Synergism in the Activity of the Mixed Oligoallene Complexes of Palladium and Group VIII Nonnoble Metals in the Hydrogenation of Dienes to Alkenes

V. M. Frolov, E. M. Khar'kova, L. E. Rozantseva, and G. N. Bondarenko

Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 117912 Russia
Received November 5, 2002

Abstract—The superadditivity of the catalytic properties of various bimetallic Pd–Ni, Pd–Co, and Pd–Fe complexes with oligodimethylallene ligands was studied. Palladium–nickel catalysts of an equimolar composition exhibited the highest activity. The complexes were studied by IR spectroscopy. Conceivable structures were proposed for the complexes. The main kinetic features of the isoprene hydrogenation reaction under the action of palladium and palladium–nickel systems were studied. A two-center mechanism, which takes into account the presence of properly arranged palladium and nickel atoms in the active center of the catalyst, was considered as a probable reason for the appearance of a synergistic effect.

INTRODUCTION

The catalytic hydrogenation of organic compounds forms the basis of many large-scale processes in petrochemical synthesis; basic organic synthesis; and the synthesis of vitamins, pharmaceuticals, etc. The selective hydrogenation of diene hydrocarbons to olefins is of interest. This process is used for the purification of lower olefins in order to remove diene traces and to obtain pure monomers for polymerization. As a rule, the catalytic systems in current use require high temperatures and pressures. Therefore, studies of homogeneous metal complex catalysts based on palladium with ligands of different natures are of particular interest. These catalysts provide an opportunity to perform hydrogenation reactions with high activity and selectivity under mild conditions.

Many of the palladium-based metal complex catalysts for hydrogenation described in the literature were prepared with the use of expensive and toxic organophosphorus and organonitrogen compounds. At the same time, the search for highly active and selective Pd-containing catalysts with less toxic and more readily available ligands, which make it possible to perform hydrogenation processes at sufficiently low temperatures and pressures, is of scientific and applied importance.

Previously [1], we found that the oligoallene complexes of palladium prepared by the reaction of bis(acetylacetonato)palladium(II) with triisobutylaluminum in the presence of allene or 1,1-dimethylallene (DMA) in an aromatic solvent are highly active and highly selective catalysts for the hydrogenation of dienes to olefins. Henceforth, complexes with an oligodimethylallene ligand will be designated as $M(DMA)^{ol}$, where M = Pd, Ni, Co, or Fe.
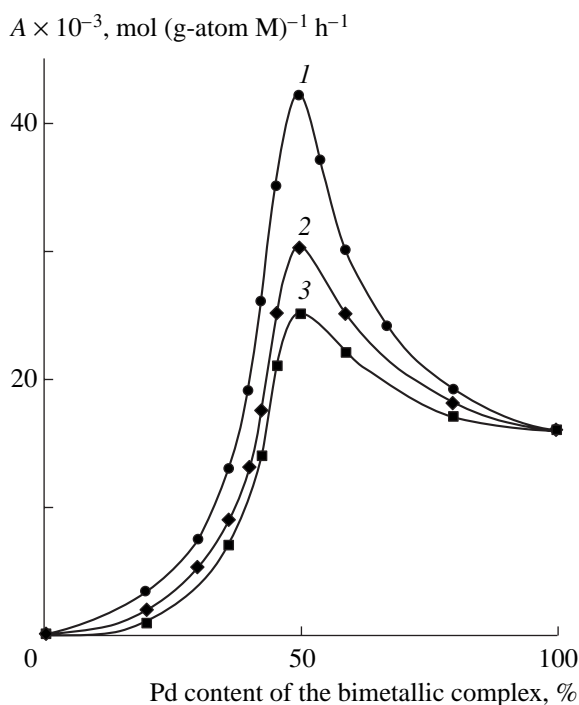
Bimetallic complexes were prepared by the interaction of equimolar amounts of Pd and Ni, Pd and Co, or Pd and Fe acetylacetonates with triisobutylaluminum in the presence of 1,1-dimethylallene [2, 3].

The apparent catalytic activity of complexes in the hydrogenation of a number of unsaturated compounds (in particular, isoprene) is very high. In terms of the turnover frequency of a hydrogenation reaction, it is as high as tens of thousand of inverse hours. A clearly defined synergistic effect takes place: bimetallic complexes containing a nonnoble transition metal in addition to palladium greatly surpass palladium complexes in activity, whereas the complexes of nonnoble metals are completely inactive. Selectivity for isopentenes at near-100% conversions was 98%, and it was somewhat lower only in the case of Pd–Fe and Pd–Co systems.
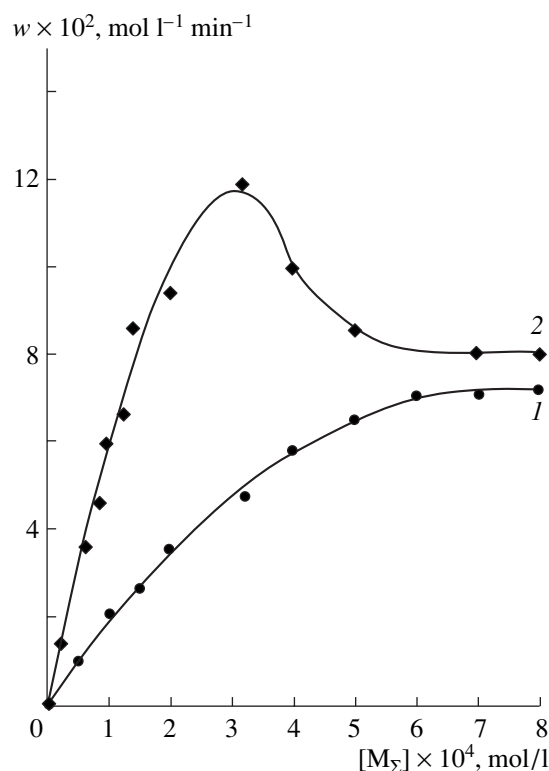
This work was devoted to the further study of the superadditivity of the catalytic properties of bimetallic complexes. It includes an IR-spectroscopic study of palladium and palladium–nickel oligoallene compounds and a study of the main kinetic features of the reaction of isoprene hydrogenation under the action of these systems.

EXPERIMENTAL

The synthesis of mono- and bimetallic complex catalysts based on transition metal (Pd, Ni, Co, and Fe) acetylacetonates was performed with intense stirring in an argon atmosphere at 20°C and a total metal (Pd, Pd + Ni, Pd + Co, or Pd + Fe) concentration $[M_\Sigma] = 2 \times 10^{-3}$ mol/l. A calculated amount of 1,1-dimethylallene (8×10^{-3} mol/l) was added to a salt solution; next, a required amount of a triisobutylaluminum solution in toluene (4×10^{-3} mol/l) from a dropping funnel was added. The ratios between reactants were

$A \times 10^{-3}$, mol (g-atom M)$^{-1}$ h^{-1}

Fig. 1. Specific activities (A) of catalysts in the reaction of isoprene hydrogenation as functions of the palladium content of bimetallic complexes: (*1*) Pd–Ni(DMA)^{ol}, (*2*) Pd–Fe(DMA)^{ol}, and (*3*) Pd–Co(DMA)^{ol}. [M$_\Sigma$] = 2 × 10^{-4} mol/l; isoprene amount, 3 mmol.

$w \times 10^2$, mol l^{-1} min^{-1}

Fig. 2. Rates of isoprene hydrogenation (w) in the presence of (*1*) Pd(DMA)^{ol} and (*2*) Pd–Ni(DMA)^{ol} of an equimolar composition as functions of complex concentration. Isoprene amount, 3 mmol.

(iso-C$_4$H$_9$)$_3$Al/M$_\Sigma$ = 2 and DMA/M$_\Sigma$ = 4. The synthesis time was 8 h. For a more detailed study of the synergistic effect, complexes with other ratios between metals were synthesized in addition to the systems of an equimolar composition.

The resulting complexes were active in diene hydrogenation without additionally adding an organoaluminum compound.

The hydrogenation of dienes was performed in a long-necked flask reactor at 20°C and a constant pressure of hydrogen equal to 68 kPa in toluene as a solvent (V = 17 ml) with intense stirring.

The specific activity of a catalyst was calculated as the number of moles of a substrate reacted in 1 h (1 mol of hydrogen per 1 mol of a substrate) per g-atom of a metal at 20°C and a hydrogen pressure of 0.1 MPa.
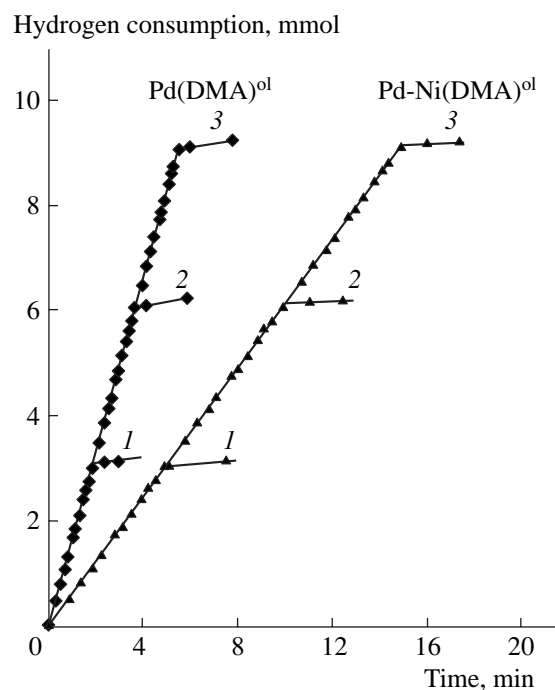
RESULTS AND DISCUSSION

Figure 1 demonstrates the dependence of the activity of catalysts in the hydrogenation reaction of a model substrate, isoprene, on the percentage of palladium in the palladium–nonnoble metal system (the activity was calculated on a total metal basis). The activity of individual nickel, cobalt, and iron complexes corresponds to a zero value of this quantity. The activity of a palladium complex corresponds to 100%. A maximum cor-

responds to an approximately equimolar composition; a bimetallic complex of palladium and nickel exhibited the highest activity (42 000 mol (g-atom M)$^{-1}$ h^{-1}). The lowest activity was found in a complex of palladium and cobalt; an analogous system with iron occupies an intermediate position.

It is of interest that the synergistic effect also clearly manifested itself in a comparison between the rates of isoprene hydrogenation on an individual complex of palladium and a bimetallic Pd–Ni complex of an equimolar composition as functions of catalysts concentration (Fig. 2). The monometallic system exhibited a monotonic increase in the rate of reaction with palladium concentration (curve *1*). At [Pd] > 6 × 10^{-4} mol/l, the rate of reaction remained constant; this can be explained by a decrease in the fraction of the most active centers due to their association into coarser and less active particles.

Curve *2* in Fig. 2 is intricate, and it passes through a maximum at a total concentration of the metals (3.2 × 10^{-4} mol/l), which is followed by a portion characterized by a negative kinetic order with respect to [M$_\Sigma$]. It is likely that these complexes participate in equilibrium association reactions to result in an increase or decrease in the amount of catalytically active centers in different concentration ranges. At [Pd + Ni] > 7 × 10^{-4} mol/l, the rate of the process does not depend on [M$_\Sigma$].

Hydrogen consumption, mmol

Fig. 3. Kinetic curves of isoprene hydrogenation at the following initial isoprene concentrations, mol/l: (*1*) 0.18, (*2*) 0.36, and (*3*) 0.54. Catalysts: Pd(DMA)^{ol} (P_{H_2} = 68 kPa) and Pd–Ni(DMA)^{ol} (P_{H_2} = 44 kPa). [M$_\Sigma$] = 2×10^{-4} mol/l.

$w \times 10^2$, mol l^{-1} min^{-1}

Fig. 4. Rates of isoprene hydrogenation (*w*) in the presence of (*1*) Pd(DMA)^{ol} and (*2*) Pd–Ni(DMA)^{ol} as functions of hydrogen pressure. [M$_\Sigma$] = 2×10^{-4} mol/l.

At low concentrations of complexes ($<1 \times 10^{-4}$ mol/l), the rate of hydrogenation is directly proportional to [M]; that is, a first order with respect to the catalyst is observed under these conditions.
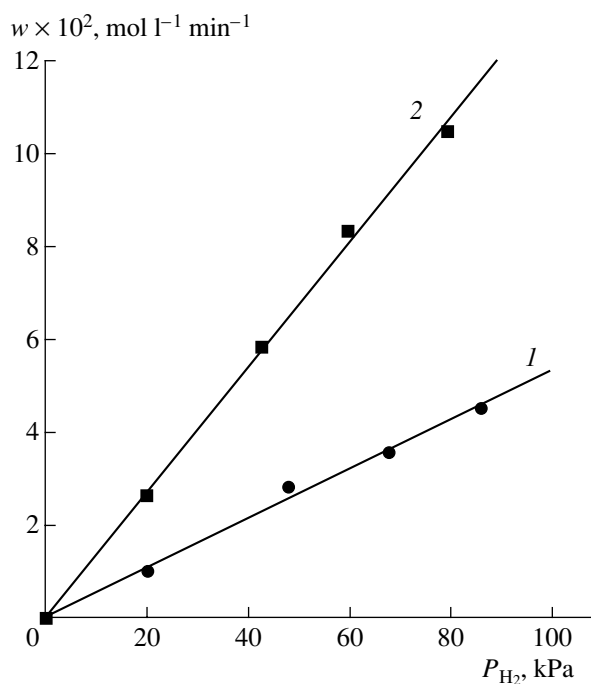
Figure 3 demonstrates the kinetic curves of isoprene hydrogenation at various initial concentrations of isoprene. A zero order of the reaction with respect to the substrate was found, which is indicative of a maximum degree of coordination of isoprene molecules at the active centers. Figure 4 suggests a first order of the hydrogenation reaction with respect to hydrogen.

The activation energies calculated with consideration for hydrogen dissolution in toluene are equal to 14.7 ± 0.9 and 17.2 ± 1.8 kJ/mol for Pd(DMA)^{ol} and Pd–Ni(DMA)^{ol} catalysts, respectively.

The complexes were studied by IR spectroscopy in order to characterize their structures.
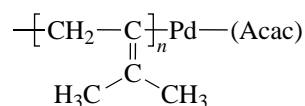
The product of the reaction of bis(acetylacetonato)palladium(II) with triisobutylaluminum in the presence of 1,1-dimethylallene exhibited absorption bands in the region 280–425 cm^{-1}, which rapidly disappeared on exposure to air; this fact suggests the presence of Pd–C bonds. Intense bands at 1376 (split), 1424, 1456, and 2952–2882 cm^{-1} can be attributed to the deformation and stretching vibrations of CH groups in CH$_2$ and CH$_3$ [4].

The metal-containing center at which a polymer chain grows by the insertion of allene monomer molecules into the Pd–C bond can be schematically represented as the following fragment:
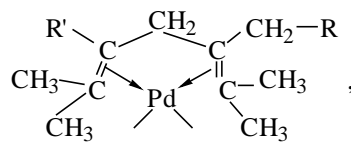

The presence of a π-alkenyl structure is improbable because of the absence of corresponding absorption bands.

The above metal-containing center can be stabilized by the π coordination of double bonds in the oligoallene ligand. A band at 1605–1615 cm^{-1} (which disappeared in air) can be attributed to the stretching vibrations of the C=C double bond π-coordinated to palladium (ν_{C-C}) in the oligomer fragment. The occurrence of bands at 820, 1068, and 1136 cm^{-1} in the IR spectrum, whose intensities dramatically decreased upon oxidation of the sample in air, can be ascribed to a Pd-containing fragment of the following type:

where R = *iso*-C$_4$H$_9$, R' =

The IR spectrum of the mixed (bimetallic) palladium–nickel complex exhibited bands characteristic of a π-alkenyl group at a metal [4, 5]: 550, 910, 1490, and 1540–1555 cm^{-1}. Because they were observed in the individual oligoallene complex of nickel, they should be attributed to a nickel-containing fragment in the case of the mixed complex. The bands due to a palladium-containing fragment in the mixed complex were somewhat shifted: 815, 1065, and 1120 cm^{-1}.

According to data obtained by chromatography–mass spectrometry, hydrocarbons with molecular weights corresponding to the dimeric, trimeric, and tetrameric (which was predominant) forms of oligo-1,1-dimethylallene were detected in the acidolysis products of the mixed complex of palladium and nickel.

It is believed that a bimetallic complex, which exhibits an activity synergism, is formed by the *in situ* interaction of a π-alkenyl complex of nickel with an oligodienyl compound of palladium. We cannot exclude the possibility of the formation of a polynuclear active center, whose constituents are the atoms of both of the metals (palladium and nickel).

Note that we did not observe an increase in activity with the use of a mixture of separately prepared Pd and Ni complexes in isoprene hydrogenation.

The occurrence of a two-center mechanism in the presence of properly arranged Pd and Ni atoms in the active center of a catalyst is a conceivable reason for the appearance of a synergistic effect on the reaction of isoprene hydrogenation under the action of a palladium–nickel complex. The reaction scheme of diene hydrogenation in the presence of a bimetallic Pd–Ni complex can be represented as follows: hydrogen is coordinated to a palladium center; the coordination and activation of a diene occur at a nickel center of the catalyst. The transfer of activated hydrogen to the substrate results in the formation of a reaction product. The assumption of the coordination of hydrogen at a palladium center is based on the greater affinity of palladium to hydrogen than to nickel.

It is probable that the complex ligand environment of metals stabilizes the resulting hydride species, which are active intermediates in the hydrogenation reactions of unsaturated compounds.

Thus, we found a pronounced synergistic effect (which is unusual for metal complex catalysis) on activity with the use of bimetallic systems containing, in addition to palladium, a Group VIII nonnoble metal, which dramatically increases the activity of catalysts for liquid-phase hydrogenation.

REFERENCES

1. Khar'kova, E.M., Novikova, A.V., Rozantseva, L.E., and Frolov, V.M., *Kinet. Katal.*, 1993, vol. 34, no. 5, p. 866.
2. Khar'kova, E.M., Rozantseva, L.E., and Frolov, V.M., *Kinet. Katal.*, 1998, vol. 39, no. 3, p. 389.
3. Khar'kova, E.M., Rozantseva, L.E., and Frolov, V.M., *Neftekhimiya*, 2001, vol. 41, no. 4, p. 287.
4. Ballamy, L., *The Infra-Red Spectra of Complex Molecules*, London: Wiley, 1961.
5. Bondarenko, G.N. and Kotov, A.V., *Dokl. Akad. Nauk SSSR*, 1974, vol. 219, no. 5, p. 1150.