow. After closing with Teflon stopper with a rubber gasket (for sampling), the hydrogen pressure was raised to 1 at and the stirring was switched on. The course of the hydrogenation was monitored by the drop in hydrogen pressure. Analysis of the products of anthracene hydrogenation was carried out using gas chromatography–mass spectrometry. Cobalt catalyst formed in this way had the maximum catalytic activity.

b. Differs from the method *a* that in the hydrogenation vessel under a hydrogen flow were successively charged a solution of LiAlH(*t*-BuO)$_3$ in 1 ml of THF, dry anthracene, and 13 ml of THF at stirring. To the resulting white suspension a solution of Co(acac)$_2$ (2×10^{-4} to 5×10^{-4} mol) in THF (10 ml) was poured. In this case, the catalyst has less activity than the catalyst obtained by the method *a*.

When to the solution of Co(acac)$_2$ (1×10^{-4}–5×10^{-4} mol) in THF (20 ml) was added dropwise a solution of LiAlH(*t*-BuO)$_3$ in the presence of dissolved anthracene, the formed catalytic system is not active in the hydrogenation under the above conditions.

ACKNOWLEDGMENTS

This work was performed under the Federal Target Program “Research and scientific-pedagogical staff of innovation in Russia” (State contract no. P1344).

REFERENCES

1. Sloan, M.F. and Matlack, A.S., and Breslow, D.S., *J. Am. Chem. Soc*., 1963, vol. 85, p. 4014.
2. Kalechits, I.V. and Shmidt, F.K., *Kinetika i Kataliz*, 1966, vol. 7, no. 4, p. 614.
3. Shmidt, F.K., *Kataliz kompleksami metallov pervogo perekhodnogo ryada reaktsii gidrirovaniya i dimerizatsii* (Catalysis of Hydrogenation and Dimerization Reactions by the Complexses of the Metals of First Transition Row), Irkutsk: Irkutsk. Gos. Univ., 1986.
4. Alley, W.M., Hamdemir, I.K., Johnson, K.A., and Finke, R.G., *J. Mol. Catal. (A),* 2010, vol. 315, no. 1, p. 1.
5. McManus, N.T. and Rempel, G.L., *J. Macromol. Sci. Rev. Macromol. Chem. Phys. C*, 1995, vol. 35, no. 2, p. 239.
6. Bonnemann, H., Braun, G., Brijoux, W., Brinkmann, R., Tilling, A.S., Seevogel, K., and Siepen, K., *J. Organomet. Chem*., 1996, vol. 520, p. 143.
7. Shmidt, F.K., Nindakova, L.O., Shainyan, B.A., Saraev, V.V., Chipanina, N.N., and Umanetz, V.A., *J. Mol. Catal. (A),* 2005, vol. 235, nos. 1–2, p. 161.
8. Belykh, L.B., Goremyka, T.V., Skripov, N.I., Umanets, V.A., and Shmidt, F.K., *Kinetika i Kataliz*, 2006, vol. 47, no. 3, p. 373.
9. Ganem, B. and Osby, J., *Chem. Rev*., 1988, vol. 86, p. 763.
10. Belykh, L.B., Titova, Yu.Yu., Rokhin, A.V., and Shmidt, F.K., *Zh. Prikl. Khim.,* 2010, vol. 83, no. 11, p. 1778.
11. Belykh, L.B., Titova, Yu.Yu., Umanets, V.A., and Shmidt, F.K., *Zh. Prikl. Khim*., 2006, vol. 79, no. 8, p. 1285.
12. Shmidt, F.K., Levkovskii, Yu.S., Ryutina, H.M., and Bakunina, T.I., *Kinetika i Kataliz*, 1982, vol. 23, no. 10, p. 360.
13. Soloveichik, G.L. and Bulychev, B.M., *Usp. Khim*., 1983, vol. 52, no. 1, p. 72.
14. Fedotov, M.A., Molchanov, V.V., Zotov, R.N., and Tuzikov, F.V., *Zh. Neorg. Khim*., 2008, vol. 53, no. 10, p. 1735.
15. Horne, D.A., *J. Am. Chem. Soc*., 1980, vol. 102, no. 19, p. 6011.
16. Gordon, A.J. and Ford, R.A., *The Chemist’s Companion. A Handbook of Practical Data, Techniques and References*, New York: Wiley, 1972.
17. Ellern, J.B. and Ragsdale, R., *Inorg. Syntheses*., 1968, vol. 11, p. 82.
18. Shalhoub, G.M., *J. Chem. Education*., 1980, vol. 57, no. 7, p. 525.
19. Schuldt, B., Heller, D., Storz, F., and Madeja, K., *J. Mol. Catal*., 1993, vol. 81, no. 2, p. 195.