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Heterogeneous Iron-Containing Catalysts for the Reaction of CCl_4 Addition to a Multiple Bond

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Abstract—The catalytic properties of iron complexes with monoethanolamine chemically immobilized on the surface of silica were studied in the reaction of CCl_4 addition to 1-octene. Unlike the previously studied complexes of other transition metals, the activity of the iron complexes increased with increasing metal content. The analysis of the catalyst composition and reaction products demonstrated that the reaction occurred by a coordination mechanism at low metal concentrations. At high concentrations, the metal mainly occurred in the form of an oxychloride and the catalytic process occurred nonselectively, probably, by an ionic mechanism. The addition occurred in an analogous manner in the presence of iron chloride supported onto unmodified silica gel.

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INTRODUCTION

The addition of CCl_4 at multiple bonds (Kharash reaction) is of interest as a means for hydrocarbon functionalization. The optimization of this reaction is still in progress. It is well known that the process occurs with the participation of free radicals. Its detailed mechanism and the composition of products depend on the nature of the initiator [1]. With the use of peroxides and other traditional initiators, the reaction develops in accordance with an ordinary chain mechanism; chain propagation is assisted by trichloromethyl and chloroalkyl radicals in solution. As a result, telomerization and substitution products (in particular, chloroalkenes) and a number of other compounds are formed in addition to an addition product. In the presence of metal complex initiators, the process can occur in the coordination sphere of a metal complex; in this case, the addition product is formed with a high selectivity. Previously, we found that this development of the process is characteristic of the complexes of a number of transition metals (Cu, Mn, V, and Co) with monoethanolamine (MEA), which are chemically immobilized on the surface of silica. In addition to high activity and selectivity, the reaction in the presence of the above compounds is generally characterized by activity as an extremal function of metal concentration on the surface; this is due to a dramatic difference in the activities of mononuclear and bridging metal complexes [2–4].

The catalytic activity of corresponding iron-containing systems was found to be higher than the activity of the immobilized complexes of other transition metals. However, the regularities of catalysis were essentially different in this case. First, the dependence of the activity of catalysts on metal content had a monotonic form. Second, the composition of products depended on the metal content of the catalyst. The above facts suggest that the mechanism of catalysis in the presence of iron-containing catalysts can be different from that characteristic of the amine complexes of other transition metals. The aim of this work was to find the main regularities and mechanism of carbon tetrachloride addition at multiple bonds in the presence of immobilized iron complexes using the reaction of CCl_4 with 1-octene as an example.

EXPERIMENTAL

The KSK-2 silica gel ($S_{sp} = 300$ m^2/g; pore diameter $d_p = 15$ nm) modified with MEA was prepared in accordance with a previously described procedure [2]. Iron(II) chloride was synthesized by the interaction of iron metal with gaseous hydrogen chloride in an electric tube furnace at 900°C [5]. The resulting light yellow powder (Fe content of 44 wt %, which is consistent with the theoretical value) was evacuated and kept in sealed ampoules. Iron chloride was supported onto the modified silica gel in an acetonitrile solution in accordance with a procedure described elsewhere [2, 4]. The above chloride was chosen because its solubility in acetonitrile is higher than that of Fe(III) compounds; this allowed us to vary the metal concentration over a wide range. Analogously, the iron chloride was supported onto silica gel free of the amino alcohol. Then, the catalysts were evacuated and kept in sealed ampoules. The concentrations of the metal in the samples were determined by atomic absorption spectrometry. The catalytic experiments were performed in evacuated and sealed ampoules with intense stirring under the following standard conditions: heterogeneous catalyst, 0.02 g; 1-octene, 0.05 ml; CCl_4, 0.45 ml; temperature, 130°C. The rate of the reaction did not depend on the rate of

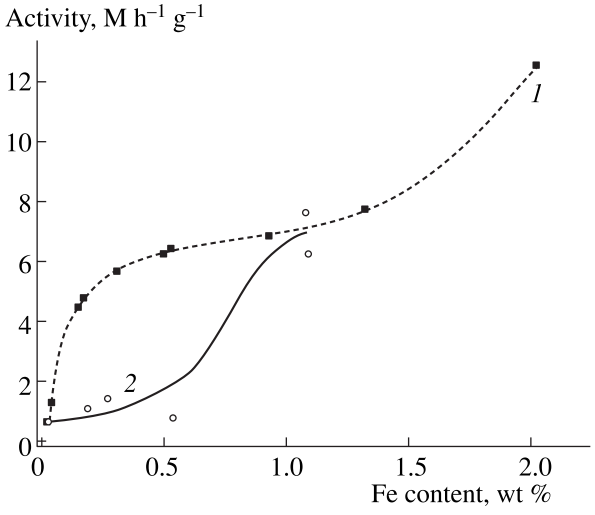

Fig. 1. Dependence of the activity of (*1*) Fe/MEA/KSK-2 and (*2*) Fe/KSK-2 catalysts on the iron content of the catalysts.

stirring. The yield of reaction products was determined by chromatography on an LKhM 3700 instrument with a flame-ionization detector using a column with an SE-30 nonpolar phase. The catalyst activity was calculated as the initial rate of 1-octene conversion per unit weight of the catalyst. In preliminary experiments, it was found that the kinetic curves were smoothly shaped and an induction period was absent.

RESULTS AND DISCUSSION

The product composition of the reaction of CCl_4 with 1-octene depends on the iron content of the catalyst. The main product is the addition product, 1,1,1,3-tetrachlorononane. The formation of chlorooctene and telomerization products was also detected at high iron concentrations. Figure 1 (curve *1*) shows the dependence of the activity of catalysts under identical conditions on the iron content of the catalysts. Here, unlike experiments with copper-containing systems [2, 3], the activity monotonically increases with increasing metal content of the samples. In this case, in the region of low metal concentrations, the run of the curve is qualitatively identical to that in the presence of catalysts based on other metals. As found previously using copper-containing catalysts as an example, the increase in activity in the region of low surface metal concentrations is due to the accumulation of complexes containing various amounts of amino groups in the coordination sphere of the metal. Differences manifest themselves in the region of higher (>0.4 wt %) concentrations. At these metal concentrations, the activity of previously studied complexes decreased, whereas the growth of activity only somewhat slowed down in the case of iron; after reaching a critical metal concentration, the activity rapidly increased again. Under these conditions, as can be seen in Table 1, the composition of products changed: telomers and chlorooctene were formed along with the addition product.

Table 1. Comparison of the catalytic properties of Fe-containing systems

Entry	Metal/ligand/support system	Metal content, wt %	Total C_8H_{16} conversion, %	Octene conversion[a] into telomers, %	Yield of chlorooctene, %
1	Fe/MEA/KSK-2	0.15	33	–	0.3
2	″	0.17	36	–	0.3
3	″	0.31	41	–	0.3
4	″[b]	0.31	34	6	0.8
5	″	0.93	47	–	0.4
6	″	1.32	57	11	1.0
7	″	2.02	73	12	1.2
8	Fe/KSK-2	0.19	11	3.0	0.5
9	″	0.27	15	4.2	0.8
10	″	0.93	51	5.3	3.6
11	″	1.08	55	5.0	3.7
12	$FeCl_3$ solution	(1.2×10^{-2})[c]	43	25	5.2
13	$FeCl_3$ solution + KSK-2[d]	(1.2×10^{-2})[c]	91	22	6.4

Note: [a] Calculated from a material balance.
[b] The same sample after storage for a long time (see text).
[c] Concentration in mol/l.
[d] KSK-2 (0.02 g) was added to a homogeneous reaction mixture.

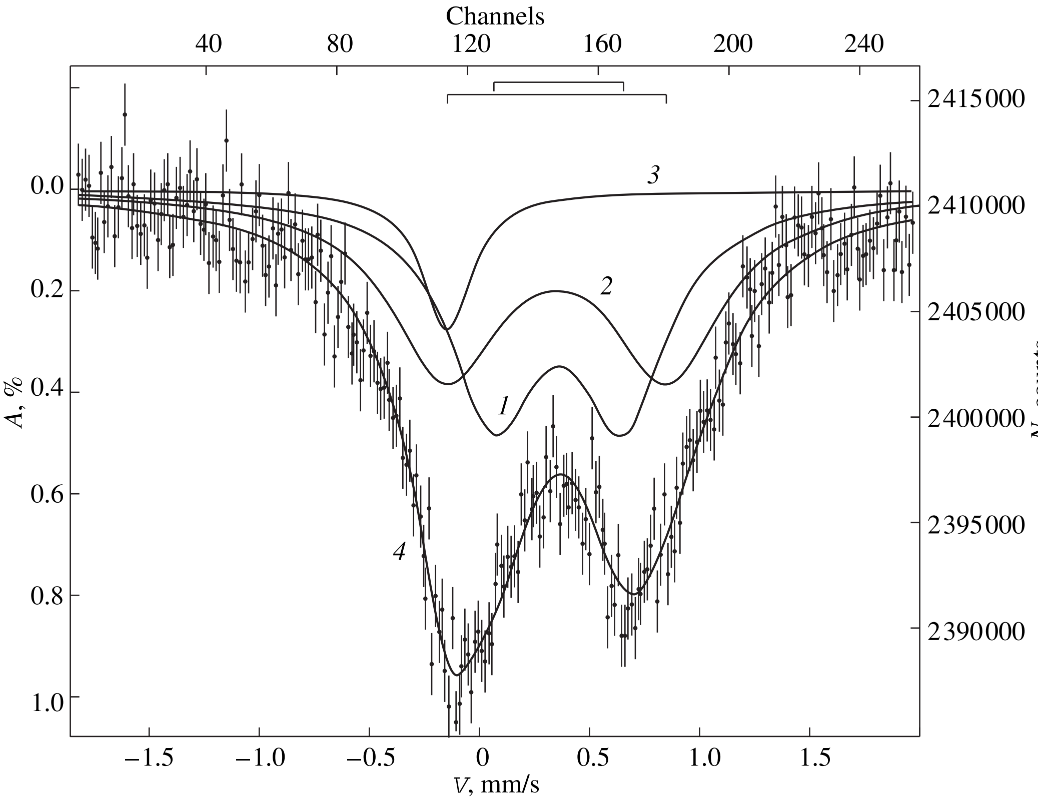

Fig. 2. (*4*) Mössbauer spectrum of the Fe/MEA/KSK-2 catalyst (Fe content of 0.80 wt %). Spectrum *4* is the superposition of two doublets *1* and *2* and singlet *3*.

Evidently, the observed differences are due to the presence of active centers other than those in the case of copper and other metals on the surface of Fe-containing catalysts. Based on published data, we can assume that iron chloride unbound to amino groups plays the role of these centers. Indeed, it is well known that the telomerization of CCl_4 with olefins in the presence of iron(II) chloride can also occur in the absence of an amine [5]. We compared the activity and selectivity of action of the Fe/MEA/KSK-2 system and an analogous Fe/KSK-2 system (without MEA) at various metal concentrations. Figure 1 and Table 1 summarize the data obtained. As can be seen in Fig. 1, only the samples containing MEA exhibited noticeable activity at low iron concentrations. As the iron content was increased, the activity of samples containing no MEA began to increase rapidly and became equal to the activity of the metal complex initiator starting with 1 wt %. In other words, the role of complexes with the amino alcohol is negligibly small in this concentration region.

The nature of active centers on the surface of the Fe/MEA/KSK-2 catalyst (0.8 wt % Fe) was studied by Mössbauer spectroscopy.[1] The experimental spectrum (Fig. 2) is the superposition of signals from various compounds: two doublets and a singlet. Components 1 and 2 (Table 2) correspond to the absorption of Fe(III) in an octahedral environment. The isomer shifts and quadrupole splittings of these subspectra are close to the corresponding parameters of the spectrum of $Fe(OH)_3$ [6]. It is likely that the small deviation of the experimental parameters from the parameters given in the cited work is due to the fact that the symmetry of the environment of the iron ion is distorted by the partial replacement of O atoms by Cl. A small isomer shift of the singlet line (component 3) allowed us to attribute this subspectrum in the Fe/MEA/KSK-2 system to the amine complexes of iron with a maximum probability.

Thus, iron on the catalyst surface completely occurs in a trivalent state. In this case, hydroxide or oxychloride species were predominant in samples with high metal concentrations. The oxidation of parent Fe(II) resulted from contact with atmospheric oxygen in the presence of (amine and acetonitrile) donors even in the course of catalyst preparation. We observed an analogous oxidation process in a study of Cu-containing systems, where the metal, which did not participate in complexation with the functional groups of a modifier, occurred in the form of a hydroxychloride [1, 3]. The hydroxychlorides of copper and other transition metals tested did not exhibit catalytic properties, and the deriv-

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[1] We are grateful to D.A. Pankratov (Faculty of Chemistry, Moscow State University) for his assistance in the recording and interpretation of the spectra.

Table 2. Isomer shifts (δ), quadrupole splittings (Δ), and line widths (Γ) of the components of the Mössbauer spectrum of the Fe/MEA/KSK-2 catalyst (Fe content of 0.80 wt %)

Subspectrum*	δ, mm/s	Δ, mm/s	Γ, mm/s	Relative area, %
1 (doublet)	0.35 ± 0.01	0.60 ± 0.01	0.50 ± 0.01	45.26
2 (doublet)	0.34 ± 0.01	1.00 ± 0.00	0.62 ± 0.02	43.23
3 (singlet)	–0.15 ± 0.01	–	0.27 ± 0.01	8.51

* See Fig. 2.

atives of these elements adsorbed on silica did not exhibit activity in the absence of an amino alcohol.

Another situation was observed in the case of iron. As the concentration of Fe was increased to 0.35–0.40 wt %, the surface of a modified support was gradually saturated with the metal because of complexation with immobilized amino groups. In this case, an insignificant amount of iron(III) hydroxide or hydroxychloride, which was coordinated to the free silanol groups of silica, was present on the surface. However, in this concentration range, the contribution of the above species to the total activity of the system was small; the complex with the amino alcohol played the main role. The reaction occurred with high selectivity, and the only reaction product was formed by a coordination-type radical mechanism, as in the case of other transition metals. Data on the metal contents of the catalyst before and after the reaction provided support to the conclusion that Fe is a constituent of grafted amine complexes. As can be seen in Table 3, the metal content of the Fe/MEA/KSK-2 catalyst after the reaction changed only slightly; that is, iron was strongly retained in a complex with the amino groups of the modifier.

Note that the storage of the catalyst in air for several days changed its activity and selectivity (Table 1, entry 4). This was likely due to the gradual cleavage of hydrolytically unstable Si–O–C bonds on the surface of silica and the degradation of amine complexes. Tetrachloroheptadecane (a 2 : 1 telomer) was detected by gas chromatography–mass spectrometry as a constituent of reaction products obtained on these catalysts. The fraction of this compound in the mixture of products was about 2.5%. The other products were chlorooctene and, probably, heavier oligomers, which cannot be identified by gas chromatography–mass spectrometry. To all appearances, the presence of immobilized amine complexes on the surface is a necessary condition for selective addition on Fe-containing catalysts.

Table 3. Metal contents of Fe/MEA/KSK-2 and Fe/KSK-2 heterogeneous catalysts before and after the reaction of CCl_4 addition to 1-octene (standard conditions)

Catalyst	Iron content, wt %	
	before reaction	after reaction
Fe/MEA/KSK-2	0.17	0.15
Fe/KSK-2	0.27	0.12

The behavior of catalysts prepared by supporting an aqueous solution of iron chloride onto unmodified silica was essentially different. A considerable portion of the metal passed into solution in the course of the reaction; Fe(III) hydroxychloride was retained on the surface much more weakly. As the iron content of the catalyst was increased, the fraction of iron(III) hydroxychloride coordinated to the silanol groups of silica increased; correspondingly, its contribution to olefin conversion increased (Fig. 1, curve *2*). The rapid increase in activity with increasing metal content indicates that, in this case, unlike reactions with the participation of typical metal complex initiators, the formation of bridging and polymer (in terms of the metal) structures not only does not interfere with the catalytic process but also, on the contrary, facilitates an increase in the activity.

It is likely that, at a high metal concentration, the reaction at Lewis acid sites was predominant; this reaction occurred by an ionic rather than radical mechanism. The processes of CCl_4 addition at multiple bonds in the presence of strong Lewis acids have long been known; they are characterized by a comparatively low selectivity of the formation of a 1 : 1 adduct and by the formation of telomers (for example, see [7]). Based on published data concerning cationic telomerization in the presence of Fe(III) compounds [8], we can propose the following scheme for the reaction catalyzed by iron(III) hydroxychloride, which is tentatively represented by the formula $Fe(OH)Cl_2$:

$$2\mathrm{Fe(OH)Cl_2} \rightleftarrows \mathrm{Fe(OH)Cl^+} + \mathrm{Fe(OH)Cl_3^-},$$

$$\mathrm{Fe(OH)Cl^+} + \mathrm{CCl_4} \longrightarrow \mathrm{Fe(OH)Cl_2} + \mathrm{CCl_3^+}$$

(chain initiation) (I)

or

$$\mathrm{Fe(OH)Cl_2 + CCl_4 \longrightarrow Fe(OH)Cl_3^- + CCl_3^+}$$

(chain initiation) (II),

$$\mathrm{CCl_3^+ + Ol \longrightarrow R_1^+} \quad \text{(chain propagation)},$$

$$\mathrm{R_1^+ + CCl_4 \longrightarrow R_1Cl + CCl_3^+}$$

(chain transfer, addition),

$$\mathrm{R_1^+ + Ol \longrightarrow R_2^+ \longrightarrow R_{\mathit{n}}^+}$$

(chain propagation, telimerization),

$$\mathrm{CCl_3^+ + Ol \longrightarrow CHCl_3 + R_1'^+}$$

(chain propagation),

$$\mathrm{R_1'^+ + CCl_4 \longrightarrow R_1'Cl + CCl_3^+}$$

(chain transfer, substitution)

(here, Ol is the molecule of an unsaturated compound).

The occurrence of the reaction at Lewis acid sites was supported by data obtained in the reaction performed in homogeneous iron chloride solutions (Table 1, entry 12), where it is difficult to assume a catalysis mechanism other than acid catalysis. In this case, the conversion of reactants was comparable to that observed in the presence of a heterogeneous catalysis with a high metal content. The compositions of products differed only slightly. It is of interest that the addition of SiO_2 to a homogeneous chloride solution resulted in a noticeable (more than twofold) increase in the conversion of octene. Taking into account that the intrinsic activity of silica gel is low (the conversion of octene under the specified conditions was lower than 5%), we can believe that the polar hydroxyl groups and adsorbed water in silica gel facilitate the autoionization of iron and the formation of additional active acidic species.

Thus, active centers of different natures occurred in catalysts prepared by the immobilization of iron chloride on the surface of silica modified with MEA. At a low metal content (to 0.4 wt %), the reaction occurred with high selectivity on amine complexes by a coordination mechanism. In samples with high metal concentrations, iron hydroxychlorides, which form Lewis acid sites, were responsible for catalysis. Under these conditions, the rate of reaction was high; however, telomers and chlorooctene were formed along with the addition product. Thus, varying the metal concentration in the catalyst can be considered a convenient and effective means for regulating the direction and rate of reactions of polychloroalkanes with unsaturated compounds.

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