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CATALYSIS

In Situ Formation of Al(Fe)/Cl Metal Chloride Complexes and Evaluation of Their Catalytic Properties in the Reaction of Ethylene Oligomerization

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Abstract—According to FT-IR and UV spectroscopic data, the interaction of the Al/Fe alloy with *tert*-butyl chloride results in that $AlCl_4^-$, $Al_2Cl_7^-$, and $FeCl_2^+$ ion complexes, Fe^{3+} ions, and $AlCl_3$ molecular form are produced in situ in the reaction medium. Ethylene was oligomerized in *n*-hexane on metal chloride complexes produced in situ from Al/Fe alloys and *tert*-butyl chloride.

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Raising the selectivity of practically important reactions in which hydrocarbons are converted, such as alkylation, oligomerization, and isomerization, is among fundamental tasks of organic chemistry and catalysis. Recently, in situ methods have become widely accepted for synthesis of catalytic aluminum chloride complexes from activated aluminum and organochlorine compounds, which are active in the liquid-phase alkylation of isobutane with butenes [1], oligomerization of decene-1 [2], and transformations of cyclohexene into dimethyldecalines [3]. However, to raise the selectivity of the corresponding reactions, it is necessary to use aluminum chloride complexes containing ions of transition metals: iron, nickel, cobalt, copper, etc. [4–6]. It is known that iron-based complexes produced from metallic Fe and CCl_4 in acetonitrile and dimethylacetamide are active in the telomerization of ethylene [7]. Of scientific interest in this context is the in situ formation in the reaction medium of aluminum chloride complexes containing ions of transition metals from the corresponding alloys and organochlorine compounds, among which *tert*-butyl chloride (TBC) has gained wide acceptance.

The goal of our study was to examine the reactivity of the Al/Fe alloy with respect to organochlorine compounds for producing in situ catalytic (Fe-, Al/Cl) complexes from the systems Al/Fe/TBC and Al/Fe/TBC in *n*-hexane and to determine their catalytic properties under the chosen conditions in the reaction of ethylene oligomerization.

EXPERIMENTAL

We used in the study the A/Fe alloy containing 2.15 wt % Fe [8].

In situ formation of metal chloride complexes.

(a) A 0.05–0.15-g alloy sample was placed in a Teflon reactor and then 10 mL of TBC was added. After the sample was completely dissolved at a temperature of 25°C, a red fluid was formed with a separate dense phase of tarry compounds. A 40-μL portion of the liquid phase was dissolved in 1 mL of acetone and analyzed by gas chromatography/mass spectrometry (GC/MS). Additionally, FT-IR spectra were recorded. The tarry compounds were analyzed by FT-IR spectroscopy and UV-Vis spectrophotometry. Then, 3–5 mL of water was added to the tarry compounds until a complete hydrolysis occurred and a 3-fold extraction with 1 mL of n-hexane was performed. The resulting extract was analyzed by GC/MS.

(b) A 5 × 5 mm 0.1-g alloy sample with a thickness of 2.0 m was placed in a Teflon reactor of special design that enabled delivery of gases, and then 10 mL of TBC was added. Helium was delivered into the reactor under a pressure of 0.2–0.4 MPa. The reaction mixture was kept in a thermostat at 80°C for 6–7 h. The reaction products were analyzed as noted above.

(c) An alloy sample with mass of 0.1–1.15 g, dimensions of 5 × 7 mm, and thickness of 1.8–2.0 mm was placed in a Teflon reactor of special design that enabled delivery of gases, and then a 4-fold excess of TBC and 15 mL of n-hexane were added. Helium was delivered into the reactor under a pressure of 0.2–0.4 MPa. The reaction mixture was kept in a thermostat at 80°C for 9–10 h. The alloy sample did not react completely: the conversion of the alloy was only 1.91%. The reaction alloy was partly covered by a layer of raspberry-red products, which confirms that compounds of unknown composition are formed and hinder further dissolution of the alloy. The GC/MS method was used to analyze the liquid phase.

Reaction of Ethylene Oligomerization

(a) Ethylene was passed at a flow rate of 1 mL min^{-1} for 1 h under a pressure of 0.11–0.12 MPa at a temperature of 15°C through metal chloride complexes formed in situ by procedure (a). The reaction products were analyzed by the GC/MS method.

(b) A 0.1–0.15-g portion of an Al/Fe alloy (2.15 wt % Fe) was placed in a Teflon reactor of special design, 10 mL of TBC was added, and ethylene was delivered to create an excess pressure of 0.2–0.4 MPa. The reaction mixture was kept in a thermostat for 80°C for 7–8 h and then cooled and analyzed.

(c) Ethylene was added under an excess pressure of 0.2–0.4 MPa to metal chloride complexes formed in situ by procedure (c) (in hexane). The reaction mixture was kept in a thermostat at a temperature of 80°C for 1 h. Liquid reaction products were analyzed by GC/MS, and tarry compounds formed on the alloy plate were scraped off with a putty knife and analyzed by multiple attenuated total reflectance FT-IR (ATR-FT-IR) spectroscopy.

The composition of the products being formed was analyzed by gas chromatography/mass spectrometry on a 6890/5973N instrument (Agilent Technologies) with a mass spectrometer of the quadrupole type with ionization energy of 70 eV.

To obtain FT-IR and UV-Vis spectra, a demountable cell with 0.015-mm-thick absorbing layer and KBr glasses was used. FT-IR absorption spectra were obtained on a NICOLET 5700 Fourier-transform IR spectrometer with a deuterated triglycine sulfate detector in the spectral range 7400–400 cm^{-1} with resolution of 4 cm^{-1}. ATR-FT-IR spectra were obtained on the same instrument with an additional special attachment. A ZnSe crystal served as the internal reflection element.

UV-Vis absorption spectra were obtained with a Shimadzu UV 2501PC spectrophotometer at 190–900 nm. The UV-Vis spectrum of the cuvette was subtracted from these spectra.

RESULTS AND DISCUSSION

After a prolonged (~20 h) interaction of the Al/Fe alloy (2.15 wt %) with TBC at 25°C, release of tarry compounds and a change in the coloration of the liquid reaction mixture were observed. The FT-IR spectrum of the tarry reaction products demonstrated in the low-frequency spectral range a strong absorption band at 493 cm^{-1} (Fig. 1, spectrum *1*). According to published data, this band is associated with stretching vibrations of Al–Cl bonds in the tetrahedral ion $AlCl_4^-$ [9, 10]. Additionally, the FT-IR spectrum exhibited absorption bands at 523 and 608 cm^{-1}, associated with stretching vibrations of the Al–Cl bonds in the binuclear ion $Al_2Cl_7^-$ and molecular form $AlCl_3$, respectively [11, 12]. In addition, absorption bands at 2730 and 2414 cm^{-1} were recorded in the FT-IR spectrum, these bands being associated with stretching vibrations of H–Cl bond in hydrogen chloride molecules interacting with aluminum chloride complexes and olefins, respectively [13, 14]. The absorption band at 1644 cm^{-1} corresponds to the frequency of stretching vibrations of C=C bonds in olefins.

The qualitative composition of aluminum chloride complexes formed in situ in the interaction of the Al/Fe alloy (2.15 wt %) with TBC at 80°C is not changed significantly (Fig. 1, spectrum *2*). However, the appearance of an absorption band was recorded in the FT-IR spectrum at 1601 cm^{-1}, this band being characteristic of vibrations of C=C bonds in dienes and polyenes.

Figure 2 shows UV-Vis spectra of the tarry compounds formed in the reactions at 25 and 80°C. A strong absorption is recorded in the spectral range 220–400 nm. According to the available published data, the absorption band at 334 nm is due to the electron transitions in $FeCl^{2+}$ ions [15], and the absorption bands at 307 and 388 nm, to transitions in Fe^{3+} ions [16]. Additionally, the spectrum shows $\pi \rightarrow \pi^*$ electron transitions in polyenes.

An analysis of hydrolyzed tarry reaction products by the GC/MS method demonstrated the presence of a

Fraction composition of ethylene conversion products obtained on different catalytic systems

Catalytic system	Fraction composition, mol %							
	hydrocarbons	olefins			chloroalkanes			C_{9+}
		C_4	C_6	C_8	C_6	C_8	C_5, C_7	
Al/Fe/TBC alloy (procedure a)	4.3	–	–	–	25.2	4.6	22.9	43.0
Al/Fe/TBC alloy (procedure b)	1.4	–	–	–	9.2	13.8	5.8	69.8
Al/Fe/TBC alloy (procedure c)	–	70.6	–	29.4	–	–	–	–

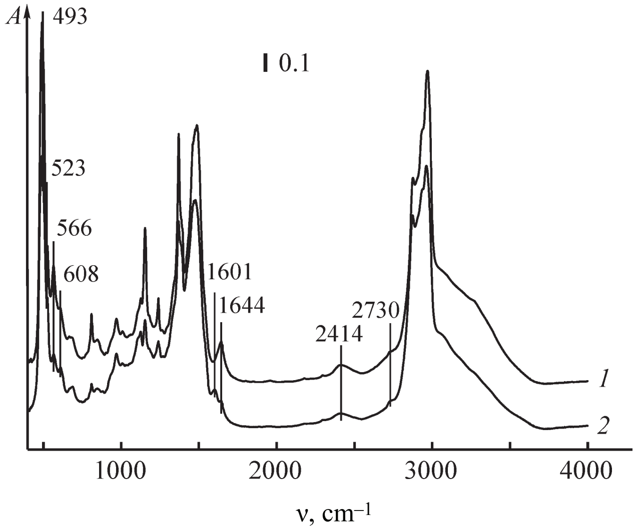

Fig. 1. FT-IR spectra of aluminum chloride complexes formed in situ by procedure (*1*) a and (*2*) b. (*A*) Absorption and (ν) wave number.

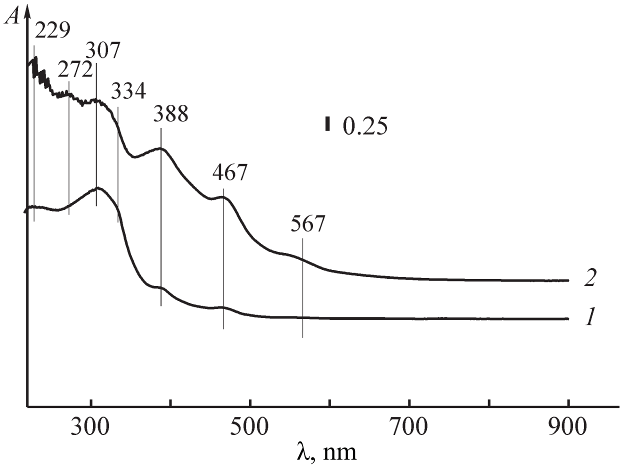

Fig. 2. UV-Vis spectra of Fe/Cl complexes formed in situ by procedure (*1*) a and (*2*) b. (*A*) Absorption and (λ) wavelength.

wide variety of cyclopenta-1,3-diene and cyclohexa-1,3-diene derivatives. The liquid reaction products are for the most part represented by 2,2,4-trimethylpentane and organochlorine compounds: 2-chloro-2-methylbutane, 2-chloro-2,3-dimethylbutane, and 2-chloro-2,5,5-trimethylhexane.

Table 1 presents the results of catalytic tests of the oligomerization of ethylene. It can be seen that oligomers are predominantly formed in the liquid reaction medium on catalytic complexes produced in situ from the Al/Fe alloy (2.15 wt %) and TBC in n-hexane. In the absence of this solvent, chloroalkanes are predominantly formed in the liquid reaction medium, which is possibly due to the occurrence of reactions in which ethylene oligomers are hydrochlorinated. The GC/MS revealed in the tarry reaction products cyclopenta-1,3-diene and cyclohexa-1,3-diene derivatives with molecular masses of up to 388 g mol^{-1}, which indicates that there occurs the coupled oligomerization reaction.

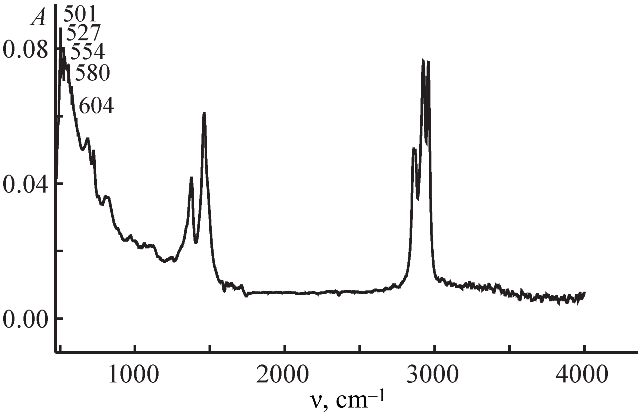

Fig. 3. ATR-FT-IR spectra of the catalytic system Al/Fe/TBC alloy in *n*-hexane, produced by procedure c under the conditions of the ethylene oligomerization reaction. (*A*) Absorption and (ν) wave number.

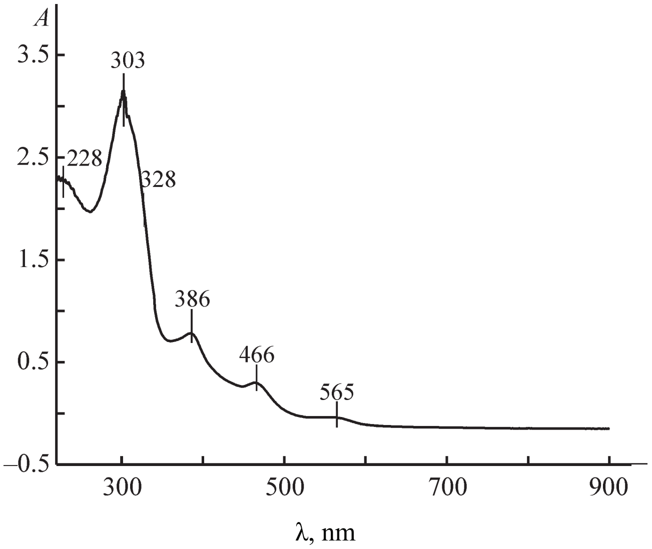

Fig. 4. UV-Vis absorption spectrum of a Fe/Cl complex formed in situ by procedure a, under the conditions of the reactions of coupled ethylene oligomerization and hydrochlorination of olefins. (*A*) Absorption and (λ) wavelength.

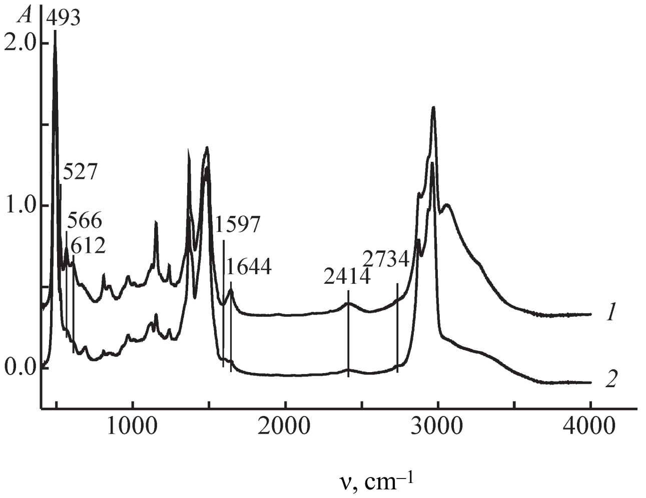

Fig. 5. FT-IR absorption spectra of aluminum chloride complexes formed in situ by procedure (*1*) a and (*2*) b under the conditions of the reactions of coupled ethylene oligomerization and hydrochlorination of olefins. (*A*) Absorption and (ν) wave number.

Figure 3 shows ATR-FT-IR spectra of aluminum chloride complexes produced in situ under the conditions of the ethylene oligomerization reaction. Together with the absorption bands of the Al$_2$Cl$_7^-$ ion (527 cm^{-1}), there appear new absorption bands at 501 and 580 cm^{-1}, characteristic of stretching vibrations of Al–Cl bonds in the AlCl$_4^-$ ions with C3v symmetry [17]. Additionally, the ATR-FT-IR spectrum exhibited absorption bands at 554 and 604 cm^{-1}, which are presumably associated with stretching vibrations of Al–Cl bonds in molecular complexes of the type AlCl$_3$/olefin [18].

In the conditions of the reactions of coupled oligomerization and hydrochlorination of olefins, the main changes were observed by UV-Vis spectroscopy in the spectral range 250–400 nm (Fig. 4). For example, an increase was recorded in the intensity of the absorption bands at 303 and 386 nm, associated with electron transitions in Fe^{3+} ions. It can be assumed that both FeCl^{2+} and Fe^{3+} ions are involved in the transformations of ethylene. According to FT-IR spectroscopic data, the qualitative composition of aluminum chloride complexes produced in situ is not changed significantly in the reactions of coupled oligomerization and hydrochlorination of olefins (Fig. 5). Presumably, this may indicate that the aluminum chloride complexes are not involved in separate stages of the catalytic cycle.

Comparing the ATR-FT-IR data with the results of our catalytic tests, we can assume that molecular complexes of the type AlCl$_3$/olefin are necessary for the reaction of ethylene oligomerization to occur.

CONCLUSIONS

(1) According to FT-IR and UV-Vis spectroscopic data, the interaction of the Al/Fe alloy (2.15 wt %) with *tert*-butyl chloride yields in situ ion complexes of composition AlCl$_4^-$,Al$_2$Cl$_7^-$, and FeCl$_2^+$, Fe^{3+} ions and molecular form AlCl$_3$.

(2) ATR-FT-IR spectroscopy demonstrated that AlCl$_3$/ethylene molecular complexes are necessary for the reaction of ethylene oligomerization to occur.

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