Nature of Active Sites of Supported Chromic Oxide Polymerization Catalysts

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The active sites of chromic oxide polymerization catalysts form by interaction of the catalyst surface with monomer. Part of the Cr^{6+} atoms are reduced to the trivalent state and alkylated. The active sites are alkylated trivalent chromium atoms in combination with a Lewis acid. By lowering the electron density on the Cr^{3+} atom, the Lewis acid strengthens the Cr^{3+}–C bond in the polymer chain and increases the ability of the Cr^{3+} atoms to coordinate with the monomer molecules. On the other hand, coordination weakens the Cr^{3+}–C bond, which grows stronger again after the monomer molecule enters the chain. Polymerization occurs as a result of alternative strengthening and weakening of this bond. An effective carrier increases the oxidative power of the chromic anhydride and enhances the donor–acceptor properties of the chromium atoms. There is a direct dependence between the oxidative power of chromic oxide catalysts and the polyethylene yield on them, which persists up to a certain limit. The subsequent drop in activity is due to decreasing stability of the catalyst.

INTRODUCTION

Most workers relate the activity of supported chromic oxide–olefin polymerization catalysts to the presence of pentavalent chromium atoms on their surface *(1–13)*. But sufficient experimental data to confirm this point of view have not been obtained. To account for the fact that the most intense narrow EPR signal ascribed to Cr^{5+} atoms is observed, in contradiction to theory, in alumo–chromium catalysts, which are much less active than chromia–aluminosilicate catalysts it had to be assumed *(11–13)* that Cr^{5+} atoms could exist in two modifications, namely, an active one (tetrahedric coordination) and inactive one (octahedric coordination), and that the latter modification was the predominant one on aluminium oxide *(11)*.

In a previous paper *(14)* it was asserted that pentavalent chromium atoms could not be responsible for the catalytic activity of chromic oxide catalysts. An active surface can form only as a result of interaction between catalyst and monomer. Pretreating the catalyst with heptane under the conditions of the experiment almost completely deactivates it, whereas according to published data when a chromic oxide catalyst is reduced by a hydrocarbon solvent, a considerable amount of pentavalent chromium atoms come out on its surface. It was also shown in that paper that to be active in the absence of a promoter, the initial catalyst must contain hexavalent chromium atoms, and that the beginning of the reaction always coincides with the beginning of reduction of Cr^{6+} atoms, and hence it was suggested that reduction of these atoms to the trivalent state by monomer involves alkylation with the formation of a Cr^{3+}–C bond. The following structure was ascribed to the active complex

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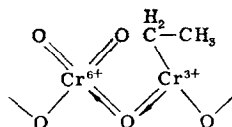
The pronounced Lewis acid properties of CrO_3 cause a redistribution of electron density in the complex, displacing it towards the hexavalent chromium atoms. The decrease in positive charge of the hexavalent chromium atoms accounts for the appearance of Cr^{5+} atoms on the surface. However, since the complex is active only if trivalent chromium atoms are alkylated during its formation, which occurs only when the catalyst is reduced by monomer, and there is no Cr^{3+}–C bond in the chromium chromate formed as a result of mild reduction of the catalyst by solvent, pentavalent chromium atoms obviously have no direct relation to the activity of catalyst. The only condition for catalyst activity is the presence of a Cr^{3+}–C bond and of a Lewis acid. The latter need not necessarily be only CrO_3, but also the carrier. For example, a chromia–aluminosilicate catalyst deactivated as a result of reduction of Cr^{6+} to Cr^{3+} by alcohol, is reactivated in the presence of the alkylating agent $Al(i-Bu)_3$.

By decreasing the electron density on the Cr^{3+} atom of the active complex, the Lewis acid increases its ability to coordinate with the olefin molecule, on the one hand, and increases the strength of the Cr^{3+}–C bond, on the other. Coordination of the monomer molecule with the Cr^{3+} atom, involving passage of its π-electrons on to the incomplete d-levels of the chromium atom, weakens the Cr^{3+}–C bond of the growing polymer chain, and thus facilitates instillation of the coordinated olefin molecule at this bond. After the monomer molecule has entered the chain the Cr^{3+}–C bond again grows stronger until a new monomer molecule enters into coordination linkage with the Cr^{3+} atom. Thus, chain propagation proceeds by alternative weakening and strengthening of the Cr^{3+}–C bond, and this is possible only if the chromium atoms have a high donor–acceptor capacity.

Hence, chromic oxide polymerization catalysts must be of high oxidative power to ensure easy transition of Cr^{6+} into Cr^{3+} and simultaneously alkylation of trivalent chromium atoms by monomer, and have high donor–acceptor capacity to facilitate alternative strengthening and weakening of the bond, which makes possible the very process of polymerization.

This paper gives experimental data demonstrating that these conditions can be set up by selecting a suitable carrier and confirming the ideas suggested previously concerning the nature of active sites, the conditions of their formation, and the mechanism of polymerization of α-olefins on them.

EXPERIMENTAL

Chromic oxide catalysts were prepared by impregnating carriers with an aqueous solution of chromic anhydride and drying subsequently at 105° and then at 160°C for 4 hr.

The carriers are characterized by the data of Table 1. The pumice surface area was tentatively taken to be 10 m²/g. Carrier particle size was in the 0.25–0.5 mm range.

The silica gel and pumice were pretreated repeatedly by boiling with concentrated hydrochloric acid solution, and then washed with distilled water to negative reaction to chloride ion, dried and calcined at 500°C.

SiO_2 was applied to pumice by impregnating it with Na_2SiO_3 solution, drying, treating with hydrochloric acid solution, and washing to remove chloride ion. Aluminium oxide was applied to aluminosilicate by impregnating the latter with solutions of aluminium nitrate of different concentrations and subsequently drying at 105°C and calcining at 500°C. The aluminosilicate

TABLE 1

SPECIFIC SURFACE AREA AND AVERAGE
PORE RADIUS OF CARRIERS

Carrier	Specific surface area (m²/g)	Average pore radius (Å)
Commercial aluminosilicate (3% Al₂O₃)	412	40
Aluminium oxide (I)	142	42
Aluminium oxide (II)	327	36
Silica gel (I)	424	38
Silica gel (II)	704	8
Pumice	~10	—

treated with 0.2 N NaOH solution was also dried and then calcined at 500°C.

The measure of oxidizing power of the resulting samples was the degree to which they were reduced by benzene at 140°C in 1 hr. The degree of reduction is here defined as the ratio of reduced hexavalent chromium to its total initial content. Reduction was carried out by the method described earlier (14–15).

The thermal stability of the initial samples and their capacity for oxidation by atmospheric oxygen after complete reduction by alcohol was determined by calcining at 500°C for 2 hr in a muffle furnace. The measure of thermal stability and of degree of oxidation was the ratio of residual or newly formed CrO_3 to its total content in the sample.

CrO_3 content was determined by extraction by boiling weighed portions (0.3–0.5 g) of the sample repeatedly with sulphuric acid solution (1:50). The solution was decanted on a No. 2 glass filter, collecting the filtrate in a flask with a ground glass stopper. Then 15–20 ml of 10% KI solution and 30 ml of 2 N H_2SO_4 were added, and the iodine liberated was titrated 20 min later with 0.1 N hyposulphite solution.

The catalyst was activated in glass am-

pules at 350°C and 10^{-1} mm Hg for 3 hr and at 10^{-4} mm for 2 hr, after which the ampules were sealed. Activity was determined by the yield of polyethylene.

Ethylene polymerization was conducted in a 300-ml autoclave with a screened electromagnetic stirrer, a device for breaking the ampule in the course of the test and a pocket for a thermocouple. The solvent was heptane. The conditions of purification of solvent and ethylene were described in earlier papers (14, 15). After ampules containing 0.25 g of catalyst were placed in the autoclave the latter was evacuated with a forepump during 4 hr at 250°C and then cooled to 0°C; then 140 ml of solvent was added, ethylene was admitted (initial pressure 15 atm), and the heater was switched on. When the temperature reached 140°C, the pressure was raised to 40 atm with ethylene and the ampule with the catalyst was broken. The test lasted 10 min, ethylene being added periodically. Then the autoclave was cooled quickly with a water–ice mixture, and 3 min later the ethylene was let out and it was discharged.

The polymer was dried to constant weight, and the yield was calculated in g/g of catalyst/hour, taking into account the weight of ampule with catalyst. To obtain

TABLE 2

Effect of Carrier in Chromic Oxide Catalysts on Oxidizing Power and Thermal Stability of Chromic Anhydride[a]

Carrier	Oxidizing power (degree of reduction by benzene at 140°C, %)	CrO_3 content after calcining at 500°C, % of initial content	
		Dried samples	Reduced with alcohol
Aluminosilicate	60.5	64.0	57.0
Silica gel (I)	67.8	61.5	53.5
Silica gel (II)	—	80.5	74.0
Aluminium oxide (I)	31.8	51.0	—
Aluminium oxide (II)	13.7	77.9	76.5
Pumice	0.0	0.0	—
Pumice with 15% SiO_2 applied	62.0	31.0	—
Aluminosilicate treated with 0.2 N NaOH	0.0	100	—
No carrier	—	0.0	—

[a] Samples contained ca. 6.5% CrO_3.

comparable results, each run of tests was carried out with ethylene and solvent of the same purification batch. The entire system, including purification and solvent feed, was completely hermetical.

RESULTS AND DISCUSSION

Table 2 contains comparative data on the oxidizing power of chromic anhydride on various carriers, determined by treating the samples with benzene at 140°C for 1 hr. It is evident from these data that reduction is highest on aluminosilicate and silica gel. On an inert carrier, namely, pumice, CrO_3 was practically not reduced at all, but after 15% SiO_2 was applied to its surface, it was reduced to a degree of 62%. The sample obtained by applying CrO_3 to aluminosilicate pretreated with 0.2 N NaOH had no oxidizing power either. Hence, the nature of carrier affects the oxidizing power of chromium anhydride.

Table 3 and Fig. 1 show the dependence of the activity of catalyst samples on their oxidizing power. In these samples the carrier was aluminosilicate with various amounts of aluminium oxide additionally applied to its surface, and aluminosilicate pretreated with 0.2 N NaOH. The carrier for one of the samples was silica gel of specific surface area and pore radius close to those of the aluminosilicate.

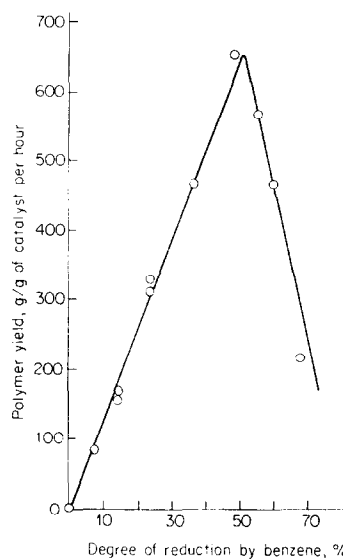It is evident that with increasing oxidizing power of the samples the polymer

FIG. 1. Dependence of polyethylene yield over chromic oxide catalysts on their oxidizing power.

yield rises linearly at first and then falls off abruptly. The existence of an inverse linear dependence is obviously related to the fact that after a definite oxidizing power is reached the stability of the catalyst begins to decrease. The stability of the Cr^{6+} atoms in the active complex against reduction by monomer and solvent is due to the decrease in their positive charge owing to redistribution of electron density between Cr^{3+} and Cr^{6+}. If the oxidizing power is too high, such stabilization is insuffi-
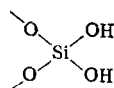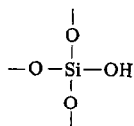
TABLE 3

POLYETHYLENE YIELD ON CHROMIC OXIDE CATALYSTS OF DIFFERENT OXIDIZING POWER[a]

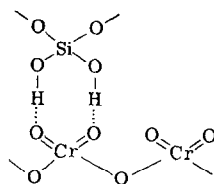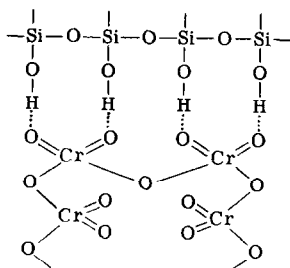| Carrier	Oxidizing power (degree of reduction by benzene at 140°C, %)	Polymer yield (g/g-cat./hr)
Aluminosilicate treated with 0.2 N NaOH	0	0
Aluminosilicate with Al₂O₃ applied (%) 20	7.5	85
15	14.5	158
13	23.5	316
6.5	36.5	470
3.0	49.5	655
1.5	56.0	570
Aluminosilicate	60.5	470
Silica gel (I)	68.0	220

[a] Experimental conditions: temperature 140°C; pressure 40 atm; duration 10 min; solvent, heptane; CrO_3 content in samples ca. 6.5%.

ciently effective and the number of active sites decreases. The oxidizing power of the sample containing an additional 3% Al_2O_3 was optimal.

The high oxidizing power of CrO_3 on silica gel and on aluminosilicate should be attributed to the acidic properties of the surfaces of these carriers. In the case of silica gel, the oxygen atoms of the chromic anhydride evidently coordinate with the protons of the hydroxyl groups, forming a compound of the conjugated acid type. Since there are two types of hydroxyl groups on the surface of silica gel (16), corresponding to the structures

benzene under the conditions used became possible only after its content in the sample began to exceed the amount necessary to form a chemical compound with the surface. The amount of chemically bound, CrO_3 increased with increasing surface area, and the degree of reduction declined accordingly (see Tables 1 and 2). However, since the aluminium chromate has a strong Lewis acid, namely, aluminium oxide, as its substrate, it has a higher oxidizing power than pure aluminium chromate and initiates electron shift in the CrO_3 monolayers not bound chemically to the surface, thus increasing their reducibility. The structure

the conjugated acids accordingly have the following forms:

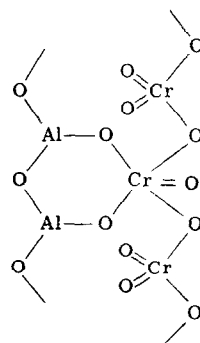of the alumo–chromium catalyst can be imagined as follows:

The formation of a coordination bond between the oxygen atoms of chromic anhydride and the protons of the silica-gel hydroxyl groups lowers the electron density on the chromium atom of chromic anhydride and thus increases its oxidizing power. The shift of electron density in the first monolayer of chromic anhydride initiates a similar shift in the subsequent monolayer, which are tied to each other with oxygen cross-links.

The reaction of CrO_3, with the surface hydroxyl groups of aluminium oxide results in a compound of the type of aluminium chromate. Like any other salt of chromic acid, aluminium chromate possesses a much lower oxidizing power than chromic acid itself. Therefore, reduction of CrO_3 with

The aluminosilicate contains montmorillonite- and aluminosilica-gel-type structures (16). Neither of these structures have any hydroxyl groups at their silicon atoms, because their protons are substituted by

aluminium ions. The number of hydroxyl groups tied to the aluminium atoms in the aluminosilica-gel-type structure is very insignificant, and in the montmorillonite-type structure these groups are inaccessible to the reactant molecules. For this reason the high oxidizing power of chromia–aluminosilicate catalysts can be due only to the formation of a coordination bond between the oxygen atoms of chromic anhydride and the exchangeable and inexchangeable surface aluminium atoms.
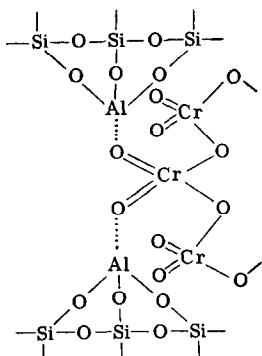
The coordination bond with the surface can probably be accomplished by two or by one of the chromic anhydride oxygen atoms.

Hexavalent chromium atoms can pass into a lower valency state only if the oxygen atoms tied to them are simultaneously removed; in the first monolayer the latter are bound coordinationally to the hydroxyl group protons of silicon atoms or to the aluminium atoms of aluminosilicate, and in aluminium oxide they are bound chemically to the surface. Therefore, reduction of this layer is difficult in chromic oxide catalysts. With increasing chromic anhydride content, the degree of reduction of catalyst increases. The dependence of the degree of reduction on the CrO$_3$ content for

the case of a chromia–aluminosilicate catalyst is shown in Table 4.

Increase of the oxidative power of chromic anhydride should favor greater shift of the electron density from Cr^{3+} to Cr^{6+}, which is probably the reason for the narrowing of the EPR signal on carriers possessing the property of an aprotonic acid, compared to pure chromium chromate.

It follows from the data of Table 2 that all the carriers used, except for pumice, were able to increase the thermal stability of chromic anhydride. This ability is evidently due to the formation of a coordination or chemical bond between the oxygen atoms of the chromic anhydride and the carrier surface, as a result of which passage of electrons of the oxygen atoms to the d-orbital of the hexavalent chromium atoms accompanied by reduction of the latter to the trivalent state and liberation of free oxygen, becomes difficult. With increasing CrO$_3$ content in the sample thermal stability decreases (Table 4). At the same time, when a sample containing only Cr^{3+} atoms owing to reduction with alcohol, is calcined in air at 500°C, part of the trivalent chromium atoms are reoxidized to the hexavalent state, the degree of oxidation achieved coming close to the thermal stability of the initial sample at the same temperature (Table 2). The slightly lower value of the former of these values is probably due to the fact that on reduction with alcohol part of the Cr$_2$O$_3$ loses its linkage with the surface as a result of rupture of the oxygen cross-link.

The readier reducibility of hexavalent chromium atoms on the carrier suggests that the carrier increases the ability of chromium ions both to accept and to give away electrons.

TABLE 4

DEPENDENCE OF DEGREE OF REDUCTION AND THERMAL STABILITY OF CHROMIA–ALUMINOSILICATE CATALYST ON ITS CrO$_3$ CONTENT

CrO$_3$ content of initial sample (%)	0.5	1	3	6	10	20
Degree of reduction by benzene at 140°C (%)	50	54	—	60.5	72.0	89.0
Thermal stability (CrO$_3$ content, % of initial after calcining at 500°C)	—	100	100	60.9	42.7	31.0

Thus, in chromic oxide catalysts an effective carrier will increase the oxidizing power of the chromic anhydride and enhance the donor–acceptor properties of the chromium atoms.

Since aluminium oxide forms a chemical compound with CrO_3, it does not fully satisfy one of these conditions and is, therefore, a less effective carrier in chromic oxide catalysts than silica gel or aluminosilicate. The Lewis acid evidently plays a similar part in Ziegler–Natta-type catalytic systems, i.e., it lowers the electron density on the atom of the transition metal, increases its donor–acceptor properties and strengthens the transition metal carbon bond, subsequent weakening of which is not due to formation of a cross-linkage of the type
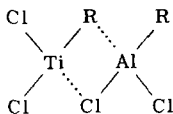
but to coordination of the monomer molecule with the transition metal atom.

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