

Preparation Method Effect on the Properties of Ziegler-Type Hydrogenation Catalysts Based on Bis(acetylacetonato)cobalt

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Abstract—The turnover frequency and turnover number of Ziegler-type systems based on $\text{Co}(\text{acac})_2 \cdot n\text{H}_2\text{O}$ ($n = 0, 0.5, \text{ and } 2$) and AlEt_3 or $\text{AlEt}_2(\text{OEt})$ are reported in relation to the Al : Co molar ratio and to the concentrations of the initial components. Proton donor compounds have an effect on the catalytic characteristics of the systems. ESR data are presented for the interaction of $\text{Co}(\text{acac})_2$ with organometallic compounds (AlEt_3 , $\text{AlEt}_2(\text{OEt})$, $\text{Li}(n\text{-Bu})$, and $(\text{C}_6\text{H}_5\text{CH}_2)\text{MgCl}$) in the presence of various arenes. Seven preparation methods and a formation scheme are suggested for catalytic species that are active in styrene hydrogenation and are based on $\text{Co}(\text{acac})_2$ combined with AlEt_3 or $\text{AlEt}_2(\text{OEt})$ and.

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Hydrogenation catalysts based on bis(acetylacetonato)cobalt ($\text{Co}(\text{acac})_2$) and its complexes with Lewis bases have long been attracting attention from researchers engaged in hydrogenation catalysis. Ziegler-type systems are very sensitive to oxygen, water, and other proton donors, which are inevitably present in the initial reactants. This is the reason why catalytic experiments aimed at determining the turnover frequency (TOF) and turnover number (TON) yield discrepant data. Using cobalt systems as examples, Shmidt [1, 2] demonstrated for the first time that water (at concentrations comparable to those of the components of the catalytic system) exerts a favorable effect on the quantitative characteristics of these systems.

Elucidation of mechanisms of the formation of efficient Ziegler-type hydrogenation catalysts and development of targeted methods for the synthesis of these catalysts involve serious problems. For systems based on $\text{Co}(\text{acac})_2$ combined with organoaluminum compounds, it was found that paramagnetic $\text{Co}(0)$ complexes form at the hydrogenation catalyst preparation stage [3–6]. All attempts to isolate $\text{Co}(0)$ complexes forming in the Ziegler-type systems have been unsuccessful, because these compounds are unstable near room temperature. Much work has been done to study the effect of the composition of a catalytic system on the ESR spectroscopic parameters of the system, and these studies made it possible to determine the most likely composition of the paramagnetic $\text{Co}(0)$ complexes [4–7]. It was simultaneously demonstrated that the $\text{Co}(0)$ complexes detectable by the ESR spectroscopy are

inactive in hydrogenation catalysis and are only precursors of catalytically active systems.

It was shown [8, 9] that catalysis in Ziegler-type systems takes place on nanosized particles. Later, this finding was verified by Finke and their colleagues for bis(neodecanoato)cobalt as an example [10]. The activity of the catalyst was much higher in case it had been formed in the presence of the substrate to be hydrogenated.

However, these previous studies failed to formulate a scientifically grounded approach to the synthesis of effective catalysts. The importance of investigating the formation of Ziegler-type systems based on cobalt complexes is also due to the fact that it is the cobalt-based systems that are employed in the industrial-scale hydrogenation of styrene–butadiene copolymers [11–15].

Here, we report the effect of preparation conditions on the properties (TOF and TON) of $\text{Co}(\text{acac})_2$ –Red (Red = AlEt_3 , $\text{AlEt}_2(\text{OEt})$) systems in hydrogenation catalysis and refine the ESR parameters of the paramagnetic $\text{Co}(0)$ complexes and their role in the formation of catalytically active particles.

EXPERIMENTAL

Materials

Solvents (toluene, octane, hexane, and diethyl ether) and substrates (styrene, 1-hexene, and cyclohexene) were purified using standard procedures [16]. Toluene, octane, and hexane were further dried by distillation from LiAlH_4 using a distillation column and were stored in an argon atmosphere over molecular

sieve 4 Å in sealed tubes. After being purified from peroxides, diethyl ether was distilled from sodium benzophenone ketyl and was stored in an argon atmosphere over sodium foil in sealed tubes. As determined by the Fisher method [17], the water concentration in octane, hexane, and toluene was $\sim 1.1 \times 10^{-3}$ mol/L and the water concentration in diethyl ether was 1.6×10^{-3} mol/L.

p-Xylene (1,4-dimethylbenzene), mesitylene (1,3,5-trimethylbenzene), durene (1,2,4,5-tetramethylbenzene), and 1,2,3,4,5,6-hexamethylbenzene were dried via standard procedures [18] and were stored in an argon atmosphere in sealed tubes.

Argon was dried and deoxygenated by successively passing it through columns filled with P_2O_5 , a granular alkali, zeolite CaA, and silica-supported activated copper preheated to 200°C. Hydrogen (brand A, Russia) was purified from oxygen and water traces by successively passing it through columns filled with a nickel–chromium catalyst and zeolite CaA.

Triethylaluminum was vacuum-distilled at 48–49°C/1 Torr and was then stored in an argon atmosphere in sealed tubes. $AlEt_3$ was dissolved in *n*-hexane or *n*-octane in an argon atmosphere in Schlenk flasks. The $AlEt_3$ concentration in the solutions was determined volumetrically by decomposing a solution aliquot with water. The purity of $AlEt_3$ was checked by NMR spectroscopy. The 1H NMR spectrum of an $AlEt_3$ solution in C_6D_6 showed the following signals (δ , ppm): 0.45 (CH_2 , q, $^1J = 8.24$ Hz) and 1.22 (CH_3 , t, $^1J = 8.24$ Hz).

Benzylmagnesium chloride ($C_6H_5CH_2$)MgCl was synthesized via a standard procedure [19] using a solution of butyllithium $Li(n-C_4H_9)$ in hexane (Acros Organics). The butyllithium concentration was determined via a standard procedure [20].

n-Butanol was refluxed over freshly calcined CaO (12.5 g) for 4 h in an argon atmosphere and was then distilled using a Vigreux column. The distillate was boiled over sodium and was then distilled off, and the fraction boiling at 117°C ($n^{25} = 0.80572$) was collected [21].

Bis(acetylacetonato)cobalt samples were synthesized via a procedure reported in the literature [22].

Co(acac) $_2$ · 2H $_2$ O (sample 1) was synthesized by combining an aqueous solution of $CoCl_2 \cdot 6H_2O$ (0.2 mol, 47.6 g) with an aqueous solution of Na(acac) (0.4 mol, 48.8 g) [22]. The resulting $Co(acac)_2$ precipitate was vacuum-dried (40–50°C/14 Torr) for 3 h. The crystalline hydrate synthesized in this way, $Co(acac)_2 \cdot 2H_2O$, was a pale pink powder.

Co(acac) $_2$ · 0.5H $_2$ O (sample 2) was synthesized by dehydrating the crystalline hydrate $Co(acac)_2 \cdot 2H_2O$ (sample 1) by azeotropic distillation with toluene. The resulting lilac powder was vacuum-dried (40–50°C/2 Torr) for 10 h.

Anhydrous Co(acac) $_2$ (sample 3), a dark lilac powder, was obtained by sublimating sample 2 at 105–110°C/0.1 Torr.

The water content of the bis(acetylacetonato)cobalt samples was determined by thermogravimetric analysis combined with differential scanning calorimetry on an STA 449 F3 Jupiter thermoanalytical system (Netzsch, Germany) under the following conditions: nitrogen supply rate, 30 mL/min; heating rate, 5 K/min.

Hydrogenation Experiments

Hydrogenation experiments were performed in a temperature-controlled duck-shaped vessel at a preset temperature and an excess hydrogen pressure of 1 atm under vigorous agitation preventing the reaction from being diffusion-controlled. $Co(acac)_2$ (0.0256 g, 1×10^{-4} mol) and benzene or toluene (15 mL) were placed in a prepumped, hydrogen- or argon-filled, temperature-controlled, duck-shaped vessel under flowing hydrogen or argon, and the mixture was agitated for 10 min to obtain a light lilac transparent solution. Styrene (1 mL, 8.7 mmol) and a solution of $AlEt_3$ in *n*-octane (2 mL) were added to this solution. The Al : Co ratio was varied between 1 and 15. The vessel was closed with a Teflon stopper with a rubber septum (intended for sampling), an excess hydrogen pressure (1 atm) was produced, and hydrogenation was then carried out. The hydrogenation reaction was monitored as the pressure drop indicated by a manometer. The composition of the reaction mixture was determined by gas–liquid chromatography (GLC) on a Khromatek-Kristall 5000.2 chromatograph (Khromatek, Russia) fitted with a flame-ionization detector and an SGE BPX5 (0.53 mm \times 30 m) capillary column. Catalysts were analyzed by the GC–MS method on a GCMS-QP-2010 mass spectrometer (Shimadzu, Japan).

The interaction between $Co(acac)_2$ and $AlEt_3$ or another reductant ($AlEt_2(OEt)$, $Li(n-C_4H_9)$, or $(C_6H_5CH_2)MgCl$) at different ratios between the initial reactants were studied in a dry and deoxygenated argon and/or hydrogen atmosphere. For example, a solution of a reductant in octane (Red = $AlEt_3$ or $AlEt_2(OEt)$), tetrahydrofuran (Red = $(C_6H_5CH_2)MgCl$), or hexane (Red = $Li(n-Bu)$) was added to a stirred solution of $Co(acac)_2$ (0.0256 g, 1×10^{-4} mol) in toluene (9 mL). The total volume of the system was 10 mL. The Red : Co molar ratio was varied between 1 and 15, depending on the reductant type. The resulting solution was analyzed at different point in time by ESR spectroscopy at room temperature and at the liquid nitrogen temperature.

The $Co(acac)_2$ – $AlEt_3$ reaction systems were analyzed by ESR spectroscopy under hydrogenation catalysis conditions. For this purpose, after the cobalt catalyst was prepared as described in the *Hydrogenation Experiments* section, samples of the reaction mixture were syringed from the reactor through the sep-

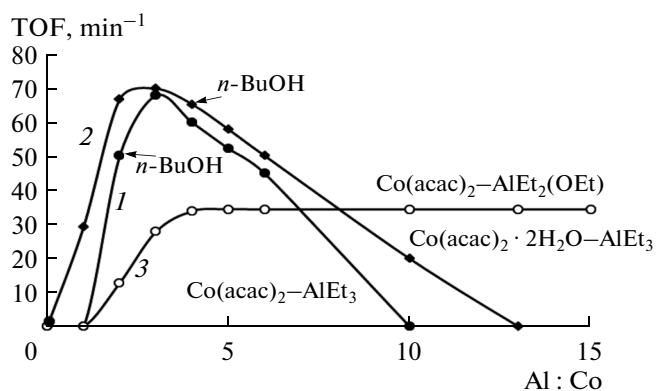


Fig. 1. Activity of $\text{Co}(\text{acac})_2 \cdot n\text{H}_2\text{O}$ -Red (Red = (1, 2) AlEt_3 and (3) $\text{AlEt}_2(\text{OEt})$) system in styrene hydrogenation as a function of the Al : Co molar ratio at $n = (1, 3) 0$ and (2) 2.0. (1, 2) $[\text{Co}] = 6.25 \text{ mmol/L}$, $[\text{styrene}] = 0.48 \text{ mol/L}$, $P_{\text{H}_2} = 2 \text{ atm}$, $T = 30^\circ\text{C}$, $[\text{n-C}_4\text{H}_9\text{OH}] : [\text{AlEt}_3] = 3$; (3) $[\text{Co}] = 10.0 \text{ mmol/L}$. The arrows indicates the points at which the $\text{n-C}_4\text{H}_9\text{OH}$ activator is introduced.

tum in its Teflon stopper during the reaction. The samples were transferred in prepumped, argon-filled ESR tubes.

ESR spectra were recorded on an ESP 70-03 XD/2 spectrometer (KBST BGU, Belarus) operating at a frequency of 9.3 GHz. The magnetic field sweep was calibrated using diphenylpicrylhydrazyl (DPPH) or the *N,N*-diphenyl-*N'*-picrylhydrazyl radical. ESR spectra were simulated on a Tesla GPU computer cluster [23] using the EasySpin module for the Matlab software package [24]. Only the electron Zeeman interaction and hyperfine coupling in the first-order approximation were taken into account. The spin concentration was calculated by comparing the given spectrum with the spectrum of the reference $\text{Cu}(\text{acac})_2$ solution.

Samples to be examined by transmission electron microscopy (TEM) were taken out of the reaction mixture just during the experiment. Part of each sample was studied by ESR spectroscopy. (The ESR sample was placed in two tubes, one to be examined at room temperature and the other at the liquid nitrogen temperature.) For preparing TEM specimens, the solutions of the samples were diluted fivefold with a solvent (toluene : octane = 15 : 2). A drop of the diluted solution was applied to a carbon-coated copper grid (200 mesh) and was dried at room temperature in an inert atmosphere in a glovebox. TEM images were obtained on a JEM-2010 microscope (JEOL, Japan) at an accelerating voltage of 200 kV and a lattice resolution limit of 0.14 nm. The images were recorded using a CCD camera (Soft Imaging System, Germany). Local elemental analyses of specimens on 10-nm areas were carried out on a JEM 2010 electron microscope equipped with an EDAX energy-dispersive X-ray spectrometer (Phoenix, United States) with a Si(Li) semiconductor detector.

RESULTS AND DISCUSSION

Catalytic Properties of the Systems in Hydrogenation

In order to develop methods for preparing efficient $\text{Co}(\text{acac})_2$ -based hydrogenation catalysts, we investigated how the quantitative characteristics of these catalysts in alkene hydrogenation depend on the concentration of the catalytic system components, on the order in which the components were introduced, and on the atmosphere in which the catalyst was formed. In case the catalytic system based on anhydrous $\text{Co}(\text{acac})_2$ and AlEt_3 was formed in an argon atmosphere, irrespective of whether a substrate (styrene, 1-hexene, or cyclohexene) was present, alkene hydrogenation at 30°C does not take place. A slight catalytic activity ($\text{TOF} = 2 \times 10^{-2} \text{ min}^{-1}$) at 70°C is observed only after the introduction of *n*-butanol into the $\text{Co}(\text{acac})_2$ - AlEt_3 reaction system. The activating effect of butanol and other proton donors was earlier discovered for nickel catalysts formed under the action of not only AlEt_3 [25] but also LiAlH_4 [26]. In the case of the $\text{Co}(\text{acac})_2$ and AlEt_3 solutions mixed in a hydrogen atmosphere, TOF and TON did not depend on the time at which the substrate (styrene) was subsequently introduced (in the 1–60 min range), on the $\text{Co}(\text{acac})_2$ concentration (2.5×10^{-3} – $2.0 \times 10^{-2} \text{ mol/L}$), or on the molar ratio of the catalyst components (Al : Co = 2–4). The TOF value calculated from the initial styrene hydrogenation rates was $8.4 \pm 0.8 \text{ min}^{-1}$, and the TON value was $38 \pm 9 \text{ mol}_{\text{styrene}}/\text{mol}_{\text{Co}}$.

Figure 1 plots TOF as a function of the Al : Co molar ratio for the systems based on $\text{Co}(\text{acac})_2$ and $\text{Co}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$ before and after the introduction of the activator (*n*- $\text{C}_4\text{H}_9\text{OH}$).

Note that, for the catalytic systems based on anhydrous $\text{Co}(\text{acac})_2$ (sample 3), styrene hydrogenation in the Al : Co = 2–10 molar ratio range occurs only after the introduction of *n*-butanol ($[\text{n-C}_4\text{H}_9\text{OH}] : [\text{AlEt}_3] = 3$) into the system (Fig. 1, curve 1). The hydrogenation activity of the $\text{Co}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$ - AlEt_3 systems with Al : Co = 1–3 is observed in the absence of *n*- $\text{C}_4\text{H}_9\text{OH}$ ($\text{TOF} = 70 \text{ min}^{-1}$, $\text{TON} = 200 \text{ mol}_{\text{styrene}}/\text{mol}_{\text{Co}}$). At Al : Co = ≥ 4 , the $\text{Co}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$ - AlEt_3 system shows catalytic activity only after the introduction of an additional amount of activator. For example, at Al : Co = 4, TOF increases from 0 to 65 min^{-1} upon the introduction of *n*-butanol ($[\text{n-C}_4\text{H}_9\text{OH}] : [\text{AlEt}_3] = 3$), the TON value becoming $496 \text{ mol}_{\text{styrene}}/\text{mol}_{\text{Co}}$ (Fig. 1, curve 2).

Thus, without a proton donor, no hydrogenation catalyst forms in the $\text{Co}(\text{acac})_2$ - AlEt_3 systems. Excess AlEt_3 acts as an inhibitor, completely suppressing the hydrogenation activity of the sample 3- AlEt_3 system at Al : Co = 10 and that of the sample 1- AlEt_3 system at Al : Co = 12. The poisoning effect of AlEt_3 on the cobalt-containing catalysts is partly reversible (eliminated by *n*-butanol) and partly irreversible (e.g., due to the oxidative addition of AlEt_3 to $\text{Co}(0)$) [27, 28].

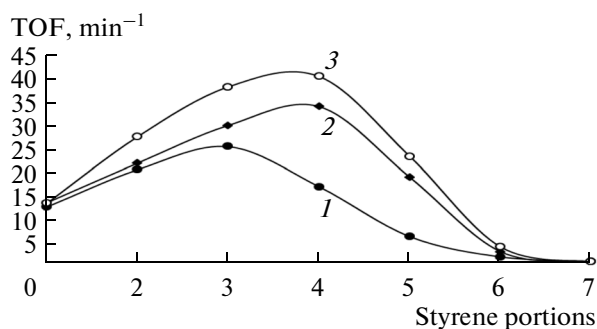


Fig. 2. Activity of the $\text{Co}(\text{acac})_2\text{-AlEt}_3$ system in styrene hydrogenation in heptane–arene (1) mesitylene, (2) durene, and (3) hexamethylbenzene) media as a function of the number of hydrogenated styrene portions. Reaction conditions: one styrene portion is 1 mL (8.7 mmol); heptane volume, 9 mL; arene : Co = 10; Al : Co = 4; $[\text{Co}] = 10.0 \text{ mmol/L}$; $P_{\text{H}_2} = 2 \text{ atm}$; $T = 30^\circ\text{C}$.

With $\text{AlEt}_2(\text{OEt})$ as the cocatalyst, a hydrogenation-active system forms at Al : Co ≥ 2 without an activator (Fig. 1, curve 3). The highest activity (TOF = 34.5 min^{-1} , TON = $522 \text{ mol}_{\text{styrene}}/\text{mol}_{\text{Co}}$) is observed at Al : Co = 4. Note that, after the $\text{Co}(\text{acac})_2\text{-AlEt}_2(\text{OEt})$ system reaches its steady-state activity, the productivity of the system decreases as the Al : Co ratio is increased. For example, TON = $550 \text{ mol}_{\text{styrene}}/\text{mol}_{\text{Co}}$ at Al : Co = 5 and it decreases to $370 \text{ mol}_{\text{styrene}}/\text{mol}_{\text{Co}}$ as Al : Co is increased to 15.

The largest TOF values for the $\text{Co}(\text{acac})_2\text{-AlEt}_3$ system in styrene hydrogenation are observed when the reaction was conducted in heptane. The dependence of TOF on the cobalt precursor concentration is uncommon, antibatic in nature. For example, at $[\text{Co}(\text{acac})_2] = 0.25 \times 10^{-3} \text{ mol/L}$, TOF = 500 min^{-1} ; at $[\text{Co}(\text{acac})_2] = 0.5 \times 10^{-3} \text{ mol/L}$, TOF = $150\text{--}200 \text{ min}^{-1}$; at $[\text{Co}(\text{acac})_2] = 1.0 \times 10^{-2} \text{ mol/L}$, TOF = $25\text{--}30 \text{ min}^{-1}$.

The marked decrease in TOF observed with an increasing $\text{Co}(\text{acac})_2$ (sample 3) concentration is likely due to the aggregation of catalytically active particles and the inhibiting effect of free AlEt_3 .

In the case of the catalyst formed in heptane in the presence of a polyalkylarene, TOF and TON increase in the mesitylene < durene < hexamethylbenzene order (Fig. 2). This is possibly explained by excess AlEt_3 being bound by polyalkylarene through their acid–base interaction and by the weakening of the inhibiting effect of free AlEt_3 .

Paramagnetic $\text{Co}(0)$ complexes were earlier detected in Ziegler-type systems based on cobalt acetylacetonato complexes [4–7]. In order to elucidate the effect of the catalytic system composition on ESR spectrum parameters and to understand the role of the paramagnetic $\text{Co}(0)$ complexes in the formation of cobalt-containing hydrogenation catalysts, we studied the interaction of $\text{Co}(\text{acac})_2$ with organometallic compounds (AlEt_3 , $\text{AlEt}_2(\text{OEt})$, $\text{Li}(n\text{-Bu})$, $(\text{PhCH}_2)\text{MgCl}$) in the presence of various arenes by ESR spectroscopy.

Investigation of Components Interaction in the Ziegler-Type $\text{Co}(\text{acac})_2$ Systems

The ESR spectra of the $\text{Co}(\text{acac})_2\text{-AlEt}_3$ catalytic system in toluene are shown in Fig. 3.

It was demonstrated earlier [6] that the spectrum presented in Fig. 3a is due to a cobalt complex in which the cobalt atom is formally in the oxidation state 0 and is in a rhombically distorted tetragonal field; in the ground state, the unpaired electron occupies an $|x^2 - y^2\rangle$ type orbital. The first coordination sphere of $\text{Co}(0)$ includes an arene molecule, an alkyl group of AlEt_3 , and the acetylacetonate ligand of diethylacetylacetonatoaluminum. The significant variation of the ESR parameters of the $\text{Co}(0)$ complexes from one arene to another is mainly due to the steric effects exerted by the

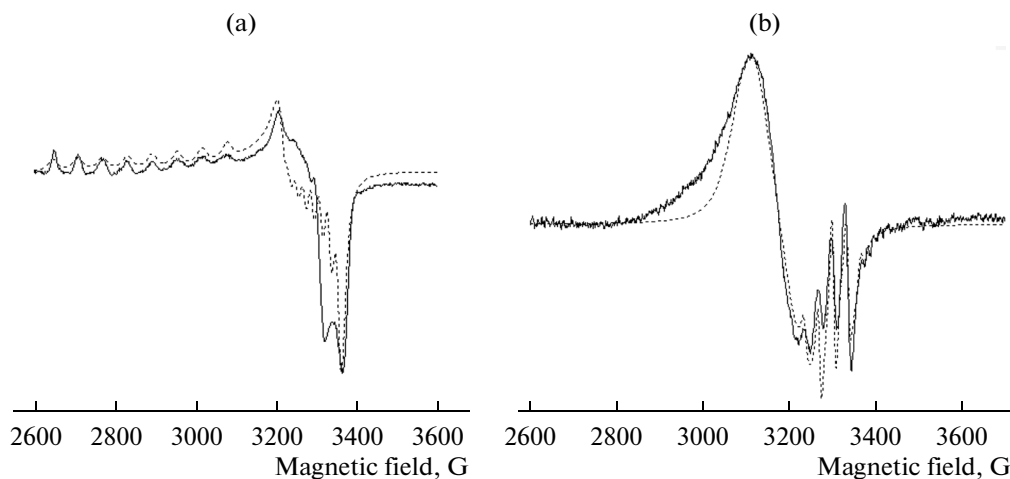


Fig. 3. Observed (solid line) and simulated (dashed line) ESR spectra of the $\text{Co}(\text{acac})_2\text{-AlEt}_3$ catalytic system at (a) 77 and (b) 293 K. $[\text{Co}] = 1 \times 10^{-2} \text{ mol/L}$, Al : Co = 4, toluene solvent, argon atmosphere, catalyst formation temperature of 298 K. Sampling was carried out after 10-s-long mixing of the components.

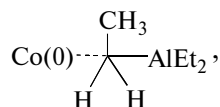
Table 1. Parameters of the ESR spectra of Co(acac)₂–Red–arene based catalytic systems

Entry	Solvent	Arene	Reductant	<i>g</i>		<i>A</i>	
				<i>g</i> _⊥	<i>g</i> _∥	<i>A</i> _⊥	<i>A</i> _∥
1		Toluene	AlEt ₃	2.050	2.355	16.0	56.9
3		Mesitylene		2.053	2.358	16.2	53.2
4		<i>p</i> -Xylene		2.052	2.357	16.5	54.5
5	Heptane	Mesitylene		2.052	2.360	16.3	53.2
6		Durene		2.050	2.354	16.3	56.9
7		Hexamethylbenzen		2.048	2.355	16.5	56.9
8		Toluene		AlEt ₂ (OEt)	2.050	2.355	18.0
9	Heptane	Hexamethylbenzen	Li(<i>n</i> -C ₄ H ₉)	2.052	2.357	15.8	57.3
10			(C ₆ H ₅ CH ₂)MgCl	2.061	2.360	16.7	61.0

* The catalysts were formed at 298 K in an argon atmosphere, and their ESR spectra were recorded at 77 K.

alkyl groups of AlEt₃ in the coordination of an arene to cobalt (Table 1).

Note that the coordination between Co(0) and AlEt₃, which leads to the formation of complexes containing a



fragment, takes place via the carbon atom in the α -position with respect to the aluminum atom, yielding an electron-deficient bond between the cobalt, carbon, and aluminum atoms. The ESR data presented in this work are in agreement with the results of Wilke and their colleagues [29–31] concerning the synthesis of Ni(0) complexes with organometallic compounds of lithium, magnesium, and aluminum. These complexes were isolated in pure form and were characterized by physical methods, including molecular structure determination.

We were the first to record the room-temperature ESR spectrum of the Co(0) complex forming in the Co(acac)₂–AlEt₃ system (Fig. 3b). Note that the spectrum of the Co(0) complex at 293 K can be observed for no longer than 1–2 min, and the stability of this complex depends on the arene type and increases in the benzene < toluene < *p*-xylene < mesitylene < durene < hexamethylbenzene order. If the reductant is AlEt₂(OEt) or Li(*n*-Bu) rather than AlEt₃, no signal from the Co(0) arene complex will be observed at room temperature. An analysis and simulation of this spectrum demonstrated that it consists of a weak ferromagnetic resonance signal from [Co]_{*n*} and its hyperfine structure arises from the interaction of the unpaired electron with cobalt, aluminum, and hydrogen nuclei. This ESR spectrum can be interpreted as a result of AlEt₂(acac) coordination to Co(0), as was hypothesized in earlier works [6, 7]. A detailed investigation of the room-temperature ESR spectra of the Co(acac)₂–AlEt₃ system will be the subject of our forthcoming studies.

The ESR spectrum recorded at 77 K for the Co(0) complex forming in the Co(acac)₂–AlEt₃ system var-

ies with time (Fig. 4a). Initially (Fig. 4a, curve 1), the shape of the spectrum and its *g* factors are characteristic of a biaxially anisotropic signal (*g*_⊥ = 2.050, *g*_∥ = 2.355). A similar signal was reported in earlier works [3, 4]. In 5 min, a triaxially anisotropic signal (*g*₁ = 2.0185, *g*₂ = 2.051, *g*₃ = 2.332) appears (Fig. 4a, curve 2), which was described in earlier works [4, 9]. In 10 min, this signal turns into a signal showing no additional splitting lines due to the cobalt nucleus (*J* = 7/2) (Fig. 4a, curve 3). These lines can clearly be seen in the initial spectra, particularly for the parallel orientation. The introduction of *n*-butanol into the reaction system causes the instantaneous disappearance of the signals from the Co(0) complexes.

The time dependence of the concentration of paramagnetic Co(0) complexes in the Co(acac)₂–AlEt₃ system in the toluene medium is illustrated in Fig. 4b (curve 1). Three segments can be distinguished in this kinetic curve. Initially (0–10 min), the intensity of the ESR signal decreases sharply (segment I); thereafter (30–75 min), the signal intensity remains invariable (segment II); this is followed by a rapid loss and, eventually, complete disappearance of paramagnetism (5- to 10-min-long segment III). The intensity of the Co(0) signal in the steady-state segment of the curve increases practically linearly with an increasing concentration of the initial cobalt complex (Fig. 5).

The formation of the Co(0) complexes in the systems considered takes place not only in aromatic hydrocarbons (Table 2, entries 1–12) but also in solvents like heptane upon the addition of an arene at an arene : Co molar ratio of 1 (Table 2, entries 13–18). The intensity of the ESR spectrum depends considerably on the arene : Co ratio and on the nature of the arene itself. Possible reductants here are not only AlEt₃ and AlEt₂(OEt) but also organometallic compounds of lithium and magnesium, such as Li(*n*-Bu) and (PhCH₂)MgCl. The molar ratio maximizing the concentration of Co(0) complexes depends on the nature of the reductant. For example, other conditions being equal, the highest concentration of Co(0) complexes in the case of Li(*n*-Bu) was observed at

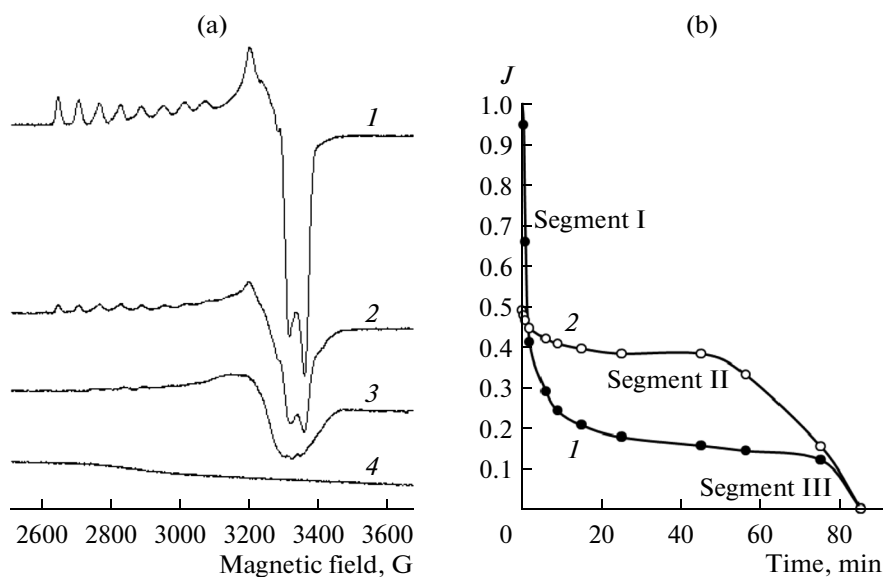


Fig. 4. (a) Time evolution of the ESR spectrum of the $\text{Co}(\text{acac})_2\text{-4AlEt}_3$ system after its formation: spectra recorded (1) 10 s, (2) 5 min, (3) 20 min, and (4) 80 min after the mixing of the components. (b) Time dependence of the relative intensity of the ESR signal (J) of $\text{Co}(\text{acac})_2\text{-Red}$ systems: (1) Red = AlEt_3 , Al : Co = 4; (2) Red = $\text{AlEt}_2(\text{OEt})$, Al : Co = 10. $[\text{Co}] = 1 \times 10^{-3}$ mol/L, toluene solvent, argon atmosphere, catalyst formation temperature of 298 K, spectrum acquisition temperature of 77 K.

Li : Co > 5–10, depending on the arene, while for $\text{AlEt}_2(\text{OEt})$, the maximum Co(0) concentration was observed at Al : Co = 10.

Note the high sensitivity of the ESR parameters of the Co(0) arene complex to the presence of water in the cobalt precursor (Table 2, entries 2, 19, 20). In the case of the interaction between anhydrous $\text{Co}(\text{acac})_2$ (sample 3) and AlEt_3 , the ESR spectrum shows a biaxially anisotropic signal ($g_{\perp} = 2.050$, $g_{\parallel} = 2.355$) from the Co(0) complex, whose intensity is ~77% of the intensity of the signal from the initial $\text{Co}(\text{acac})_2$ (Table 2, entry 2). Use of $\text{Co}(\text{acac})_2 \cdot 0.5\text{H}_2\text{O}$ (sample 2) in place of anhydrous $\text{Co}(\text{acac})_2$ gives rise to a triaxially anisotropic signal from the Co(0) arene complex ($g_1 = 2.0185$, $g_2 = 2.051$, $g_3 = 2.332$) in the ESR spectrum of the reaction system (Table 2, entry 19), and the concentration of this complex is ~70%. Replacing sample 2 with sample 1 causes a dramatic weakening and distortion of the triaxially anisotropic signal from Co(0) (Table 2, entry 20).

These data provide an explanation for the discrepancy between the ESR parameters reported in earlier works [1, 3, 6] and those observed in this study. In particular, it was demonstrated in those works that the Co(0) arene complex obtained in toluene is characterized by the following spectral parameters: $g_1 = 1.997$, $g_2 = 2.053\text{--}2.069$, and $g_3 = 2.342\text{--}2.368$. In our opinion, the discrepancy in the second decimal place between the observed g factors (g_2 , g_3) arises not from measurement errors but from the difference between the water contents of the $\text{Co}(\text{acac})_2$ samples. In addition, the AlEt_3 preparation and storage procedure used in the previous studies [1, 3, 6] (which involved Schlenk flasks) did not rule out partial hydrolysis of

triethylaluminum or its oxidation with oxygen. As a consequence, a solution containing AlEt_3 and its hydroxy and ethoxy derivatives instead of a solution of AlEt_3 was possibly examined in those studies.

For verifying this hypothesis, we carried out a series of ESR spectroscopic experiments on the interaction between the components of the sample 1– $\text{AlEt}_2(\text{OEt})$ system in toluene. The components of the g factor for the Co(0) complexes in this case ($g_{\perp} = 2.050$, $g_{\parallel} = 2.355$) are in better agreement with those reported earlier [1, 9], and the same is true for the time dependence of the rate of decomposition of the Co(0) arene complexes (Fig. 4b, curve 2).

As the components of the sample 1– AlEt_3 system interact in a hydrogen atmosphere, the initial intensity

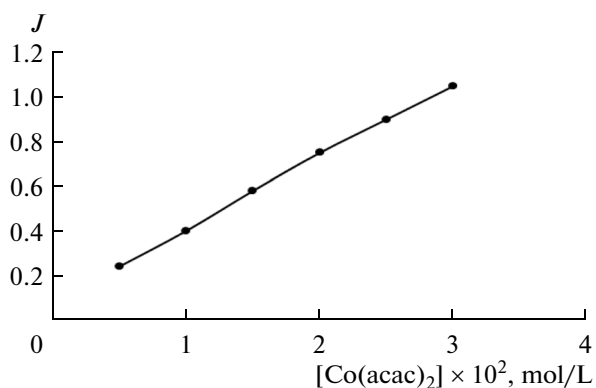


Fig. 5. Relative intensity of the ESR signal (J) from Co(0) in segment II (steady state) as a function of the $\text{Co}(\text{acac})_2$ concentration in the $\text{Co}(\text{acac})_2\text{-4AlEt}_3$ system $[\text{Co}] = 1 \times 10^{-3}$ mol/L, toluene solvent, Al : Co = 4, $T = 293$ K.

Table 2. Quantitative ESR spectroscopic data for the Co(0) complexes forming in the Co(acac)₂–AlEt₃ system in the presence of some arenes

Entry	[Co(acac) ₂], mol/L	Al : Co	Solvent	Arene	Arene : Co	[Co(0)], mol/L (ESR data)
1	5 × 10 ⁻³	4	Toluene	Toluene	940	3.9 × 10 ⁻³
2	1 × 10 ⁻²	4	Toluene	Toluene	940	7.7 × 10 ⁻³
3	2 × 10 ⁻²	4	Toluene	Toluene	940	1.5 × 10 ⁻²
4	3 × 10 ⁻²	4	Toluene	Toluene	940	2.0 × 10 ⁻²
5	2 × 10 ⁻²	2	Toluene	Toluene	940	1.2 × 10 ⁻²
6 ^a	2 × 10 ⁻²	2	Toluene	Toluene	940	4.9 × 10 ⁻³
7	2 × 10 ⁻²	6	Toluene	Toluene	940	7.0 × 10 ⁻³
8	2 × 10 ⁻²	8	Toluene	Toluene	940	7.0 × 10 ⁻³
9	5 × 10 ⁻³	4	Mesitylene	Mesitylene	720	4.9 × 10 ⁻³
10	1 × 10 ⁻²	4	Mesitylene	Mesitylene	720	1.0 × 10 ⁻²
11	2 × 10 ⁻²	4	Mesitylene	Mesitylene	720	8.9 × 10 ⁻³
12	1 × 10 ⁻²	4	<i>p</i> -Xylene	<i>p</i> -Xylene	820	8.2 × 10 ⁻³
13	1 × 10 ⁻²	4	Heptane	Mesitylene	10	2.4 × 10 ⁻³
14	1 × 10 ⁻²	4	Heptane	Mesitylene	4	2.1 × 10 ⁻³
15	1 × 10 ⁻²	4	Heptane	Durene	10	2.2 × 10 ⁻³
16	1 × 10 ⁻²	4	Heptane	Durene	4	2.1 × 10 ⁻³
17	1 × 10 ⁻²	4	Heptane	Hexamethyl–benzene	10	2.9 × 10 ⁻³
18	1 × 10 ⁻²	4	Heptane	Hexamethyl–benzene	4	2.7 × 10 ⁻³
19 ^b	1 × 10 ⁻²	4	Toluene	Toluene	940	7.1 × 10 ⁻³
20 ^c	1 × 10 ⁻²	4	Toluene	Toluene	940	5.5 × 10 ⁻³

The catalysts were formed at 298 K in an argon atmosphere, and their ESR spectra were recorded at 77 K.

^a The system was formed in hydrogen.

^b The cobalt precursor was Co(acac)₂ · 0.5H₂O.

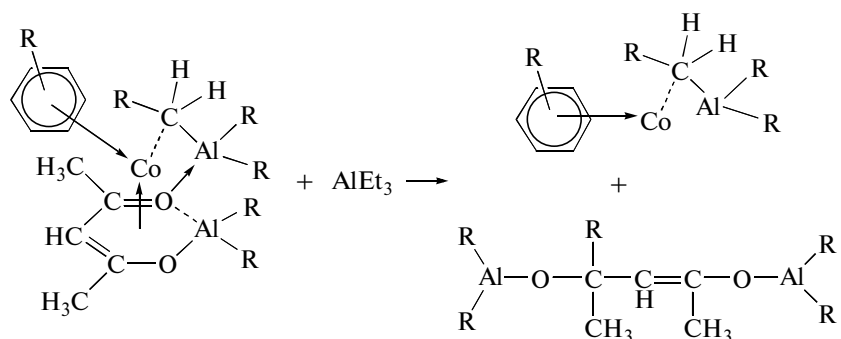
^c The cobalt precursor was Co(acac)₂ · 2H₂O.


of the ESR signal from the Co(0) complex decreases by a factor larger than 2, and this signal disappears completely in 4 min. Note that, when the reaction is conducted under the same conditions but in an argon atmosphere, the ESR signal from the paramagnetic Co(0) complex is observable for at least 80 min. This result is not surprising, because intermediate cobalt alkyl complexes are very reactive compounds. The hydrogenolysis of LCoEt (L = arene, AlEt₃, AlEt₂(acac)) or the oxidative addition of a hydrogen molecule to Co(0) causes a rapid loss of paramagnetism under hydrogenation catalysis conditions.

The main gaseous products of the interaction between triethylaluminum and bis(acetylacetonato)cobalt for all of the three samples are hydrogen (2–3%), ethane (75–90%), ethylene (no more than

1%), butene (3–14%), and butane (1–6%). As the Al : Co ratio is increased, the proportion of ethane decreases and the proportions of butenes and butane increase. In addition, the total yield of gaseous products increases with an increasing Al : Co ratio. For example, at Al : Co = 1 the total gas yield is 1.9–2.0 mol_{gas}/mol_{Co}; at Al : Co = 8, the total gas yield is 5 mol_{gas}/mol_{Co}. This fact is direct evidence of AlEt₃ decomposition taking place under the action of intermediate cobalt compounds forming in the system.

It was demonstrated [6, 7] by UV and IR spectroscopy that, in the course of the reaction between Co(acac)₂ and AlEt₃, the resulting diethylacetylacetonatoaluminum undergoes the following conversion as a result of the nucleophilic addition of AlEt₃ to the carbonyl group of AlEt₂(acac):



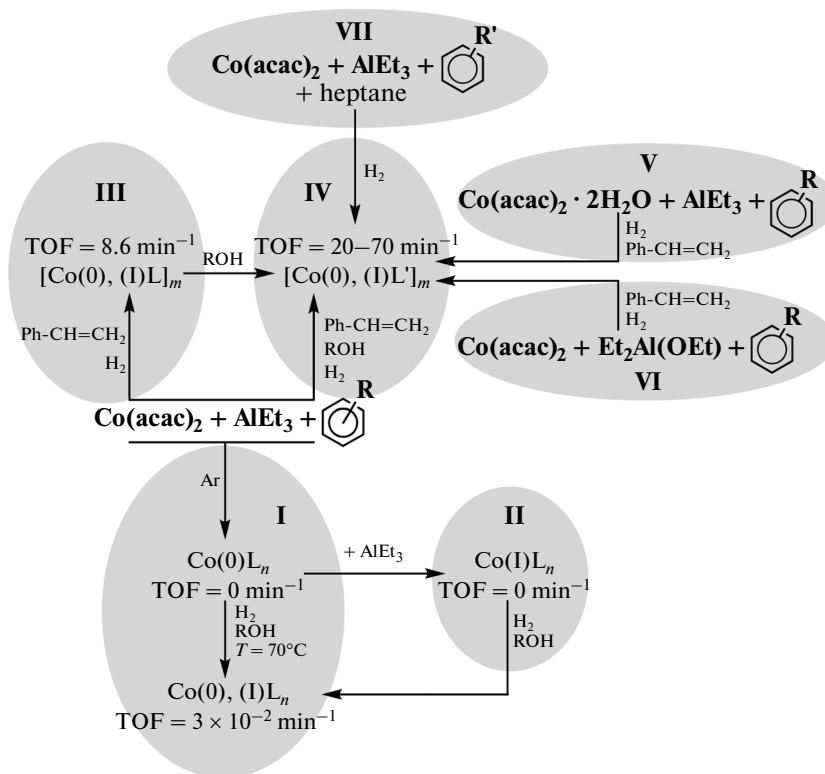
where  is benzene, toluene, *p*-xylene, mesitylene, durene, or hexamethylbenzene.

The rate constant of the interaction between AlEt_3 and $\text{AlEt}_2(\text{acac})$ in the presence of the $\text{Co}(0)$ complexes is 1.7 times smaller than the rate constant of the same interaction in the absence of cobalt, indicating that $\text{AlEt}_2(\text{acac})$ is stabilized in the coordination sphere of $\text{Co}(0)$. The resulting paramagnetic $\text{Co}(\text{Ar})\text{AlEt}_3$ (Ar = arene) species either are undetectable by ESR or dimerize to yield a diamagnetic complex (via the interaction



of two $\text{Co}(0)$ complex molecules), a paramagnetic complex (via the interaction of three $\text{Co}(0)$ complex molecules), and so on. No better substantiated hypothesis can be suggested now. Having reached a critical size, these complexes form diamagnetic compounds. No nanoparticles were detected by TEM in the systems containing the highest $\text{Co}(0)$ concentration, although the resolving power of the electron microscope used (see Experimental) allowed >0.7 -nm particles to be detected.

The main hydrogenation catalyst preparation methods described in this work are presented in the following scheme.

Effect of formation conditions on the quantitative characteristics of Ziegler-type hydrogenation catalysts based on $\text{Co}(\text{acac})_2$



where L = arene, AlEt_3 , $\text{AlEt}_2(\text{acac})$; L' = $\text{AlEt}_2(\text{OEt})$;

 – is benzene or toluene;  – is mesitylene, durene, or hexamethylbenzene.

Scheme.

(1) Reaction of anhydrous $\text{Co}(\text{acac})_2$ in a toluene medium at a water concentration of $\sim 1 \times 10^{-3} \text{ mol/L}$ in an argon atmosphere (see I in the scheme). After the replacement of argon with hydrogen, practically no hydrogenation occurs under mild conditions ($T \leq 30^\circ\text{C}$, $P_{\text{H}_2} = 2 \text{ atm}$). Under these conditions, the high-

est concentration of paramagnetic $\text{Co}(0)$ complexes is attained. The fact that the yield of gaseous products (C_2H_4 , C_2H_6 , C_4H_{10} , and C_4H_8) exceeds $2 \text{ mol/mol}_{\text{Co}}$ indicates AlEt_3 decomposition in the coordination sphere of $\text{Co}(0)$. The decomposition of AlEt_3 in the coordination sphere of the $\text{Co}(0)$ complexes was

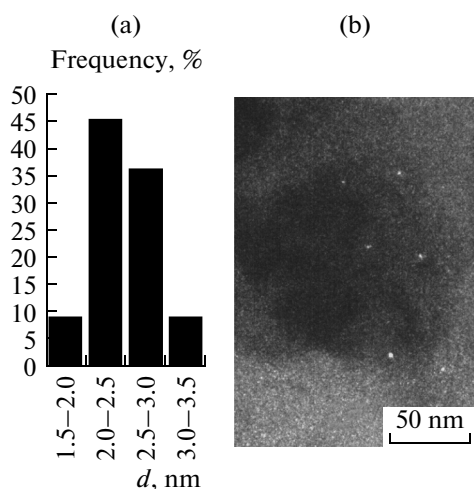
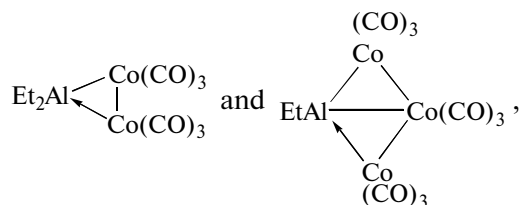


Fig. 6. TEM data for the $\text{Co}(\text{acac})_2$ (sample 3)– 3AlEt_3 system activated with $n\text{-C}_4\text{H}_9\text{OH}$ after the hydrogenation of 3 mL of styrene ($[\text{Co}] = 5.8 \times 10^{-3}$ mol/L): (a) particle size distribution and (b) dark-field image.

proved [32] by identifying the heterometallic compounds



which result from the interaction between $\text{Co}(\text{acac})_2$ and AlEt_3 in the presence of carbon monoxide. The introduction of a proton donor (e.g., $n\text{-C}_4\text{H}_9\text{OH}$) into the system at 70°C initiates styrene hydrogenation with a very low TOF of about $3 \times 10^{-2} \text{ min}^{-1}$. It was demonstrated by TEM and ESR spectroscopy that this catalyst formation method yields a homogeneous solution.

(2) The oxidative addition of AlEt_3 to $\text{Co}(0)$ (see **II** in the scheme) followed by the decomposition of the resulting $\text{LCo}(\text{Et})\text{AlEt}_2$ ($\text{L} = \text{arene}, \text{AlEt}_3, \text{AlEt}_2(\text{acac})$) complexes leads to $\text{Co}(0)$ oxidation to $\text{Co}(I)$, and the cobalt complexes lose their capability to activate molecular hydrogen and to catalyze hydrogenation reactions. Thus, the formation of the complexes having an Al–Co bond irreversibly poisons the hydrogenation catalyst.

(3) In case the catalytic system is formed in the presence of styrene, the hydrogenation of the substrate proceeds at $\text{TOF} = 8.6 \pm 0.8 \text{ min}^{-1}$ and $\text{TON} = 30 \text{ mol}_{\text{styrene}}/(\text{g-at Co})$ (see **III** in the scheme). Note that, with this catalyst formation method, the concentration of $\text{Co}(0)$ arene complexes is lower than in the case of catalyst formation in an argon atmosphere, and TEM data indicate the formation of a homogeneous solution or a solution containing $<0.7\text{-nm}$ nanoparticles.

(4) The addition of a proton donor (e.g., $n\text{-C}_4\text{H}_9\text{OH}$) to the systems formed via the procedure described in (2) (see **IV** in the scheme) dramatically increases TOF to $60\text{--}70 \text{ min}^{-1}$ and TON to

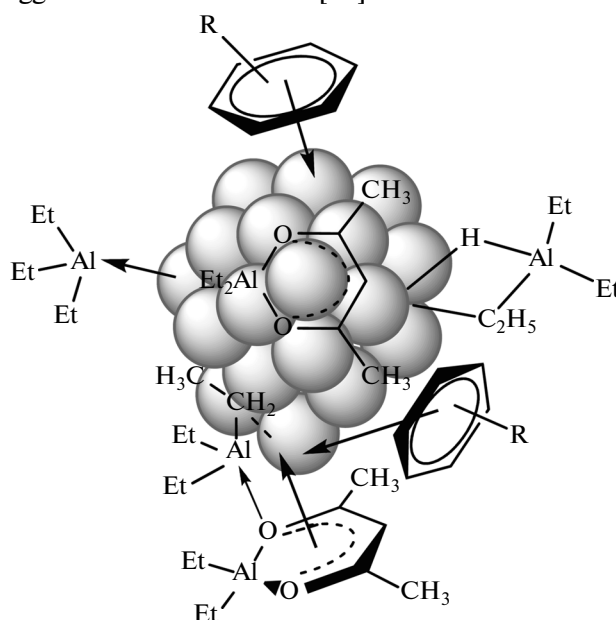
$350 \text{ mol}_{\text{styrene}}/(\text{g-at Co})$. A broad signal due to ferromagnetic cobalt nanoclusters ($g = 2.1\text{--}2.2$, line width of 150.0 mT) appears in the ESR spectrum. According to TEM data, the average size of the particles forming in this way is $2.5 \pm 0.5 \text{ nm}$ (Fig. 6).

(5) In the case of $\text{Co}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$ used as the initial component (see **V** in the scheme), the resulting catalytic systems are characterized by a TOF of up to $60\text{--}70 \text{ min}^{-1}$ and a TON of up to $350 \text{ mol}_{\text{styrene}}/(\text{g-at Co})$, depending on the Al : Co ratio. Again, a signal due to ferromagnetic cobalt nanoclusters appears in the ESR spectrum, and, according to TEM data, the average particle size is $2.5 \pm 0.5 \text{ nm}$.

(6) Replacing AlEt_3 with $\text{AlEt}_2(\text{OEt})$ leads to the formation of a catalytic system active in styrene hydrogenation, whose maximum activity is 34.5 min^{-1} ($\text{TON} = 522 \text{ mol}_{\text{styrene}}/(\text{g-at Co})$) at Al : Co = 4 (see **VI** in the scheme). The ESR spectrum of this system shows a ferromagnetic resonance signal.

(7) Forming the catalytic system in a heptane–polyalkylarene solution (see **VII** in the scheme) affords a hydrogenation catalyst (Fig. 2). The initial activity of the catalyst is the same for all arenes, and TOF increases as the number of hydrogenated styrene portions is increased. As the number of substituents in the aromatic ring (its basicity) is increased, TOF grows slightly. This is possibly due to Lewis acid–Lewis base complexation between AlEt_3 and the methyl-substituted arenes, which diminishes the inhibiting effect of free AlEt_3 on the catalytic properties of reduced cobalt. As the catalyst develops, the intensity of the ESR signal from the $\text{Co}(0)$ arene complex falls to zero, but a ferromagnetic resonance signal from cobalt nanoparticles appears and increases.

The data presented in this article refine the previous model of a catalytically active cobalt nanoparticle formed in hydrogen (before its activation by a proton donor) [8, 9] on the basis of an analogy with the model suggested earlier for nickel [25]:



The ligand shell of the nanosized particle consisting of Co(0) includes coordinated triethylaluminum (as in the case of the paramagnetic Co(0) complexes), arene molecules, AlEt₃ bonded to Co(0) through acid–base interaction (AlEt₃ is an acid, and the cobalt atom is a base), and AlEt₂(acac) coordinated to cobalt through the acetylacetonate ligand. In addition, there can be surface compounds between excess AlEt₃ and hydride (or alkyl) derivatives on the surface of the [Co]_n particle [25].

These data elucidate the essence of catalyst activation by a proton donor. The interaction between ROH (H₂O) and AlEt₃ coordinated to Co(0) results in the formation of Et₂Al(OEt) and in its leaving the coordination sphere of Co(0). The clustering of the latter yields cobalt nanoparticles that are more active in hydrogenation. Unlike triethylaluminum, Et₂Al(OEt) exerts no noticeable inhibiting effect in hydrogenation catalysis, as was demonstrated above.

The above regularities in the effect of the catalyst preparation method on the quantitative characteristics of the resulting catalysts in hydrogenation arise from the complex process of the formation of cobalt clusters varying in the number of nuclei and degree of unsaturation. A detailed mechanistic investigation of the mechanism of cluster and nanoparticle formation in these systems will be the purpose of our forthcoming works.

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