# Reports of the Academy of Sciences of the USSR

Yu. I. PECHERSKAYA, V. B. KAZANSKII

1965

SovietRxiv

## Abstract

## Full Text

Reports of the Academy of Sciences of the USSR

1965, Volume 162, No. 5

## PHYSICAL CHEMISTRY

**Yu. I. PECHERSKAYA, V. B. KAZANSKII**

# ON THE MECHANISM OF INHIBITION OF THE ETHYLENE POLYMERIZATION REACTION ON CHROMIUM OXIDE CATALYSTS

*(Presented by Academician V. V. Voevodskii, December 3, 1964)*

It is known that the rate of the ethylene polymerization reaction, proceeding in the presence of supported chromium oxide catalysts, is strongly affected by impurities present in the ethylene and in the solvents. The strongest inhibitors are water, oxygen, carbon monoxide, and organic oxygen-containing compounds (alcohols, aldehydes, ketones) (1). In this connection, the starting materials require a very high degree of purification. For example, an oxygen impurity in the solvent in an amount above 0.1% almost completely suppresses polymerization, and the water content must not exceed five parts per million (2). Such a high degree of purification greatly increases the cost and complicates the process of ethylene polymerization. To overcome these difficulties, it is very important to establish the detailed mechanism of inhibition. In the present work a new approach to solving this question is proposed, using the e.p.r. method.

In our previous works it was shown that the active centers in chromium oxide catalysts for ethylene polymerization are pentavalent chromium ions stabilized on the surface (3–5). Analysis of the form of the e.p.r. signals of catalysts supported on silica gel and aluminosilicate led us to the conclusion that their asymmetry is caused by anisotropy of the $g$-factor, and made it possible to propose a model for the structure of the active centers (5). According to this model, on the surface of silica gel and aluminosilicate with a low content of aluminum oxide, the $Cr^{5+}$ ions are located at the center of a distorted tetrahedron of oxygen atoms. When carrying out the polymerization reaction directly in the resonator of the e.p.r. spectrometer, we found that the form of the signals from $Cr^{5+}$ ions changes during the reaction (3). We also observed an analogous phenomenon upon separate treatment of the catalyst with the components of the ethylene polymerization reaction, which was explained by their chemisorption on the active centers (4). The observed effects make it possible to approach in a

Figure 1

Figure 1: Figure 1

new way the elucidation of the mechanism of the inhibiting action of catalytic poisons in the ethylene polymerization reaction on chromium oxide catalysts. Indeed, by studying changes in the e.p.r. spectra upon adsorption on the catalyst surface of inhibitors, both in pure form and in a mixture with ethylene, one can draw definite conclusions about the nature of their interaction with the active centers and establish whether they act by the same mechanisms.

The catalyst used by us, supported on aluminosilicate of composition 97% $SiO_2$ and 3% $Al_2O_3$, contained 2.5% chromium. The method of its preparation is described in work (3). Thermal activation of the samples was carried out by heating them in vacuum at 400° for 4 hours in ampoules of special design (4). After completion of activation, the ampoules were sealed off, and the catalyst samples were subsequently not exposed to air. Measurements of the e.p.r. spectra were carried out on an RE-1301 instrument in the temperature interval from room temperature to 150°. A constant temperature in the resonator was maintained with the aid of a jet of heated air (6).

If vapors of butanol, butyraldehyde, or water are introduced at room temperature into an ampoule with a catalyst sample evacuated at 400°, an instantaneous change is observed in the form of the e.p.r. signal from pentavalent chromium ions: its amplitude increases strongly, and the width

decreases (see Fig. 1). Pumping at room temperature does not restore the original shape of the signals.

The analysis we carried out of the shape of the EPR lines after treatment of the catalyst with the listed substances showed that, just as in the initial catalysts, it is due to anisotropy of the *g*-factor. This is seen from Fig. 1b, where the theoretical anisotropic line, calculated on an electronic computer (7, 8), is superimposed on the signal observed after treatment of the catalyst with butanol. The satisfactory agreement of these curves confirms our conclusion.

**Fig. 1.** Change in the EPR spectrum of an activated chromaluminosilicate catalyst upon treatment with butanol vapors at room temperature:
*a*—catalyst in vacuum, *b*—after treatment with butanol (1—theoretical shape of the anisotropic line, 2—experimental line). (Instrument gain was the same in both cases.)

Table 1 gives the values of $g_\perp$ and $g_\parallel$, characterizing the anisotropy of the *g*-factor of the EPR signals from $Cr^{5+}$ ions before and after treatment of the catalyst with alcohol, water, and aldehyde. Comparison of these values shows that, under the action of catalytic poisons, the anisotropy of the *g*-factor of the signals decreases. The value of $g_\perp$ remains unchanged, while $g_\parallel$ approaches 2. The action of water, alcohol, and aldehyde leads in practice to identical changes in the shape of the signals.

Changes in the shape of the EPR signal from the $Cr^{5+}$ ion upon treatment of the catalyst with catalytic poisons, as already stated above, are explained by adsorption of inhibitor molecules on active centers. Since the changes in the signals under the action of water, alcohol, and aldehyde are analogous, it is obvious that the adsorbed molecules form bonds of the same type with the catalyst.

Both water, alcohol, and aldehyde contain in their molecules oxygen atoms possessing unshared electron pairs. $Cr^{5+}$ ions, on the other hand, are positively charged and possess vacant *d*-orbitals. It may be assumed that adsorption involves the formation of a donor-acceptor bond with transfer of the unshared electron pair of the oxygen atoms to the vacant orbitals of the pentavalent chromium ions. In this process the coordination of surface pentavalent chromium ions and the nature of the splitting of their orbital levels change, which may lead to the experimentally observed change in the value of $g_\parallel$ while the value of $g_\perp$ is retained.

**Table 1**

**Change in the parameters of the anisotropic signal from $Cr^{5+}$ ions in the spectrum of a chromaluminosilicate catalyst treated with various substances at 20°**

| Substance | $g'_\perp$ | $g''_\parallel$ | $\Delta H_{an}$, oersted |
|---|---|---|---|
| | with accuracy ±0.005 | with accuracy ±0.005 | |
| In vacuum at 20° | 1.975 | 1.900 | 140 |
| $H_2O$ | 1.977 | 1.954 | 40 |
| $C_4H_{10}OH$ | 1.977 | 1.948 | 50 |
| $C_3H_7CHO$ | 1.977 | 1.956 | 37 |
| $(C_2H_4)_{ads} + O_2$ | 1.977 | 1.957 | 35 |
| $(C_2H_4)_{ads} + CO$ | 1.977 | 1.946 | 56 |

If adsorption of vapors of water, alcohol, and aldehyde is carried out at elevated temperature, or if samples with adsorbed on the surface···

surface at room temperature, then, in addition to a change in the shape of the EPR signals from pentavalent chromium ions, a decrease in their intensity is also observed. As an example, Fig. 2 presents experimental data on the change with time in the intensity of the EPR signals of catalysts with water preadsorbed (at room temperature) during heating. It can be seen from the figure that a sharp change in the signal intensity occurs during the first 30 min after the beginning

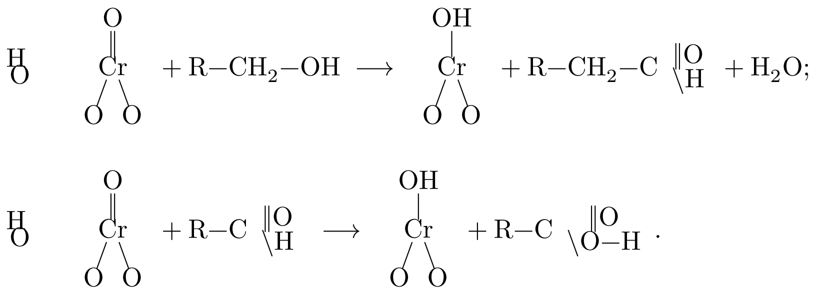
Fig. 2. Change in the intensity of the EPR signal of a catalyst preliminarily treated with water at 20° after heating it at elevated temperatures: 1 –at 40°; 2 –60°; 3 –120°

Figure 2: Fig. 2. Change in the intensity of the EPR signal of a catalyst preliminarily treated with water at 20° after heating it at elevated temperatures: 1 –at 40°; 2 –60°; 3 –120°

of adsorption, and then the line remains practically unchanged. The curves seem to tend toward a certain limiting value characteristic of each temperature; for example, at 120° the signal intensity decreases by a factor of 20, while at 40° only by a factor of 3. These results show that at elevated temperatures the relatively weak coordination form of chemisorption of alcohol, water, and aldehyde passes into a stronger one, leading to a change in the valence state of the Cr^5+ ions.

**Fig. 2. Change in the intensity of the EPR signal of a catalyst preliminarily treated with water at 20° after heating it at elevated temperatures: 1 –at 40°; 2 –60°; 3 –120°.**

In the case of alcohol and aldehyde, which are known to be strong reducing agents, Cr^5+ may pass into Cr^3+. Using the structure of the active center proposed by us, this reduction can be represented by the following reactions:



In the case of water, both reduction and oxidation of Cr^5+ ions may occur; however, in either case their valence state evidently changes, since the intensity of the EPR signals decreases. Since the signal from Cr^5+ ions can be regenerated upon reductive treatment–evacuation of water at temperatures of 300-400° (practically upon repeated activation of the sample)–it appears to us that oxidation is the more probable process.

The characteristic shape of the curves in Fig. 2, which are essentially kinetic curves of chemisorption, indicates the inhomogeneity of the active surface of chromia catalysts, which is in agreement with the data obtained in studying the kinetics of ethylene polymerization (9, 10), and with conclusions drawn by us on the basis of an analysis of the EPR spectra of activated catalysts (5). From

Fig. 3

Figure 3: Fig. 3

These curves also show that high-temperature chemisorption requires activation energy, in contrast to low-temperature chemisorption, which occurs instantaneously.

The results presented show that such catalytic poisons as water, alcohol, and aldehyde inhibit the polymerization reaction by two mechanisms: they can block active centers as a result of the formation of a donor–acceptor coordination bond, which is observed at low temperatures, and, in addition, destroy them by changing the valence state, which occurs at high temperatures. It is significant that in both cases these poisons act directly on the active centers of the catalyst.

**Fig. 3.** Change in the shape of the EPR signal of a chromaluminosilicate catalyst during its successive treatment with ethylene and carbon monoxide: *a* —catalyst in vacuum, *b*—catalyst after adsorption of ethylene at 100°, *c*—the catalyst in ethylene was treated with CO at room temperature. The instrument gain during recording of all spectra was the same.

As follows from our experimental data, poisons such as oxygen and carbon monoxide evidently act differently. These substances by themselves change neither the shape nor the intensity of the EPR signals from $Cr^{5+}$ ions either at high or at low temperatures (oxygen only reversibly broadens the signals from $Cr^{5+}$ ions by a magnetic dipole–dipole mechanism as a result of physical adsorption ([11])). If, however, oxygen or carbon monoxide is added to ethylene or is adsorbed on the surface of a catalyst previously treated with ethylene, then a change in the line shape is observed that is the same as in the case of low-temperature adsorption on the surface of catalysts of oxygen-containing compounds (Fig. 3, Table 1).

This result indicates that the mechanism of the inhibiting action of oxygen and carbon monoxide differs from the action of alcohol, water, and aldehyde. Oxygen and CO apparently do not act directly on the active centers, but break off the growing polymer chains as a result of reaction with an active complex adsorbed on $Cr^{5+}$ ions. In this process oxygen-containing compounds may be formed, the adsorption of which by a coordination mechanism leads to the changes observed experimentally in the EPR spectra. This conclusion is in agreement with observations made in works ([12,13]), where it was established that additions of oxygen to the starting feedstock decrease the molecular weight of polyethylene and increase the content of carbonyl groups in its molecules.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
29 XI 1964

## CITED LITERATURE

1. H. Gaylord, H. Mark, *Linear and Stereoregular Polymers*, IL, 1962, p. 305.
2. G. K. Boreskov, V. A. Dzis' ko, T. Ya. Tyulikova, DAN, **136**, 125 (1961).
3. F. M. Bukanayeva, Yu. I. Pecherskaya et al., *Kinetika i kataliz*, **3**, 358 (1962).
4. V. B. Kazanskii, Yu. I. Pecherskaya, *Kinetika i kataliz*, **4**, 244 (1963).
5. I. V. Aleksandrov, V. B. Kazanskii, I. D. Mikheikin, *Kinetika i kataliz*, **6**, No. 3 (1965).
6. Yu. D. Tsvetkov, Ya. S. Lebedev, V. V. Voevodskii, *Vysokomolek. soed.*, **1**, 1519 (1959).
7. Ya. S. Lebedev, *Zhurn. strukt. khimii*, **3**, 151 (1962).
8. Ya. S. Lebedev, *Zhurn. strukt. khimii*, **4**, 24 (1963).
9. A. Clark, G. Bailey, *J. Catal.*, **2**, 230 (1963).
10. A. Clark, G. Bailey, *J. Catal.*, **2**, 241 (1963).
11. V. B. Kazanskii, Yu. I. Pecherskaya, *Kinetika i kataliz*, **2**, 454 (1961).
12. V. Dalig, S. Benbenek, B. Dechkovskii, *Khim. i tekhnol. polimerov*, No. 4, 23 (1961); *Przemysl. Chem.*, **39**, No. 3, 167 (1960).
13. W. Dahlig, S. Benbenek, B. Deszkowsky, *Polimery*, **6**, No. 9, 283 (1961); *Chem. Abstr.*, **56**, 1037 (1962).

*Note: Figure translations are in progress. See original paper for figures.*

*Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.*