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The Study of Active Centers of Ethylene Polymerization over Chromium Catalysts Prepared from Tri- and Bivalent Chromium Compounds

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The catalysts prepared from the trivalent and divalent chromium compounds under conditions that prevented their oxidation were investigated in the reaction of ethylene polymerization. Also the reduced chromia catalyst prepared by standard method from sexivalent chromium compound was investigated. The valence and coordinate states of chromium ions in the catalysts were determined by EPR and reflectance optical spectroscopy. In all cases, the catalysts prepared from trivalent chromium ions had a large activity; whereas the catalysts from divalent chromium had no activity. The reduction of the trivalent chromium ions into divalent state sharply decreased the activity. The activity of the catalysts prepared by the standard method was also decreased under reduction. It is concluded that the exposed Cr^{3+} ions in low coordination state are responsible for the catalytic activity of the catalysts.

INTRODUCTION

Supported chromia catalysts of ethylene polymerization are usually prepared by impregnation of silica gel or alumina silicate with solutions of compounds of Cr^{6+} ions. Sometimes the catalysts are prepared from trivalent chromium compounds, but they are always treated at high temperature in air or oxygen. Such treatment results in oxidation of the chromium ions to sexivalent state. Further activation of catalysts in both cases involves stages of high temperature treatment in vacuum or even reduction in ammonia, carbon monoxide or other substances. Such preparation results in the formation of sexi-, penta-, tri- and divalent chromium ions in catalysts.

The available data on the state of chromium ion in the active center of chromium containing catalysts are controversial. For instance, it has been reported in (*1*) that Cr^{3+} ions are present in the active centers. Eley *et al.* (*2*) consider Cr^{5+} ions as active centers. Ermakov *et al.* (*3*) who studied chromia catalysts reduced by carbon monoxide suggest that the valent state of chromium ions in the active centers does not exceed three before the reaction is initiated. Krauss and Stack (*4,5*) supposed that the valency of the chromium ion in the active center is equal to two. This conclusion is based on the correlation between the activity and the contents of divalent chromium (*4*), and the formation of Cr^{2+}–$[CH_2–]_n$ complexes, $n = 1, \ldots, 20$, upon interaction of C_2H_4 with the reduced catalyst (*5*). Thus the question of the oxidation state of chromium ions in the active centers of the chromium containing catalysts is still unsolved. The difficulties arise from the fact that there are chromium ions of all valence states in the catalysts prepared from sexivalent chromium.

In the present work the catalysts, prepared from di- and trivalent chromium ions under conditions which prevented their oxidation into higher valence states were used. Since in such catalysts the interval of possible valence states of chromium ions is narrower than usual, it is possible to give a better answer to the question about the valence state of chromium ions in the active centers.

The second part of the paper is concerned with the study of active centers of the chromium catalysts prepared by standard procedure, namely by the impregnation of silica gel with solution of H_2CrO_4 followed by reduction in carbon monoxide.

EXPERIMENTAL METHODS

The two types of catalysts were prepared. The catalysts of type I contained only Cr^{3+} ions before activation, those of type II had only Cr^{2+} ions. They were prepared by impregnation of large porous silica gel ($S = 360$ m^2/g) with aqueous solutions of chromium compounds and in the case of the chromacetylacetonate with an alcohol solution. The chromium compounds used for the preparation of the catalysts of type I were $CrCl_3 \cdot 6H_2O$, chromium (III) acetylacetonate, chromium citrate (III), $Cr[NH_3]_6 \cdot [NO_3]_3$. Those compounds used for type II were $CrCl_2 \cdot 4H_2O$ and $CrCO_3$. The $Cr[NH_3]_6[NO_3]_3$ complex was supported on the silica gel by ion exchange according to Ref. (*6*) at pH 10, then the samples were washed out to remove the NO_3^- anions. The complex was prepared according to Ref. (*7*). The preparation of the divalent chromium compounds and their supporting on silica gel was performed either in a stream of the argon, thoroughly purified from O_2 traces, or in sealed vacuumed tubes. $CrCl_2$ was prepared according to (*8*), and $CrCO_3$ by mixing $CrCl_2$ and K_2CO_3 solutions.

The usual chromia catalyst was also investigated. It was prepared according to the standard method by the impregnation of silica gel with aqueous H_2CrO_4 solution followed by activation at 500°C in carbon monoxide at 100–300 Torr. Before reduction the catalyst was oxidized at 400°C in O_2 at 100–300 Torr for 1 hr. After reduction it was evacuated for 5 min. The preliminary experiments showed that the reduced chromia silica gel catalyst was more active than that prepared by the activation in vacuum, which is in agreement with the data reported in (*9*). The chromium concentration in the samples was about 1 wt %.

Thermal treatment in vacuum and the reduction of the catalysts were carried out in quartz ampoules where the optical and EPR spectra were also measured. The ampoules were designed to take the measurements without adsorption of air. Polymerization was carried out in two ways, in the same quartz ampoules in the gas phase at low pressure of ethylene (100–200 Torr) and in a special system at 20 atm pressure of ethylene at 80°C also in gas phase. The polymerization rate was determined from the drop of ethylene pressure in the former case and from the consumption of ethylene at constant pressure in the second case.

The EPR spectra were measured with X-range spectrometer JES-3BS "JEOL" at room and liquid nitrogen temperature. The optical reflection spectra were performed in diffused scattered light at room temperature with a "Unicam-700" spectrometer with a special accessory. The silica gel used for preparation of the catalysts was used also as the reference standard for the optical spectra.

RESULTS AND DISCUSSION

Catalysts Prepared from Di- and Trivalent Chromium Compounds

The catalyst of type I, treated in vacuum at 500°C for 2 hr showed the high catalytic activity at 20 atm pressure of ethylene, Table 1. The technique of measurement at such pressure does not allow one to examine polymerization and at the same time to study the catalysts by spectroscopic methods. Therefore some samples were

TABLE 1
THE ACTIVITY OF THE CATALYSTS OF TYPE I EVACUATED AT 500°C FOR 2 HR

Catalyst prepared from	Activity[a] (g of pol./g of cat. × hr)	Conc. of chromium (wt%)
$Cr(NH_3)_6^{3+}$	164	1
$Cr(C_5H_7O_2)_3$	66	1
$Cr(C_6H_5O_7)$	45	1.7
$CrCl_3 \cdot 6H_2O$	73	1.9

[a] The activity was determined as the amount of polyethylene formed for 2 hr at 20 atm and 80°C.

TABLE 2
THE POSITIONS OF THE ABSORPTION BANDS OF THE CATALYST OF TYPE I

Catalysts prepared from	Position of the maximum of band (10^3, cm^{-1})		
$Cr(NH_3)_6^{3+}$	39.3	28.2	21.2
$Cr(C_5H_7O_2)_3$	29.2	25.6	17.8
$Cr(C_6H_5O_7)$	33.0	23.5	17.2
$CrCl_3 \cdot 6H_2O$	28.0	22.7	15.8

studied at low pressure. For example, Fig. 1 shows the polymerization kinetics for the catalyst prepared from $Cr[NH_3]_6[NO_3]_3$ and activated under various conditions. Catalysts of type I show the catalytic activity at the activation temperature higher than 300°C or so. As the temperature of the vacuum treatment increases the activity also increases, and attains its maximum at region of 500°C, Fig. 1. Heating in CO at 500°C for 1 hr followed by pumping out of CO for 15 min at the same temperature results in the complete deactivation of the catalysts. Similar results were also obtained for other catalysts of type I.

The catalysts of type II treated at the same conditions (pumping at 10^{-6}–10^{-5} Torr in the temperature range 100–600°C) did not show any catalytic activity.

The catalysts of type I just after impregnation or the drying at moderate temperatures contain Cr^{3+} ions in the octahedral coordination. Their optical spectra (Table 2) are typical of the octahedral coordination of Cr^{3+} ions (*6,10,11*), and EPR spectra show an asymmetric line with the $g \approx 2$, Fig. 2A, characteristic of Cr^{3+} ions (*6,11*). As temperature of the vacuum treatment increases, the EPR spectra change, Fig. 2B. These changes may be caused either by H_2O desorption from the coordination sphere of Cr^{3+} ions or by reduction of Cr^{3+} ions into the divalent state. In the former case a decrease of the EPR signal intensity will be observed. This decrease is caused by a decreasing of an indirect exchange interaction between Cr^{3+} ions, which results in broadening of the EPR signal (*11*). In the second case it is caused by the absence of an EPR spectrum from Cr^{2+} ions under given conditions (*12*). The changes of the optical spectra during the vacuum treatment, Fig.

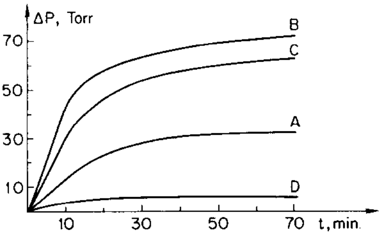

FIG. 1. The kinetics of the polymerization on the catalysts from $Cr(NH_3)_6^{3+}$ evacuated at 400°C (A), 500°C (B), 600°C (C), reduced in CO at 500°C (D).

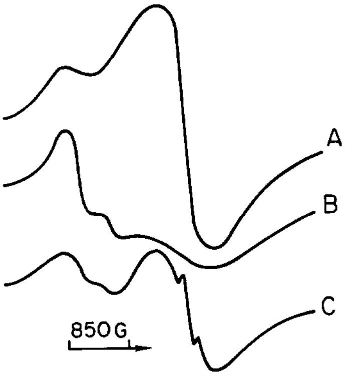

FIG. 2. EPR spectra of the catalysts from $Cr(NH_3)_6^{3+}$: (A) before the activation, (B) after the activation in vacuum at 500°C for 2 hr, (C) after H_2O adsorption on (B).

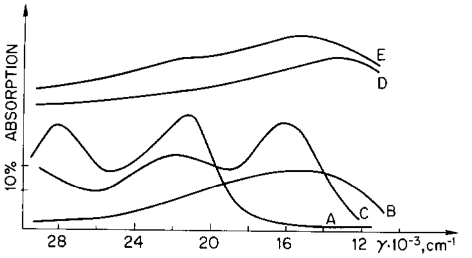

FIG. 3. The optical spectra of the catalyst from $Cr(NH_3)_6^{3+}$: (A) before activation, (B) after activation in vacuum at 500°C, (C) after H_2O adsorption on (B), (D) after reduction in CO at 600°C, (E) after H_2O adsorption on (D).

3B, can be also caused by the two above reasons. In order to understand which of these two reasons is responsible for the changes in the spectra we performed adsorption of H_2O molecules at room temperature. The H_2O adsorption gives rise to the bands of absorption in optical spectra, Fig. 3C, and the broad line with $g \approx 2$ in EPR spectra, Fig. 2C, that are characteristic of Cr^{3+} ions in the octahedral coordination. These changes provide evidence that the partial degradation of the first coordination sphere of Cr^{3+} ions takes place during the vacuum thermal treatment which results in the formation of surface exposed Cr^{3+} ions. During adsorption of water the molecules enter into the first coordination sphere of these ions changing its symmetry to the octahedral one. It should be noted that these effects are observed more clearly for the sample prepared from $[Cr(NH_3)_6]^{3+}$ complexes than for the other samples of type I. Apparently the amount of the exposed Cr^{3+} ions on their surface is less.

After reduction of the catalysts by carbon monoxide which is simultaneous with a sharp decrease of the catalytic activity, Fig. 1D, the majority of Cr^{3+} ions are reduced to the bivalent state. This is seen from the EPR and optical data. No EPR spectra are observed in the reduced catalysts both before and after H_2O adsorption at room temperature, a typical phenomenon for Cr^{2+} ions (*13*). In the optical spectra there is only one broad band, Fig. 3D and E, both before and after H_2O adsorption characteristic of Cr^{2+} ions (*4,13*). The maximum of this band shifts to the short wave region after the adsorption of water. As has been shown (*13*), such a shift indicates that the Cr^{2+} ions have a low coordination, e.g., they are the exposed ions.

It has been suggested (*14*) that the reduction in CO may result in the stabilization of these molecules in the coordination sphere of the surface ions, and hence, in the deactivation of the catalysts. But under our conditions of the reduction and pumping, as shown by ir spectra, there were no carbon monoxide molecules in the coordination sphere of the ions so far as there were no bands in the region of 2170–2200 cm^{-1} characteristic of the adsorbed and coordinated CO molecules (*15*). Moreover, reduction under these conditions does not give lines characteristic of the carbonate-carboxylate structures.

In the optical spectra of the catalysts of type II just after impregnation and drying at moderate temperature there was only a band, Fig. 4A, characteristic of Cr^{2+} ions, as we have discussed above. Thermal treatment of the samples at temperatures of 350–500°C in vacuum resulted in the absorption over a wide region of the spectra, Fig. 4B. Subsequent adsorption of water at room temperature restored the original band in part, Fig. 4C. There were no EPR from type II catalysts in all cases.

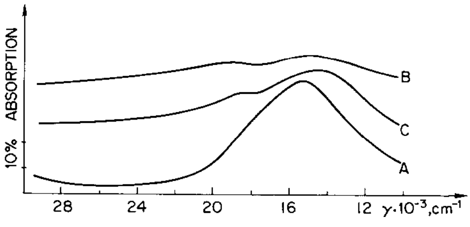

FIG. 4. The optical spectra of the catalyst prepared from $CrCO_3$: (A) before activation, (B) after vacuum treatment at 400°C for 2 hr, (C) after H_2O adsorption on (B).

These variations of the optical spectra show that the surface Cr^{2+} ions of low coordination state are formed during the thermal treatment in vacuum as well as for the catalysts of type I. Hence, not the lack of the exposed chromium ions but their valence state is responsible for the lack of the activity of the catalysts of type II.

Thus, a considerable drop of the activity upon rigid reduction in CO of the catalysts prepared from the trivalent chromium compounds and the lack of the activity in the samples prepared from the divalent chromium compounds, as well as the data obtained from the spectroscopic studies, allow one to draw the conclusion that the chromium ions in the active centers are in the trivalent state before the reaction. An increase of the activity of the catalysts with an increase of temperature of the vacuum treatment is caused by an increase of the number of Cr^{3+} ions of low coordination state.

Catalysts Prepared from Sexivalent Chromium Ions

The catalytic activity of these catalysts was studied at room temperature because at higher temperature the valency of chromium ions would be changed during the usual reduction process. Such change would make the determination of the valency of chromium responsible for the catalytic activity difficult. The kinetics of the polymerization were similar to that shown in Fig. 1. In all cases the induction period did not take place. Its absence shows that the active centers of polymerization have been formed during the activation. The polymerization rate was calculated from the linear part of the kinetic curves and is given in Table 3. As seen from Table 3, the catalyst (No. 1) activated at moderate condition has the most activity. An optimal condition of activation (time and temperature of reduction) were also referred to earlier for supported chromia catalyst (*16*).

TABLE 3

THE DEPENDENCE OF THE ACTIVITY OF THE CHROMIA CATALYSTS ON THE CONDITIONS OF THE REDUCTION IN CO

No.	Conditions		Polymerization rate (relative units)
	Temp (°C)	Time (min)	
1	300	45	220
2	500	45	60
3	500	5 hr	20

The most active catalyst contained a set of chromium ions from Cr^{6+} to Cr^{2+}. The evidence for such a conclusion are the optical and EPR data. Cr^{6+}, Cr^{3+} and Cr^{2+} ions were easily identified by the optical spectroscopy from the bands characteristic for these ions (*4,13,17*). In the EPR spectrum of the catalyst there were signals characteristic for Cr^{5+} (*17*) and the broad line characteristic for Cr^{3+}. The catalysts with the middle activity had only one wide maximum at 13,000 cm^{-1} in its optical spectrum before adsorption of H_2O, Fig. 5A. Before adsorption no EPR signals were found. H_2O adsorption gave rise to the optical spectrum with two absorption maxima at 21,000 and 15,900 cm^{-1}, characteristic of the octahedrally coordinated Cr^{3+} ions, Fig. 5B, and in EPR spectrum there was a weak broad line typical for these ions. These changes in the spectra after the H_2O adsorption, as indicated above, provide evidence for the surface

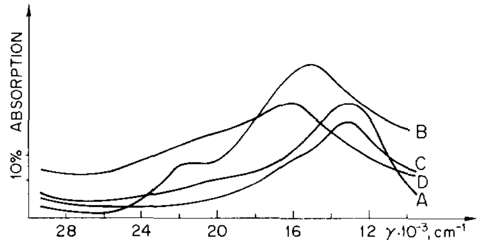

FIG. 5. The optical spectra of the catalyst prepared from H_2CrO_4: (A) after reduction in CO at 500°C for 45 min, (B) after H_2O adsorption on (A), (C) after reduction in CO at 500°C for 5 hr, (D) after H_2O adsorption on (C).

exposed Cr^{3+} ions in the catalysts. The optical spectrum of the least active catalyst had only one absorption maximum before and after H_2O adsorption, Fig. 5C and D, and no EPR signals were found. Hence only Cr^{2+} were detected within the sensitivity of EPR and optical spectroscopy methods. Cr^{2+} in this catalyst, as well as in the case of Cr^{2+} ions in the catalysts prepared from trivalent chromium compounds and reduced in CO, are exposed ions since H_2O adsorption led to a shift of the absorption maximum towards a short wave region.

A great decrease of the activity of the chromia catalysts with a degree of reduction and the optical data allow one to say that the polymerization activity is caused by the exposed Cr^{3+} ions as well as for catalysts prepared from the trivalent chromium compounds. The activity of the least active chromia catalyst (Table 3) is likely caused by Cr^{3+} ions retained in the sample in an amount that cannot be determined by EPR and optical spectroscopy.

CONCLUSION

The results obtained show that Cr^{3+} ions in the low coordinate state are present in the active centers of the catalysts of ethylene polymerization. But we have failed to obtain Cr^{2+} ions active in ethylene polymerization by the direct preparation of the catalysts from divalent chromium compounds and by the reduction of the supported trivalent chromium ions. We think that Cr^{2+} ions obtained upon reduction of the chromia catalysts which contain sexivalent chromium ions are also not active in the ethylene polymerization as was suggested in (*4*,*5*). In spite of the existence of Cr^{2+}–$[CH_2]_n$ complexes observed on the surface of chromia catalysts (*5*) the catalytic activity of the rigid reduced catalysts may be considerably less than the activity of those that were reduced under more moderate conditions.

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