PHYSICOCHEMICAL STUDIES
OF SYSTEMS AND PROCESSES

Generation and Properties of Hydrogenation Catalysts
Based on Palladium Bisacetyladonate
and Lithium Alkoxyhydroaluminates


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Palladium nanoclusters show catalytic activity in various transformations of unsaturated hydrocarbons, including hydrogenation [1]. One of the most widely used procedures for preparing metal nanoparticles is chemical condensation consisting in reduction of metal complexes in the presence of stabilizers [2]. Previously we studied how the properties of palladium hydrogenation catalysts depend on the reductant used (AlEt₃ [3], LiAlH₄ [4], NaH₂PO₂ [5], H₂ [6]) and found that the catalytic properties are influenced not only by the metal dispersity and nature of stabilizing ligands. Generation of catalytically active species is usually accompanied by a number of side reactions (degradation of phosphines taken as stabilizing ligands; catalytic decomposition of the reductant LiAlH₄, NaH₂PO₂, etc.), which can exert both promoting and inhibiting effect on the catalyst properties. In particular, for the system Pd(acac)₂-LiAlH₄ it was found that partial hydrolysis of lithium tetrahydroaluminate leads to a sharp (by a factor of 6) increase in the specific activity in hydrogenation of alkenes [4].

To develop efficient synthetic routes to high-performance palladium hydrogenation catalysts, in this study we examined the generation and properties of catalytic systems based on palladium bisacetylacetonate and lithium tetrahydroaluminate, modified with alcohols.

EXPERIMENTAL

Solvents (benzene, THF) and substrates were purified by standard procedures used in organometallic chemistry [7]. For more exhaustive drying, benzene was additionally distilled from LiAlH₄ on a distillation column and stored under argon in sealed ampules over 4Å molecular sieves. Tetrahydrofuran after removal of peroxides was distilled successively from sodium, LiAlH₄, and benzophenone ketyl and was stored under argon in sealed ampules. The concentration of water, determined by Fischer titration [8], was 1.1 × 10⁻³ in benzene and 1.6 × 10⁻³ M in THF.

Palladium bisacetylacetonate was prepared according to [9]. ¹H NMR spectrum (δ, ppm, solvent C₆D₆): 5.04 (s, 1H, CH) 1.76 (s, 6H, CH₃). IR spectrum (ν, cm⁻¹, solvent benzene): ν(C=O) + ν(C=C) 1560, 1516; UV spectrum (solvent benzene): ε₃30 = 10630 l mol⁻¹ cm⁻¹.

Commercial lithium tetrahydroaluminate LiAlH₄ was used without preliminary recrystallization. A weighed portion of LiAlH₄ was dissolved in THF, and the solution was filtered in an inert atmosphere through a glass frit. The LiAlH₄ concentration determined by the volume of hydrogen released in the course of hydrolysis was 95–98% of the theoretical value. ²⁷Al NMR spectrum (δ, ppm, solvent THF): 98 quintet (⁴J Al–H 173 Hz).
Alcohols (\textit{n}-butanol, \textit{t}-butanol) were refluxed over calcium oxide, distilled from it in an Ar atmosphere, and stored in sealed ampules under Ar.

The reactions of LiAlH\textsubscript{4} with alcohols at various component ratios were performed under dry deoxygenated argon in a temperature-controlled vessel whose design allows initial evacuation and filling with argon. The vessel connected to a volumetric syringe system was charged with a solution of LiAlH\textsubscript{4} (2.7 \times 10^{-3} M) in 5 ml of THF. The vessel was stopped with a Teflon stopper, and a definite amount of an alcohol dissolved in THF (ROH: LiAlH\textsubscript{4} = 1, 2, 3) was introduced with a syringe under vigorous stirring with a magnetic stirrer. The amount of hydrogen released in the course of LiAlH\textsubscript{4} alcoholysis was determined volumetrically. The solution was transferred into a quartz ampule 5 mm in diameter, which had been preliminarily evacuated and filled with argon, and then was analyzed by \textsuperscript{27}Al NMR spectroscopy. The NMR spectra were recorded on a Varian VX-500S pulse spectrometer. The \textsuperscript{27}Al chemical shifts were measured against an external reference, 0.1 M solution of Al(NO\textsubscript{3})\textsubscript{3}. Solutions of LiAlH\textsubscript{4}–ROH in THF for catalytic experiments were prepared similarly.

The reactions of palladium bisacetylacetonate with LiAlH\textsubscript{4} hydrolysis products were performed as follows. To a solution of Pd(acac)\textsubscript{2} (2.5 \times 10^{-4} mol, 0.0761 g) in 8 ml of benzene, placed in a temperature-controlled vessel, we added dropwise with vigorous stirring under Ar a freshly prepared (as described above) solution of LiAlH\textsubscript{4}–ROH in THF (ROH/LiAlH\textsubscript{4} = 1, 2, 3). The total volume of the solution was 10 ml. An aliquot of the resulting dark brown solution was transferred in an inert atmosphere into an all-sealed quartz cell and analyzed by UV spectroscopy. The palladium bisacetylacetonate concentration was calculated from the absorption band at 330 nm (\epsilon_{330} = 10630 \text{ mol}^{-1} \text{ cm}^{-1}); the concentration of acetylacetonate ligands bound to Al [Al(acac)\textsubscript{3}, Al(acac)\textsubscript{2}-(\textit{t}-BuO)], from the band at 288 nm (\epsilon_{288} = 14470 \text{ mol}^{-1} \text{ cm}^{-1}) per acetylacetonate group; for Pd(acac)\textsubscript{2}, \epsilon_{288} = 30901 \text{ mol}^{-1} \text{ cm}^{-1}). The UV spectra were recorded on a Specord UV VIS spectrometer in the range 280–430 nm.

Catalytic hydrogenation was performed in a duck-shaped temperature-controlled glass vessel at 30°C and initial hydrogen pressure of 1 atm in the presence of the catalytic system generated in situ. A solution of LiAlH\textsubscript{4}–ROH in THF was added dropwise in a hydrogen stream to a solution of 0.01522 g (5 \times 10^{-5} \text{ mol}) of Pd(acac)\textsubscript{2} in 8 ml of benzene, and the mixture was stirred for 5 min. The Red/Pd ratio was varied from 2 to 50. The total solution volume was 10 ml. To the resulting black-brown “solution,” we added styrene. Its hydrogenation was performed with vigorous stirring at the initial hydrogen pressure of 1 atm. The reaction progress was monitored volumetrically and by GLC with a Chrom-5 chromatograph equipped with a packed column (3.6 m, Carbowax-20M stationary phase) and a flame ionization detector. The column temperature was 100°C, and the carrier gas was N\textsubscript{2}.

It was shown previously that, for systems of the type Pd(acac)\textsubscript{2}–Red (Red = AlEt\textsubscript{3}, LiAlH\textsubscript{4}), the dependence of the catalytic activity in hydrogenation of \alpha-alkenes on the component ratio passes through a maximum [3, 4]. Studies of the formation and nature of hydrogenation-active palladium species in these reactions showed that an increase in the activity in the initial portion of the curve is due to an increase in the fraction of Pd(0) and a decrease in the size of palladium nanoparticles. The poisoning effect of excess reductant is different. Triethylaluminum acts not only as reductant, but also, when in excess, as stabilizer of palladium nanoparticles, forming surface compounds with intermediates of the catalytic cycle. Its effect as catalytic poison can be eliminated by adding alcohols which convert AlEt\textsubscript{3} into aluminum alkoxo derivatives [10]. With LiAlH\textsubscript{4}, the catalytic poison is aluminum reacting with palladium to form a substitution solid solution [4]. Aluminum can arise in the reaction system Pd(acac)\textsubscript{2}–LiAlH\textsubscript{4} from catalytic decomposition of alane formed by reaction of the components [4]:

\[
Pd(acac)_{2} + 2LiAlH_{4} \rightarrow Pd(AlH_{3})_{2} + 2Li(acac), \quad (1)
\]
\[
Pd(AlH_{3})_{2} \rightarrow Pd + 2n[AlH_{3}n] + H_{2}, \quad (2)
\]
\[
[AlH_{3}]_{n} \xrightarrow{Pd} nAl + (3n/2)H_{2}. \quad (3)
\]

It should be noted that, in contrast to palladium hydrogenation catalysts based on Pd(acac)\textsubscript{2} and AlEt\textsubscript{3} [3], the specific activity of the catalytic system Pd(acac)\textsubscript{2}–LiAlH\textsubscript{4} is low because of the inhibiting effect of aluminum and does not exceed 30 ml of substrate per mole of Pd per minute (Fig. 1).

The above facts suggest that, to prepare high-performance palladium hydrogenation catalysts, it is appropriate to use as reductant not LiAlH\textsubscript{4} but its alkoxo derivatives. To check this hypothesis, we studied the generation and properties of catalytic