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Propylene Dimerization in the Presence of Nickel Hydride Complexes Formed in situ

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Abstract—We study the influence of nickel hydride complexes formed in situ by reaction nickel(0) complexes having phosphorus-containing ligands with Brönsted acids in the presence of various modifiers on a catalyst turnover and selectivity in propylene dimerization. The activating action of boron trifluoride etherate is considered.

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Catalysis of C_2–C_6 alkene oligomerization reactions with nickel complexes has been the subject of numerous investigations for more than four decades [1–3]; these reactions were the basis of the industrial method for propylene oligomerization [4] and, in the long-range outlook, can be the basis of a number of petrochemical processes. In recent years, systems based on nickel α-diimine and bis(imino)pirydine complexes combined with organoaluminum compounds, particularly methylalumoxanes, have been intensively studied [2, 3]. The high activity of these systems, routinely calculated on the g-atom of nickel, has values on the order of 1×10^6 mol (g-at Ni h)$^{-1}$. However, when calculated per one g-atom of aluminum, these quantities drop by two to three orders of magnitude and are not higher than the activity of conventional Zigler systems of $AlEt_2Cl$–$Ni(acac)_2$ type (acac is acetylacetonate) [5, 6].

It has been shown for Zigler-type catalytic systems containing $Ni(acac)_2$, $NiX_2(PR_3)_2$ (X = Cl, Br, R = alkyl, Ph), and $AlR_{3-n}Cl_n$ ($n = 0, 1, 2$) that interaction of components of the catalytic system leads to intermediate or final nickel species of various Ni oxidation states, (Ni(II), Ni(I), and Ni(0)) containing phosphine, alkyl, and hydride ligands, in which the species play an important role in the formation and regeneration of complexes active in the catalysis of oligomerization reactions [1, 5, 6]. When Ni(II) is alkylated with organoaluminum compounds, Ni(II)-alkyl complexes form. These complexes, containing a single coordinated phosphine ligand, initiate the alkene oligomerization process to yield Ni(II)-hydride complexes that are true catalytically active species. It was first found in [6] that alkylaluminum halides oxidated Ni(0) complexes to Ni(I) complexes. Under conditions of catalytic lower alkene (ethylene, propylene) oligomerization Ni(I) species are disproportionate to both Ni(II) and Ni(0) species; i.e. intermediate Ni(I) species participate in the formation and regeneration of catalytically active species. These data have been confirmed in other reports [7, 8].

The fundamental possibility of catalyzing an oligomerization reaction under the action of Ni-hydride complexes prepared by interaction of Ni(0) complexes of phosphorus-containing ligands, PPh_3, $P(OEt)_3$, and $P(OC_6H_4CH_3\text{-}o)_3$, with Brönsted acids, H_2SO_4, CF_3COOH, and $HBF_3(OC_2H_5)$, has first been shown in [9–11].

In order to elucidate how the components of nickel hydride complexes affect both catalyst activity and selectivity in the propylene dimerization reaction, as well as the modifying action of BF_3 etherate, we studied the catalytic properties of systems based on phosphorus-containing Ni(0) complexes activated with both Brönsted and Lewis acids in the propylene dimerization reaction.

EXPERIMENTAL

Nickel complexes were synthesized according to procedures described in the literature: $Ni[PPh_3]_4$ [12], $Ni[P(OEt)_3]_4$ [13], $Ni[P(OC_6H_4CH_3\text{-}o)_2]_2(C_2H_4)$ [14], $Ni(CDT)(P(C_6H_{11})_3$ (CDT is cyclododecatriene) [15], $Ni(C_2H_4)[P(C_6H_{11})_3]_2$ [15].

Toluene was purified by treatment with concentrated sulfuric acid, washed out with a sodium carbonate aqueous solution, dried over P_2O_5, and twice distilled over sodium. Chlorobenzene and dichlorobenzene were dried over calcium chloride and distilled. Just prior to the experiment, the solvents were passed through a column packed with granulated Al_2O_3 calcined at 500°C and degassed under vacuum. BF_3 ether-

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[†] Deceased.

Table 1. Results on propylene dimerization in the presence of $Ni[P(OC_6H_4CH_3\text{-}o)]_2)(C_2H_4)$ – HX catalyst system, $c_{Ni} = 6.7 \times 10^{-3}$ mol/l, $v_{in} = 10$ ml, $p_{C_3H_6} = 1$ atm

No.	X	HX/Ni, mol/mol	T, °C	Solvent	Catalyst lifetime, min	Turnover number, $\frac{\text{mol } C_3H_6}{\text{g-at Ni}}$	Hexene composition, wt %			
							2- and 4-methylpent-2-enes	2-methylpent-1-ene	*n*-hexenes	2,3-dimethylbut-1,2-ene
1	HSO_4^-	50	10	Toluene	22	2300	53.3	2.1	43.0	0.5
2	HSO_4^-	50	10	Chlorobenzene	15	940	57	0.9	35.0	7.1
3	CF_3COO^-	40	10	Toluene	45	1800	63.6	1.3	25.0	10.1
4	CF_3COO^-	50	10	Toluene	45	2200	58.4	2.0	26.3	13.3
5	CF_3COO^-	70	10	Toluene	40	2300	63.7	1.8	25.7	8.8
6	CF_3COO^-	160	10	Toluene	36	3200	56.5	2.3	34.4	6.8
7	CF_3COO^-	250	10	Toluene	30	3800	56.6	1.5	36.3	5.6
8	CF_3COO^-	50	0	Chlorobenzene	50	1040	57.1	3.0	25.6	14.3
9	CF_3COO^-	50	30	Chlorobenzene	16	540	52.6	1.0	34.0	12.4
10	CF_3COO^-	50	50	Chlorobenzene	7	150	47.8	2.5	36.5	13.2
11	CF_3COO^-	50	10	*o*-Dichlorobenzene	29	1400	59.4	3.7	32.8	4.1

ate was distilled in vacuum over calcium hydride (53°C/46 mm Hg) and used as a 0.5 M solution in toluene or chlorobenzene. Brönsted acids were introduced into the catalytic system as a solution in toluene or chlorobenzene, or dosed by means of a micropipet.

Propylene dimerization was carried out in a temperature-controlled shaken vessel, using continuous propylene feeding to the reactor under a pressure of 1 atm. The reactor, preliminarily blown with argon, was charged with a solvent and a Ni(0) complex. Then the reaction mixture was saturated with propylene, and Brönsted acid, or BF_3 etherate, and a proton donor was added. The reactor was intensively shaken, and the rate of propylene absorption was determined. Because the propylene di- and oligomerization process in the presence of the studied catalytic systems has a nonsteady character, in order to compare their catalytic properties, the number of moles of converted propylene per one g-atom of nickel (the turnover number, TON) for the entire life of catalyst operation are given. These results and the data on hexene compositions are given in Tables 1 and 2. The concentrations of the initial Ni(0) complexes are given as notations to the tables, whereas concentrations of other components can be calculated from the molar ratios between the components given in Tables 1 and 2.

Dimerization products were analyzed by the GLC method on a Khrom-4 chromatograph at 50°C using two capillary columns 100 m in length, which have dinonyl phthalate or vacuum oil as a stationary phase.

NMR spectra were recorded on a WP200SV pulse spectrometer (Brucker).

RESULTS AND DISCUSSION

The dependence of the initial rate of propylene oligomerization in the presence of the $Ni[P(OC_6H_4CH_3\text{-}o)_2]_2(C_2H_4)$–$CF_3COOH$ catalytic system on the concentration of trifluoroacetic acid is given in Figs. 1a, 1b. It is likely that the nonlinearity of this dependence with increasing reaction rate to the limiting value is caused by the equilibrium protonation reaction of the Ni(0) complex with trifluoroacetic acid.

The PMR spectrum of the $Ni[P(OC_6H_4CH_3\text{-}o)_2]_2(C_2H_4)$–$CF_3COOH$ catalytic system has a high-field resonant signal at $\delta = -10.5$ ppm (doublet of doublets, Fig. 2). The location of the resonant signal is characteristic of hydride ligands, and the multiplicity pattern corresponds to the proton split on two nonequivalent phosphorus nuclei (Fig. 2a). The PMR spectrum agrees with the square-planar structure of the nickel complex, where phosphite ligands are in the *cis*-position with respect to each other:

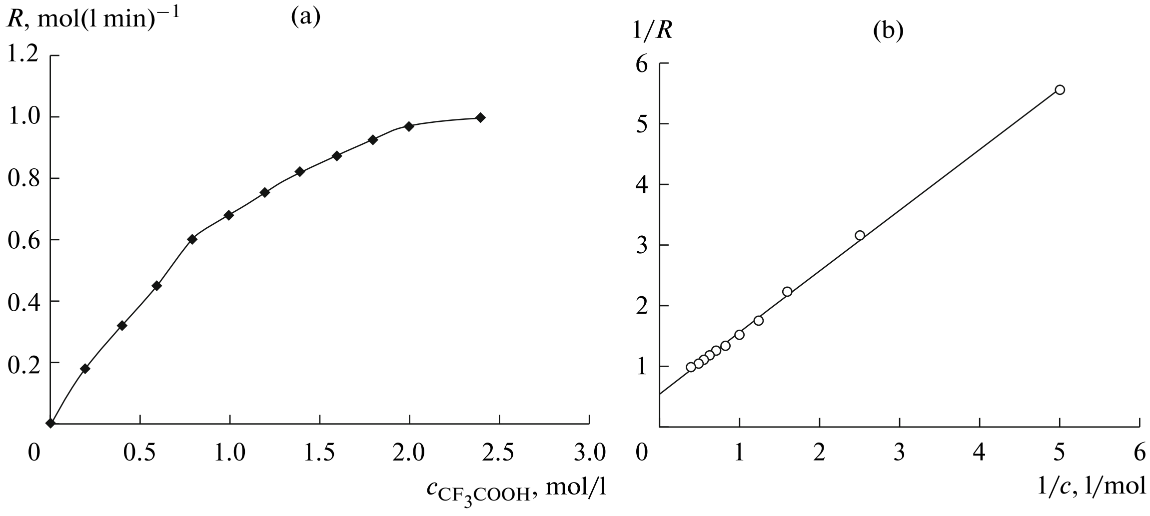
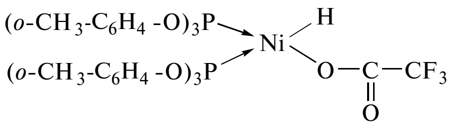


Fig. 1. Dependence of (a) propylene dimerization rate in the presence of the Ni[P(OC$_6$H$_4$CH$_3$-*o*)$_2$]$_2$(C$_2$H$_4$)–CF$_3$COOH catalyst system on CF$_3$COOH concentration; (b) reverse rate on reverse concentration, $c_{Ni} = 1 \times 10^{-2}$ mol/l, $V = 10$ ml, $T = 10$°C, solvent is toluene.



When a nickel hydride complex interacts with ethylene at $T = -30$°C, the spectral pattern varies. The resonant signal corresponding to a hydride ligand disappears, and a new broadened signal appears in the PMR spectrum at $\delta = 0.1$ ppm (Fig. 2b), which is caused by resonance of σ-alkyl protons of nickel complexes. The hyperfine structure of the signal is not observed owing to dynamic equilibrium between nickel hydride and its σ-ethyl complex. When the temperature is increased, the linewidths of this signal decrease and its intensity simultaneously decreases (Fig. 2c). Similar changes in the PMR spectrum were observed for an individual σ-alkyl complex (acac)Ni(C$_2$H$_5$)(PPh$_3$)$_2$ [16].

If we suppose that the scheme of the propylene dimerization reaction (phosphite ligands were omitted to simplify the scheme) is as follows,

$$\mathrm{Ni(0) + HX \xleftrightarrow{K_c} HNiX},$$
$$\mathrm{HNiX + 2C_3H_6 \xrightarrow{k_{ef}} HNiX + C_6H_{12}},$$

then, assuming the propylene concentration to be constant, the kinetic equation will be

$$R = \frac{k_{ef}K_c[\mathrm{Ni(0)}][\mathrm{HX}]}{1 + K_c[\mathrm{HX}]}, \qquad \text{(I)}$$

where R is the reaction rate and [HX] is the concentration of trifluoroacetic acid. The concentration of propylene is involved in the effective rate constant k_{ef}.

Kinetic equation (**1**) is linearized in $\frac{1}{R} = f\left(\frac{1}{c_{HX}}\right)$ coordinates using parametrization over Ni(0) concen-

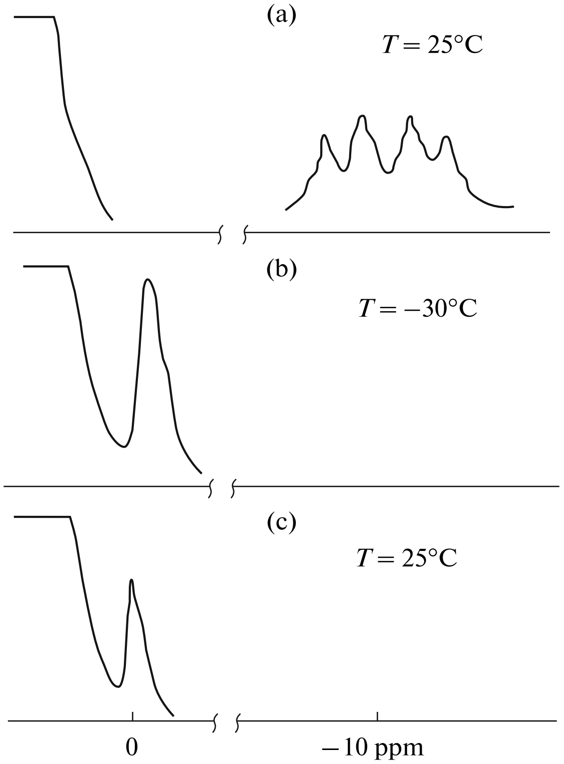


Fig. 2. ^{1}H NMR spectra of Ni[P(OC$_6$H$_4$CH$_3$-*o*)$_2$]$_2$(C$_2$H$_4$)–CF$_3$COOH catalyst system (a) prior to treatment with ethylene and (b, c) after treatment, $c_{Ni} = 0.5$ mol/l, [CF$_3$COOH]/Ni = 5, solvent is toluene-d^8.

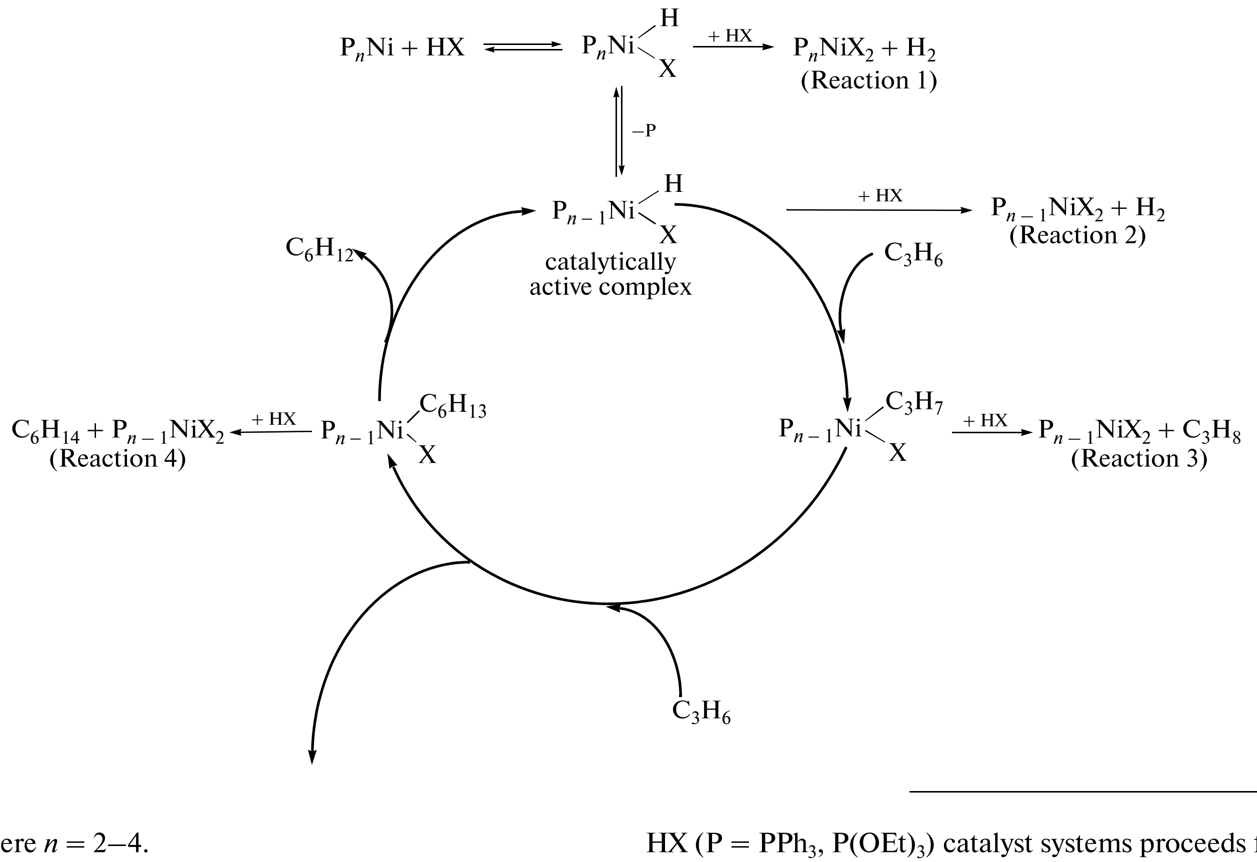
trations:

$$\frac{1}{R} = \frac{1}{k_{\text{ef}}K_{\text{c}}[\text{Ni}(0)][\text{HX}]} + \frac{1}{k_{\text{ef}}[\text{Ni}(0)]}. \quad \text{(II)}$$

Processing of the experimental results for the $\text{Ni}[\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}o)_2]_2(\text{C}_2\text{H}_4)\text{–CF}_3\text{COOH}$ catalytic system in $\frac{1}{R} = f\left(\frac{1}{c_{\text{HX}}}\right)$ coordinates (Fig. 1b) allows us to determine the equilibrium constant for a protonation reaction K_c of 0.55 ± 0.05 l/mol and an effective rate constant k_{ef} of $(1.8 \pm 0.2) \times 10^2\ \text{min}^{-1}$.

When Ni(0) phosphite nickel complexes $\text{Ni}[\text{P}(\text{OEt}_3)]_4$ and $\text{Ni}[\text{P}(\text{OPh}_3)]_4$ are used as precursors, the PMR spectrum of the reaction mixture containing these complexes and CF_3COOH also have high-field resonant signals. The signals are quintets at $\delta = -12.9$ ppm ($J_{\text{PH}} = 33$ Hz) and $\delta = -12.8$ ppm ($J_{\text{PH}} = 32$ Hz), respectively, at −40°C. Multiplicity of a signal is caused by spin–spin interaction of a proton with four equivalent phosphorus nuclei.

It follows from the data given in Table 1 that a temperature increase within a range of 0–50°C leads to a decrease in both the catalyst turnover and the lifetime. It is caused by an increase in the rates of conversion of nickel-hydride and nickel-alkyl complexes, which are intermediates of a catalyst cycle, to Ni(II) complexes of $\text{P}_{n-1}\text{NiX}_2$ type, which are inactive in catalysis, under the action of Brönsted acids:



where $n = 2–4$.

By special experiments for the $\text{Ni}[\text{P}(\text{OEt})_3]_4$–$\text{CF}_3\text{COOH}$ system, it has been shown that the oxidation rate of Ni(0) to Ni(II) under conditions of the catalytic process is higher than that in the absence of propylene. The reason for this effect is likely the higher interaction rate of Ni-alkyl complexes with acid (reactions 3, 4) in comparison with the Ni-hydride complex (reactions 1, 2). Because of the high deactivation rate of catalytically active complexes, catalysis of the propylene dimerization reaction in the presence of NiP_4–HX ($\text{P} = \text{PPh}_3$, P(OEt)_3) catalyst systems proceeds for no more than 5–15 min and the turnover has rather low values (Table 2).

The $\text{Ni}[\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}o)_2]_2(\text{C}_2\text{H}_4)$–HX catalyst system is more effective in propylene oligomerization in comparison with the systems based on $\text{Ni}[\text{P}(\text{OEt})_3]_4$ and $\text{Ni}[\text{PPh}_3]_4$ complexes. The turnover number of the $\text{Ni}[\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}o)_2]_2(\text{C}_2\text{H}_4)$–HX catalyst system is 8–20 times higher (Table 1, lines 1–7) than those based on $\text{Ni}[\text{P}(\text{OEt})_3]_4(\text{Ni}[\text{PPh}_3]_4)$–HX and $\text{Ni}(\text{PPh}_3)_4$ complexes (Table 2, lines 1–3, 9). Such

Table 2. Influence of composition of $NiP_4 - HX$ catalyst system on activity and selectivity of propylene dimerization, $c_{Ni} = 1.3 \times 10^{-2}$ mol/l, $V_{in} = 15$ ml, $p_{C_3H_6} = 1$ atm, $T = 10°C$

No.	Catalyst system	$BF_3 \cdot OEt_2$/Ni, mol/mol	HX/Ni, mol/mol	Solvent	Catalyst lifetime, min	Turnover number, mol C_3H_6/g-at Ni (TON)	Hexene composition, wt %			
							2- and 4-methylpent-2-enes	2-methylpent-1-ene	*n*-hexenes	2,3-dimethylbut-1,2-ene
1	$Ni[P(OEt)_3]_4$–CF_3COOH	0	250	Toluene	12	180	32.9	1.2	63.5	2.4
2	$Ni[P(OEt)_3]_4$–CF_3COOH	0	150	Chlorobenzene	16	120	11.4	–	87.5	1.1
3	$Ni[P(OEt)_3]_4$–H_2SO_4	0	50	Chlorobenzene	10	96	41.7	0.6	56.8	0.9
4	$Ni[P(OEt)_3]_4$–$BF_3 \cdot OEt_2$–C_2H_5OH	40	20	Toluene	60	2500	73.5	6.6	15.8	4.1
5	$Ni[P(OEt)_3]_4$–$BF_3 \cdot OEt_2$–H_2O	40	10	Toluene	45	1300	70.0	7.1	19.9	3.0
6	$Ni[P(OEt)_3]_4$–$BF_3 \cdot OEt_2$–CF_3COOH	40	150	Toluene	52	2480	72.8	4.2	21.1	1.9
7	$Ni[P(OEt)_3]_4$–$BF_3 \cdot OEt_2$–C_2H_5OH	40	20	Chlorobenzene	55	2800	71.7	14.7	32.8	2.5
8	$Ni[P(OEt)_3]_4$–$BF_3 \cdot OEt_2$–H_2SO_4	40	50	Chlorobenzene	52	2640	35.5	1.3	61.0	2.4
9	$Ni[PPh_3]_4$–H_2SO_4	0	50	Toluene	5	56	60.1	12.0	25.5	2.4
10	$Ni[PPh_3]_4$–$BF_3 \cdot OEt_2$–C_2H_5OH	5	0.5	Toluene	60	3500	50.0	14.7	32.8	2.5
11	$Ni[PPh_3]_4$–$BF_3 \cdot OEt_2$–HF	5	1	Toluene	65	3100	63.0	7.6	25.1	4.3
12	$Ni[PPh_3]_4$–$BF_3 \cdot OEt_2$–H_2SO_4	5	0.25	Toluene	70	3160	51.5	13.6	32.8	2.4
13	$Ni(CDT)(P(C_6H_{11})_3$–CF_3COOH	0	150	Toluene	10	560	55.0	3.4	5.0	36.6
14	$Ni(C_2H_4)[P(C_6H_{11})_3]_2$–$CF_3COOH$	0	150	Toluene	8	290	57.4	5.6	3.7	33.3

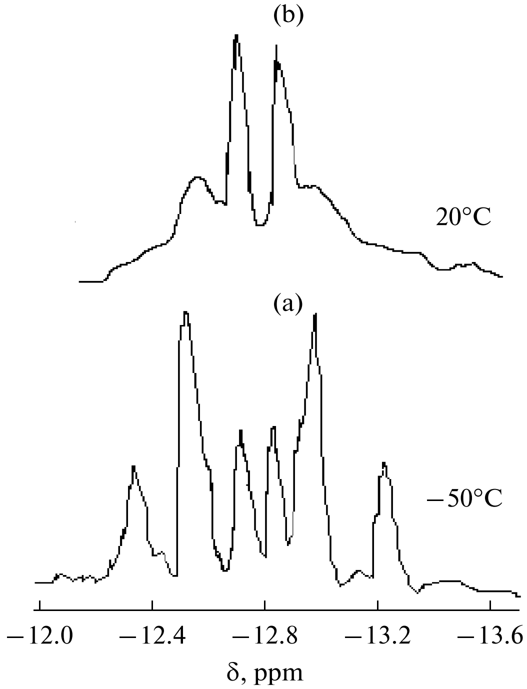


Fig. 3. ^{1}H NMR spectra of Ni(PPh$_3$)$_4$–4EtOH–20BF$_3$OEt$_2$ reaction system in toluene-d^8 at (a) –50°C and (b) 20°C ($c_{Ni} = 1 \times 10^{-2}$ mol/l).

an effect can be caused by the fact that the number of phosphorus-containing ligands of the Ni[P(OC$_6$H$_4$CH$_3$-*o*)$_2$]$_2$(C$_2$H$_4$) complex is less than those of Ni[P(OEt)$_3$]$_4$ and Ni[PPh$_3$]$_4$ complexes.

The catalytic properties of the systems under consideration are significantly affected by the nature of the solvent. Replacement of toluene by chlorobenzene and *o*-dichlorobenzene results in a TON decrease. Within the catalyst systems under consideration, chlorobenzene and *o*-dichlorobenzene act not only as a solvent, but also a reagent which deactivates the catalyst due to the oxidative addition reaction of chloroarenes to Ni(0).

Replacement of trifluoroacetic acid by sulfuric acid used as a cocatalyst within the NiP$_n$–HX, (P = P(OEt)$_3$, PPh$_3$) systems, slightly changes the catalytic properties, whereas BF$_3$ etherate introduced into the catalytic system significantly increases the operating time of the catalyst system; this is seen as an increase in TON (Table 2, lines 1, 6 and 3, 8). At first sight, it would be logical to suppose that the role of BF$_3$ in these systems can be caused by two factors: the formation of Brönsted acid in the interaction with proton donor compounds or binding of phosphorus-containing ligands, which leads to an increase in the concentration of coordinatively unsaturated Ni-hydride complexes. However, it should be noted that addition of BF$_3$ etherate not only raises the TON, but also changes selectivity in some cases. In particular, the Ni[P(OEt)$_3$]$_4$–HX catalytic system (X = CF$_3$COO$^-$, HSO$_4^-$) in both toluene and chlorobenzene is characterized by a high selectivity in the formation of linear hexenes (up to 87%). The addition of BF$_3$ · OEt$_2$ changes selectivity, increasing the methylpentene yield up to 84%.

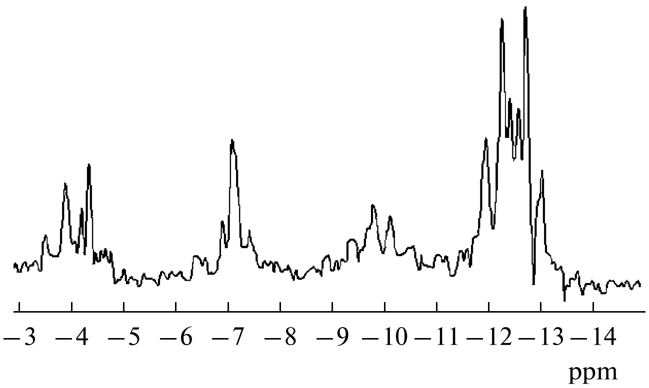
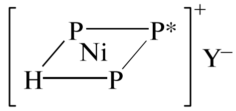


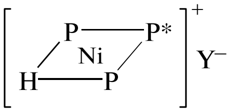
Fig. 4. ^{1}H NMR spectrum of Ni(PPh$_3$)$_4$–60BF$_3$OEt$_2$ reaction system in toluene-d^8 at –20°C ($c_{Ni} = 1 \times 10^{-2}$ mol/l, $c_{H_2O} = 3 \times 10^{-2}$ mol/l).

Examination of the Ni(PPh$_3$)$_4$–4C$_2$H$_5$OH–20BF$_3$ · OEt$_2$ catalytic system using ^{1}H NMR spectroscopy at $T = -50$°C has allowed us to register a high-field resonant signal (δ = –12.80 ppm) that is the doublet of triplets with spin–spin interaction constants of $^2J_{P-H}$ = 61.0 and $^2J_{P-H}$ = 92.8 Hz (Fig. 3). Such signal multiplicity is caused by proton interaction with two equivalent phosphorus nuclei in the nickel coordination sphere with a spin–spin interaction constant of $^2J_{P-H}$ = 61.0 Hz and one phosphorus nucleus at a larger distance from the proton with a constant of $^2J_{P-H}$ = 92.8 Hz. When temperature increases to –10°C, a badly resolved multiplet structure arises, which is transformed to a doublet at 20°C, and this is related to stereochemical nonrigidity of the [(PPh$_3$)$_3$NiH]$^+$(BF$_3$OEt)$^-$ nickel-hydride complex. This property of nickel hydrides with three phosphine ligands is a well-known fact which is described, e.g., in [17]. At $T \le -50$°C, the chemical shift difference between two types of phosphorus nuclei is large enough to give a spectrum of A$_2$X type; i.e., at low temperatures the [(PPh$_3$)$_3$NiH]$^+$(BF$_3$OEt)$^-$ complex has a static structure, where the metal complex is of square-planar geometry with two phosphines at the *cis*- and one phosphine at the *trans*-position in relation to the proton:

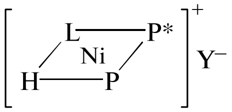


Y = BF_3OEt; P = PPh_3.

NMR monitoring of the $Ni(PPh_3)_4–BF_3 \cdot OEt_2$ reaction system (B/Ni = 60) has shown that nickel-hydride complexes were also formed in the presence of water (H_2O/Ni = 3) (Fig. 4). The ^1H NMR spectrum has high-field resonant signals characteristic of hydride ions: a doublet of triplets, $\delta = -12.60$ ppm, $^2J_{P-H} = 61.0$ Hz (triplet) and $^2J_{P-H} = 92.8$ Hz (doublet) (**1**), doublet of doublets, $\delta = -10.10$ ppm, $^2J_{P-H} = 61.0$ Hz (doublet) and $^2J_{P-H} = 92.8$ Hz (doublet) (**2**), triplet, $\delta = -7.15$ ppm, $^2J_{P-H} = 55.0$ Hz (**3**), doublet, $\delta = -4.00$ ppm, $^2J_{P-H} = 55.0$ Hz (**4**), and doublet, $\delta = -4.20$ ppm, $^2J_{P-H} = -91.0$ Hz (**5**). These resonant signals can be assigned to the following Ni(II)-hydride complexes:



(1)



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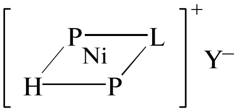

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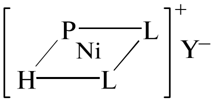

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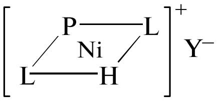


(5)

Y = BF_3OH, P = PPh_3, L =OEt_2, solvent.

Taking into account small concentrations of the complexes used in catalysis, and a degree of solvent drying, the formation of nickel-hydride complexes at the real catalytic system is inevitable. Detailed structure of these complexes and the mechanism of their transformation to Ni(I) and Ni(II) complexes will be a subject of special examination, but the fact of the formation of hydrides in these systems under conditions of catalysis does not cause doubts.

The formation of nickel-hydride complexes in the system under consideration is possible not only by two-electron oxidative addition of Brönsted acid to $Ni[PPh_3]_4$ complex. It has been previously shown that interaction of $Ni[PPh_3]_4$ with $BF_3 \cdot OEt_2$ leads to the formation of paramagnetic Ni(I) complexes of $[(PPh_3)_nNi]^+BF_4^-$ types (n = 1, 2, 3) [18], one of the routes for their formation is decomposition of Ni(II)-hydrides in reaction: $[P_nNiH]^+X^- = [P_nNi]^+X^- + 1/2H_2$, where X = BF_3OEt or BF_4.

In turn, Ni(I) complexes also can turn into catalytically active nickel-hydride complexes:

$$[P_nNi(I)](BF_4) + HBF_4 \longrightarrow [P_nNi(III)–H](BF_4)_2$$
$$\longrightarrow [P_nNi(II)](BF_4)_2 + 1/2H_2$$

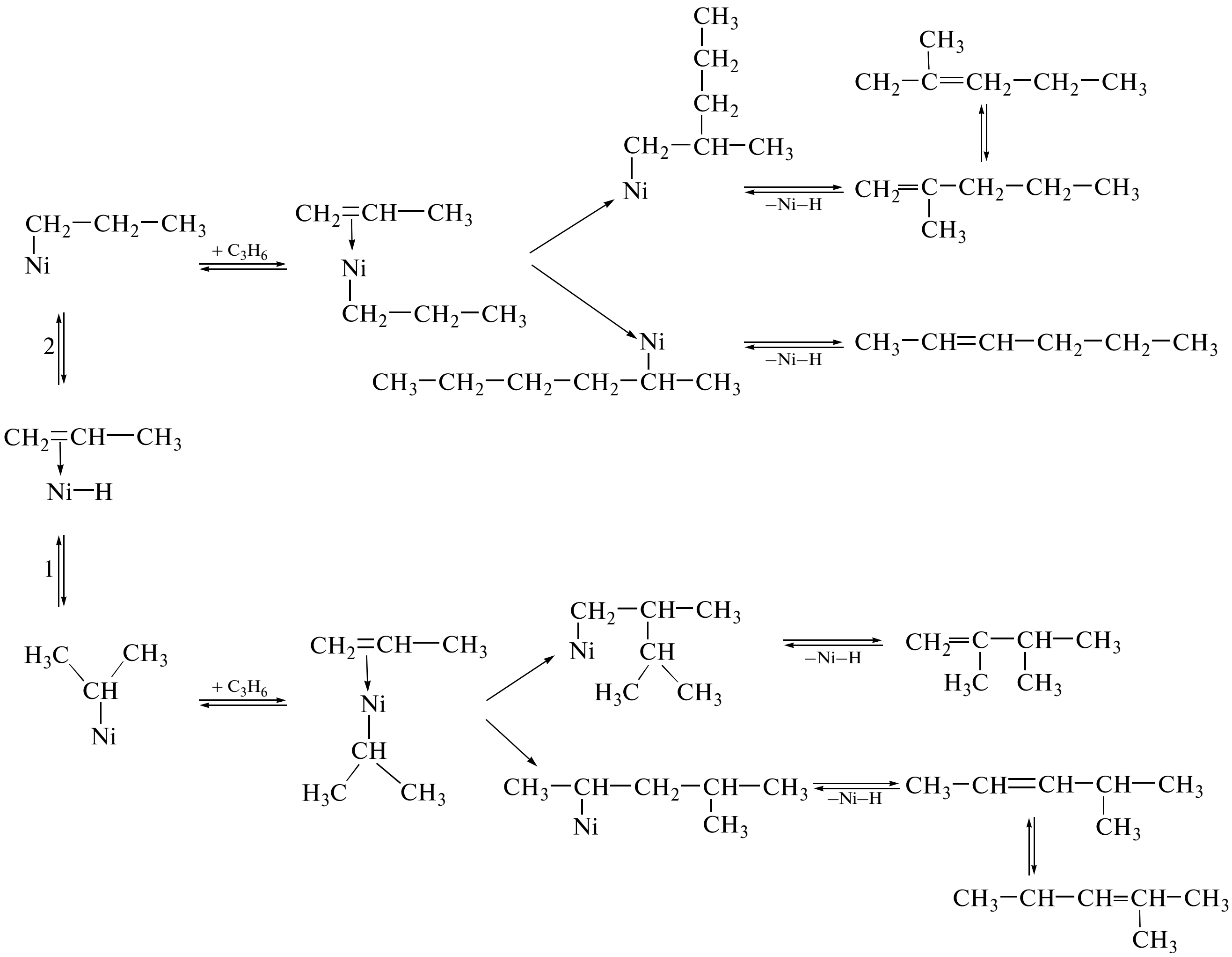
$$[P_nNi(I)](BF_4) + [P_nNi(III)–H](BF_4)_2$$
$$\longrightarrow [P_nNi(II)–H](BF_4) + [P_nNi(II)](BF_4)_2$$

$$[P_nNi(II)–H](BF_4) + HBF_4$$
$$\longrightarrow [P_nNi(II)](BF_4) + H_2$$

where n = 1, 2, 3.

The contribution of Ni(II) and Ni(III) hydride complexes to catalysis cannot yet be evaluated. However, an increase in the lifetime of catalyst systems based on $Ni[P(OEt)_3]_4$ and $Ni[PPh_3]_4$ and containing $BF_3 \cdot OEt_2$ along with a Brönsted acid causes no doubts (Table 2). The increasing catalyst lifetime and, consequently, the increasing TON is likely caused by the fact that the rate of oxidation of the $[P_3Ni]^+BF_4^-$ cation complex to Ni(II) complexes inactive in catalysis, for example, $[P_nNi](BF_4)_2$, sharply decreases because an acidic proton interacts with the nickel anion, which has an effective positive charge that is higher than that at the neutral hydride complex of $P_nNi(H)(X)$ type [19]. This suggestion demands special examination of the kinetics of the reaction of nickel complexes with Brönsted acids.

Lower alkene dimerization under the action of nickel hydride complexes follows the degenerate polymerization type. The mechanism of hexene formation can be represented in a schema (ligands at nickel are omitted):



After complexation of alkene with a coordinatively unsaturated nickel-hydride complex, hydrogen transfer to an alkene double bond occurs to give nickel-alkyl derivatives. The mode of hydrogen addition to propylene (Markovnikov and anti-Markovnikov addition, routes 1 and 2, respectively) and, as consequence, the yield ratio of linear hexenes and 2-methylpent-1-ene to 2- and 4-methylpent-2-enes and 2,3-dimethylbutene is determined by the polarity of the Ni–H bond because charges at carbon atoms of a propylene double bond are not the same owing to the electropositive effect of methyl group, namely: $\overset{-\delta}{C}H_2=\overset{+\delta}{C}H-CH_3$. Subsequent insertion of monomer molecule into the Ni–C bond leads to chain growth, whereas abstraction of hydrogen atom from alkyl β-carbon atom leads to regeneration of nickel-hydride complex to give hexene. The second stage of interaction of a nickel-alkyl complex with propylene is advantageously determined by the steric effects of the transition state [1].

It is obvious that the formation of linear hexenes and 2-methylpent-1-ene is caused by the partially negative charge at the hydrogen atom. This mode of hydrogen addition is characteristic of the $Ni[P(OEt)_3]_4$–HX system. Preferential formation of 2- and 4-methylpent-2-enes indicates a reverse charge distribution within the Ni–H bond. This is pronounced for systems where $BF_3 \cdot OEt_2$ is used in combination with ROH, where R = H^-, C_2H_5, CF_3CO. In the case of CF_3COOH as the cocatalyst, selectivity of the process also varies when $BF_3 \cdot OEt_2$ is added; however, this cannot be explained by complexation of BF_3 with CF_3COO^- because BF_3 does not form molecular complexes with CF_3COOH [20]. Apparently, within the catalytic system, there is an exchange of residue of trifluoroacetic acid for fluorine to give HF: $CF_3COOH + BF_3 \longrightarrow BF_2(CF_3COO) + HF$.

A similar exchange is observed, e.g., in the interaction of nickel bis(acetylacetonate) with BF_3. This is caused by the fact that the Ni–F binding energy is higher than that of Ni–O, and the B–O binding energy is higher than that of B–F. The presence of BF_3X^- – anion (X = OH, OEt, and F) within a coordination sphere of nickel, as it was mentioned above, results in the preferential formation of branched hexenes. A more detailed analysis of the influence of hydride complexes on selectivity of dimerization processes demands further studies of catalytic systems by physicochemical methods.

CONCLUSIONS

(1) The formation of nickel-hydride complexes in the interaction of Ni(0) complexes of phosphorus-containing ligands with Brönsted acids—CF_3COOH, $HBF_3(OEt)$, $HBF_3(OH)$—was discovered by ^1H NMR spectroscopy.

(2) Both the equilibrium constant for protonation of the $(C_2H_4)Ni[P(OC_4H_6CH_3\text{-}o)]_2$ complex with trifluoroacetic acid and the effective rate constant for propylene dimerization were determined.

(3) Selectivity of the propylene dimerization process was discussed in the context of the nickel-hydride mechanism.

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