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Influence of the Order of Introduction of Protonic Acids on the Formation of Active Complexes in the $Ni(PPh_3)_4/BF_3 \cdot OEt_2$ Catalytic System

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Abstract—The influence of the order of introduction of promoters (complex protonic acids) on the formation of active complexes in the $Ni(PPh_3)_4/BF_3 \cdot OEt_2$ catalytic system and the activity of these systems in ethylene oligomerization have been studied. The activity of the systems in which nickel exists mainly as cationic Ni(I) complexes is more than one order of magnitude higher than the activity of the systems where nickel exists mainly in the form of Ni(II) hydride complexes. The role of alcohols as promoters in the $Ni(PPh_3)_4/BF_3 \cdot OEt_2$ catalytic system is elucidated. The alcohols are the source of Ni(II) hydrides and, more importantly, the source of strong Brønsted acids, which efficiently ensure the coordinative unsaturation of the cationic Ni(I) complexes.

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INTRODUCTION

Systems based on nickel compounds are active catalysts of the low-molecular oligomerization [1–4] and polymerization [5–16] of unsaturated hydrocarbons. Although substantial success has been achieved in studying the nature of the activity of the complex nickel catalysts, the oxidation state of the transition metal in the active complex remains unclear. Most researchers hold the traditional view that processes of low-molecular olefin oligomerization are directly due to Ni(II) hydrido complexes. This view is based on the classical works on the NMR identification of Ni(II) hydrido complexes, primarily in model systems [17–24], and on the observation of the promoting effect of proton-donor compounds in real catalytic systems [25–28].

However, Ni(I) complexes are known to be formed and stabilized in solution during the formation of nickel complex catalysts [29–35]. Here, the question arises of whether the Ni(I) ions are only spin labels providing insight into the valent and structural transformations of species during catalyst formation or whether they participate directly in the catalytic conversion of the substrate.

Here, we report the influence of the order of introduction of promoters (complex protonic acids) on the formation of active complexes in the catalytic system $Ni(PPh_3)_4/BF_3 \cdot OEt_2$, as well as the activity of these complexes in ethylene oligomerization.

EXPERIMENTAL

All procedures were carried out using Schlenk techniques in dry deoxygenated argon. Schlenk glass filters were used in filtration. All prepared and synthesized chemicals were stored in sealed tubes in an argon atmosphere.

Prior to use, toluene, benzene, and heptane (Merck) were distilled from metallic sodium in the presence of benzophenone.

Boron trifluoride etherate (Merck) was distilled prior to use from LiH in an argon atmosphere.

Ethanol (96%) was dehydrated by distillation from sodium metal (10 g/l). Benzyl, isopropyl, and *tert*-butyl alcohols were distilled in a column.

Diethyl ether [36] was purified from peroxides, distilled from sodium, and stored over a sodium mirror.

HBF_3OEt was prepared as a toluene complex by reacting $BF_3 \cdot OEt_2$ with ethanol (2 : 1). Of the resulting two immiscible phases, the bottom yellow layer, which contained the reaction products, was sampled with a syringe to be immediately used [37].

The HBF_4–toluene complex was used as a toluene solution (>48% according to chromatography data). The HBF_4–toluene complex (>98% from NMR data) was synthesized by adding acetylacetone (0.352 g, 3.52 mmol) in drops to a solution of $BF_3 \cdot OEt_2$ (1 g, 7.05 mmol) in toluene (10 ml) over 2 min. The yellow layer that resulted from the reaction was transferred into a polyethylene vessel and was used within 2 h [38].

Table 1. Activity of the catalytic system $Ni(PPh_3)_4/BF_3 \cdot OEt_2$ promoted with alcohols in ethylene oligomerization

Alcohol	Ethylene oligomerization rate, (mol C_2H_4)/(mol Ni h)
C_2H_5OH	23000
$C_6H_5CH_2OH$	24000
iso-C_3H_7OH	14600
tert-C_4H_9OH	14500

Note: B : Ni = 10; ROH : Ni = 5; t = 23°C; P = 0.1 MPa.

The $Ni(PPh_3)_4$ complex was synthesized by standard procedures [39].

Ethylene oligomerization was conducted as follows. The solvent, a weighed sample of the nickel complex, and, if necessary, other compounds were successively loaded into a thermostated shaking vessel under an ethylene atmosphere. The vessel was stoppered, placed in a shaker, and fed with ethylene under vigorous shaking. The amount of reacted ethylene was measured volumetrically.

The products of ethylene oligomerization were analyzed by GLC on a GALS 370 chromatograph (50-m-long capillary column, Apiezon).

ESR spectra were recorded on a PS-100X spectrometer operating at 9.6 GHz at the nitrogen bp. The standards were Mn(II) in MgO and DPPH. ESR spectra were simulated using the program developed by us [32]. In this program, the description of hyperfine coupling (HFC) is restricted by terms of the second order of smallness and the principal axes of the g and HFC tensors coincide.

NMR spectra were obtained at 25°C on a VXR-500S spectrometer (Varian).

RESULTS AND DISCUSSION

The $Ni(PPh_3)_4/BF_3 \cdot OEt_2$ catalytic system prepared by mixing the components in toluene is among the most active systems for the oligomerization of lower olefins [30, 40]. Its activity depends on the ratio of the components. In the oligomerization of ethylene, the highest catalytic activity (~30000 mol C_2H_4 (mol Ni)$^{-1}$ h^{-1}) is observed at a B : Ni molar ratio of about 70. The major products of ethylene conversion are dimers (75%) and trimers (22%). At the molar ratio of B : Ni = 10, the activity of the catalytic system is more than two orders of magnitude lower than its maximum value. However, if ethanol is introduced into the system that has been formed at this component ratio (alcohol : Ni = 5 mol/mol), the activity of the system will increase sharply to approach its maximum value. A similar promoting effect is also exerted by benzyl alcohol. Isopropanol and *tert*-butanol are less efficient promoters (Table 1).

Proton-donor compounds can enter into donor–acceptor reactions with Lewis acids to form strong Brønsted complex acids capable of adding oxidatively to Ni(0) to yield Ni(II) hydrido complexes [41, 42]. The activity of the nickel complex catalysts is usually attributed to these nickel complexes. As shown previously [30–33, 43], the formation of the $Ni(PPh_3)_4/BF_3 \cdot OEt_2$ catalytic system is accompanied by the quantitative oxidation of Ni(0) to Ni(I) with the formation of a variety of cationic Ni(I) complexes with the general formula $[(PPh_3)_{3-n}Ni(OEt_2)_n]BF_4$ (n = 0, 1, 2), whose relative concentrations depend on the proportions of the starting components in the system. In order to see what transformations of the Ni(0) and Ni(I) complexes can occur under the action of protonic acids, let us consider the interaction of $Ni(PPh_3)_4$ and $[Ni(PPh_3)_3]BF_4$ with ethoxytrifluoroboric and tetrafluoroboric acids.

$Ni(PPh_3)_4/HBF_3X$. The ^1H NMR spectra of deuterated benzene solutions of the protonic acids HBF_3OEt and HBF_4 exhibit downfield signals from the acidic protons at δ = +9.7 and +12.5 ppm, respectively. After a protonic acid is added to the individual $Ni(PPh_3)_4$ complex in deuterated benzene (HBF_3X : Ni = 3 mol/mol), the relative intensity of these signals decreases and new broad signals appear upfield at δ = –8 and –5 ppm for HBF_3OEt and HBF_4, respectively. The upfield NMR signals are very sensitive to oxygen and immediately disappear upon the slightest contact of the solution with air. The broadening of the NMR signals to a width of Δν = 95 Hz indicates the formation of paramagnetic compounds, such as the high-spin Ni(II) complexes and Ni(I) complexes. According to ESR data, the $Ni(PPh_3)_4/HBF_3X$ systems, where X = OEt or F, contain little, if any, Ni(I) complexes under the conditions examined. Therefore, the observed paramagnetism, which is manifested in the NMR spectra as signal broadening, is due to high-spin, for example, tetrahedral, Ni(II) complexes. Note that the chemical shifts of the upfield signals, which qualitatively correspond to the hydride ion, should be considered to be estimates, because they were determined without allowance made for paramagnetic shifts. For instance, the chemical shift for the hydride hydrogen in the low-spin pentacoordinate hydrido complex $\{[P(OEt)_3]_4NiH\}BF_3OEt$ contains no paramagnetic component and is δ = –15.1 ppm [20]. Therefore, when the $Ni(PPh_3)_4$ complex reacts with ethoxytrifluoroboric and tetrafluoroboric acids, Ni(0) is oxidized to Ni(II) to form Ni(II) hydrido complexes to which the tetrahedral structure $[(PPh_3)_3NiH]BF_3X$ can be assigned.

$[Ni(PPh_3)_3]BF_4/HBF_4$. The tricoordinate Ni(I) phosphine complex $[Ni(PPh_3)_3]BF_4$ synthesized in situ in the $Ni(PPh_3)_4/BF_3 \cdot OEt_2$ catalytic system (B : Ni = 4 mol/mol) has a doubly degenerate ground state. Due to the Jahn–Teller effect, it gives rise to a broad asymmetric signal in the ESR spectrum at T = 77 K (Fig. 1, curve *1*) [30, 32, 35, 43]. The relevant ESR parameters are presented in Table 2.

Adding the protonic acid HBF_4 causes the elimination of phosphine ligands, as in the case of excess $BF_3 \cdot OEt_2$, successively yielding the $[(PPh_3)_2Ni(OEt_2)]BF_4$ and

Table 2. Parameters of the ESR spectra of the Ni(I) complexes

Complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$, mT	$A_{\perp}$, mT	References
$[(PPh_3)_3Ni]BF_4$	2.38_z	2.12_y 2.07_x	$6.1\ (1P)_z$	$6.4\ (1P)_y$ $8.1\ (1P)_x$	[32, 35]
$[(PPh_3)_2Ni(OEt_2)]BF_4$	2.44	2.10	6.0 (1P) 3.6 (1P)	7.5 (1P) 2.9 (1P)	[32]
$[(PPh_3)Ni(OEt_2)_2]BF_4$	2.30_z	2.13_y 2.03_x	$4.8\ (1P)_x$	$7.4\ (1P)_y$ $5.7\ (1P)_z$	[32]
$[(P(OEt)_3)_3NiL]BF_3X$*	2.04_z	2.10_y 2.20_x	$17.5\ (1P)_z$ $7.4\ (2P)_z$	$7.5\ (1P)_y$ $5.6\ (1P)_y$ $18.5\ (1P)_x$	–

* L = PPh_3, X = OEt.

$[(PPh_3)Ni(OEt_2)_2]BF_4$ complexes, whose ESR spectra (Fig. 1, curves *2*, *3*) are described in an earlier publication [32]. The only difference is that the elimination of one and two phosphine ligands from the cationic complex $[(PPh_3)_3Ni]BF_4$ requires only a three- and tenfold excess of HBF_4, respectively, versus 50- and 80-fold excess of $BF_3 \cdot OEt_2$ [32]. Under these conditions, the oxidation state of Ni(I) remains unchanged, and only the elimination of the last phosphine ligand under the action of both the protonic and aprotic acids decomposes the Ni(I) complexes to form colloidal nickel. The high efficiency of the protonic acid in the formation of the coordinately unsaturated Ni(I) complexes is due to the removal of the phosphine ligands from the solution through the formation of the poorly soluble phosphonium salt $HPPh_3BF_4$.

It should be mentioned that phosphonium salts are also formed in the $Ni(PPh_3)_4/HBF_3X$ system, indicating that the coordinately unsaturated Ni(II) complexes can also result from the action of protonic acids.

The experimental data obtained make it possible to optimize the experimental conditions for preparing nickel complexes with a desired composition and structure in the catalytic systems. In order to compare the activities of the catalytic systems in which nickel exists mainly as cationic Ni(I) complexes and Ni(II) hydrido complexes, let us consider ethylene oligomerization on the catalytic systems prepared by different methods from the same components ($Ni(PPh_3)_4$, $BF_3 \cdot OEt_2$, and HBF_4).

$Ni(PPh_3)_4/BF_3 \cdot OEt_2/HBF_4$. The three-component system $Ni(PPh_3)_4/BF_3 \cdot OEt_2/HBF_4$ was prepared as follows. Initially, a certain amount of $BF_3 \cdot OEt_2$ was added to a stirred toluene solution of the Ni(0) phosphine complex (B : Ni = 4 mol/mol) in an argon atmosphere, and the protonic acid HBF_4 was then added (2 mol/mol < HBF_4 : Ni < 20 mol/mol). The catalytic system thus prepared, in which nickel is mainly in the form of cationic Ni(I) complexes, shows a high activity in ethylene oligomerization. The dependence of the activity of the system on the HBF_4 : Ni molar ratio is plotted in Fig. 2 (curve *1*).

The extremum in the plot of the catalytic activity versus the amount of protonic acid is likely due to the elimination of the phosphine ligands, the formation of the coordinately unsaturated cationic Ni(I) complexes containing at most one phosphine ligand, and their decomposition in excess acid.

Note that, for the catalytic activity maximum to be reached, the three-component system $Ni(PPh_3)_4/BF_3 \cdot OEt_2/HBF_4$ requires ~6 times smaller amount of boron compounds than the two-component system $Ni(PPh_3)_4/BF_3 \cdot OEt_2$.

$Ni(PPh_3)_4/HBF_4/BF_3 \cdot OEt_2$. The three-component system $Ni(PPh_3)_4/HBF_4/BF_3 \cdot OEt_2$ was prepared using the opposite order of mixing. At first a certain amount of the protonic acid HBF_4 was added to a stirred toluene solution of the Ni(0) phosphine complex (HBF_4 : Ni = 3 mol/mol) under argon, and $BF_3 \cdot OEt_2$ was then added (2 mol/mol < B : Ni < 80 mol/mol). The system thus prepared, in which nickel exists mainly as Ni(II) hydrido complexes, exhibits a very low activity in ethylene oligomerization, which does not exceed 2% of the activity of the three-component system $Ni(PPh_3)_4/BF_3 \cdot OEt_2/HBF_4$ throughout the B : Ni range

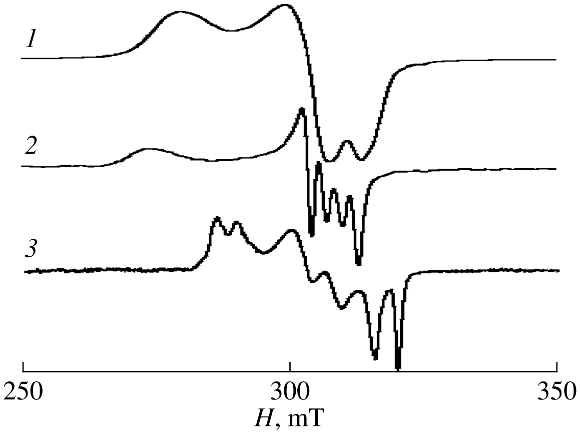

Fig. 1. ESR spectra of Ni(I) complexes: (*1*) $[Ni(PPh_3)_3]BF_4$, (*2*) $[(PPh_3)_2Ni(OEt_2)]BF_4$, and (*3*) $[(PPh_3)Ni(OEt_2)_2]BF_4$. The solvent is toluene; T = 77 K.

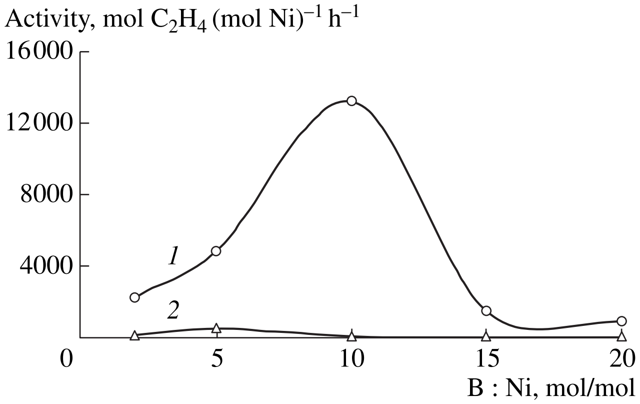

Fig. 2. Catalytic activity of the $Ni(PPh_3)_4/HBF_4$ system (*1*) activated with $BF_3 \cdot OEt_2$ and (*2*) not activated versus the amount of the protonic acid HBF_4.

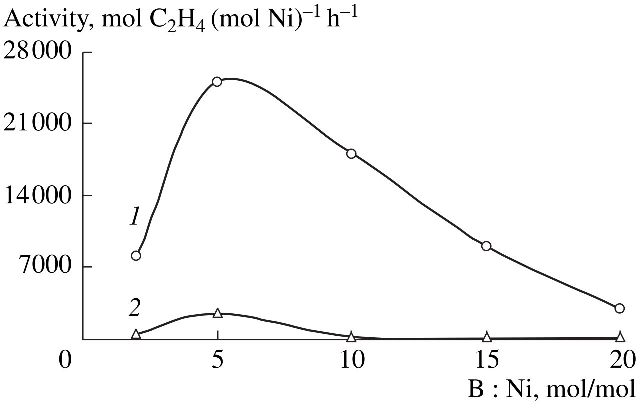

Fig. 3. Catalytic activity of the $Ni(PPh_3)_4/HBF_3OEt$ system (*1*) activated with $BF_3 \cdot OEt_2$ and (*2*) not activated versus the amount of the protonic acid HBF_3OEt.

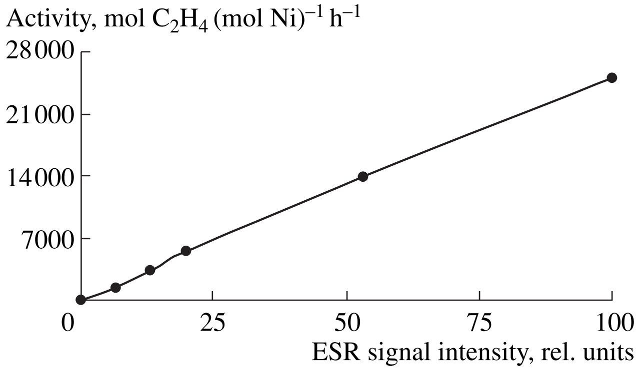

Fig. 4. Activity of the $Ni(PPh_3)_4/BF_3 \cdot OEt_2/HBF_3OEt$ system versus ESR signal intensity.

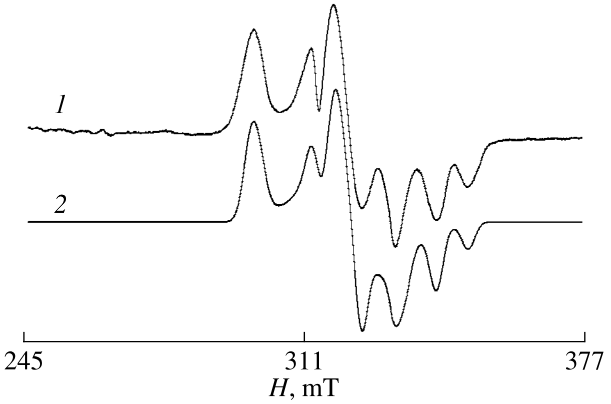

Fig. 5. (*1*) Observed and (*2*) simulated ESR spectra of the Ni(I) complex $[(P(OEt)_3)_3NiL]BF_3X$. The solvent is toluene; $T = 77$ K.

examined. The two-component system $Ni(PPh_3)_4/HBF_4$ also has a low activity, whose dependence on the HBF_4 : Ni molar ratio is plotted in Fig. 2 (curve *2*).

Similar regularities are observed in the catalytic systems in which HBF_3OEt is used as the protonic acid (Fig. 3).

Note the following characteristic feature of the catalytic systems in which nickel is mainly in the form of cationic Ni(I) complexes: the ESR signals from Ni(I) disappear once ethylene is admitted into the system and its rapid oligomerization started. This can be due to either a change in the oxidation state of Ni(I) or ion dimerization in the catalytic process. However, if the catalytic poison triethyl phosphite (P : Ni > 3 mol/mol) is introduced into the system at the highest activity moment, the oligomerization reaction stops immediately and intense ESR signals from the mononuclear Ni(I) complexes appear immediately. The ethylene oligomerization rate at the moment of catalyst poisoning is proportional to the intensity of the new ESR signals (Fig. 4). Under these conditions, the ESR spectrum of the $Ni(PPh_3)_4/BF_3 \cdot OEt_2/HBF_3OEt$ system exhibits a signal from a tetrahedral Ni(I) complex with three nonequivalent phosphorus ligands (Fig. 5), which are typical of trigonal structures with a pseudodegenerate ground state [43]. The parameters of this ESR signal are consistent with the composition $[(P(OEt)_3)_3NiL]BF_3X$, where, probably, L = PPh_3 and X = OEt (Table 2). The large width of the individual line ($\Delta H > 3$ mT) does not allow the hyperfine structure from the PPh_3 ligand to be resolved. In the ESR spectrum of the geometrically similar complex $[(P(OBu)_3)_2Ni(PPh_3)_2]BF_4$, the hyperfine structure from the PPh_3 ligands is also unresolved [43].

These data indicate that, during ethylene oligomerization, nickel in the active catalytic system is univalent and exists as diamagnetic dimers, which dissociate to mononuclear complexes upon the coordination of phosphite ligands. Further studies are required to elucidate the nature of the binuclear Ni(I) complexes.

Thus, we have investigated the influence of the order of introduction of promoters, specifically, complex protonic acids on the formation of active complexes in the $Ni(PPh_3)_4/BF_3 \cdot OEt_2$ catalytic system and the activity of these systems in ethylene oligomerization. The activity of these systems, in which nickel exists mainly as cationic Ni(I) complexes, is one order of magnitude higher than the activity of the systems in which nickel exists mainly as Ni(II) hydrido complexes.

The promoting effect of alcohols on the $Ni(PPh_3)_4/BF_3 \cdot OEt_2$ catalytic system has been revealed. The alcohols are the source of Ni(II) hydrides and, more importantly, the source of strong Brønsted acids, which efficiently ensure the coordination unsaturation of the cationic Ni(I) complexes.

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