The charge percolation mechanism and simulation of Ziegler–Natta polymerizations. Part VI. Mechanism of ethylene polymerization by supported chromium oxide

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Abstract: Despite intensive research over the last 50 years, many questions concerning ethylene polymerization by supported chromium oxide are still unanswered. Hence, the very fundamental issues of this polymerization are discussed in this paper. It is shown that a charge percolation mechanism (CPM) of olefin polymerization by Ziegler–Natta transition metal complexes, recently proposed by us, can give the answers in this case, too.

Keywords: Ethylene polymerization, Phillips CrO_x/SiO_2, charge percolation mechanism.

INTRODUCTION

Ethylene polymerization by silica supported chromium oxide was discovered some fifty years ago and has attracted a great deal of academic and industrial research.[1] It is generally believed that the insertion mechanism[2,3] of Ziegler–Natta (ZN) polymerization can also be applied in this case. Despite the very extensive research, however, there are still many open questions:[1,4–8]

1. What is the oxidation state and structure of the active center?
2. What is the mechanism of initiation?
3. What is the mechanism of polymerization?
4. What is the physico–chemical state of the Cr species at the silica?
5. How to explain the polymerization kinetics, particularly the occasional appearance of an induction period?
6. How to explain the origin of the structure and very broad molecular weight distribution (MWD) of PEHD?
7. What is the role of silica and how to correlate its properties with the results of polymerization?

The same questions have been asked since the 1950s, when Hogan and Banks claimed that the Phillips catalysts "is one of the most studied and yet controversial system". In 1985, McDaniel[8] stated, "we seem to be debating the same questions posed over thirty years ago, being no nearer to a common view". Nowadays, in a review[4] published in 2005, it is stated that "it is interesting to underline that although in the last two decades a lot of progress has been made, no unifying picture has yet been achieved."

Fifty years – the same open questions, the same "Whats" and "Hows"!

Hence, at the beginning of this article, the fundamental facts and the presumptions trying to find out what is wrong will be re-examined. Then, a recently-proposed charge percolation mechanism (CPM) of olefin polymerization in presence of transition metal compounds[9–13] will be applied. The aim of this work was to show that the CPM also can be applied to explain ethylene polymerization by CrO_x supported on SiO_2 or some other supports. In a subsequent article[14] of this series, the most important and well-known empirical facts will be presented and explained by the CPM.

EMPIRICAL FACTS AND CONTROVERSIES OF CURRENT EXPLANATION

To find a way out of the deadlock it is necessary to return to the very beginning and to analyze the process in the most fundamental manner. There is no doubt that the Phillips process includes three basis participants, *i.e.*, monomer (ethylene) molecules, active centers (based on chromium) and the support (silica). The crucial question is: Why each participant (ethylene, chromium and support) enters into the process?

Ethylene polymerizability

Concerning ethylene, there is an excess of free energy stored in the dynamic movement of π-electrons, *i.e.*, four electrons are squeezed between two carbon atoms separated by 0.133 nm. (Hence, the ethylene molecule has a quadrupole moment, *i.e.*, the C–H bonds are partially polarized. The dipole moment of the C–H bond is 3.5×10^{-30} C m, *i.e.*, 1.05 D.[15] The partially positive charges are on the H atoms, while the partially negative charges are on and between the C atoms.) The second issue is the completely restricted rotation around the C=C bond. There is a thermodynamic tendency to liberate the free energy by polymerization, *i.e.*, to transform the double bonds into the single σ-bonds, which contain the only two electrons between the two more separated carbon atoms (0.154 nm). Simultaneously, rotation around the C–C bonds would be enabled. The negative change of enthalpy ($\Delta H = -92.7$ kJ mol^{-1}),[16] *i.e.*, the heat evolved in that process, is the thermodynamic "driving force" of the polymerization. To achieve this, however, it is necessary to sacrifice the relatively free movement of the ethylene molecules and to replace it by the segmental motion of the macromolecular chain. Hence, there is a large negative change of entropy of polymerization

($\Delta S = -0.14$ kJ mol^{-1} K). Despite this, the change in free energy even at atmospheric pressure and 500 K is negative, *i.e.*, $\Delta G = \Delta H - T\Delta S = -22.9$ kJ mol^{-1}. Hence, the high negative entropy change of polymerization is not a "limiting force" of the polymerization from the thermodynamic but from the kinetics standpoint.[16] Hence, it is necessary to achieve such polymerization conditions which enable both a negative change of free energy ($\Delta G = \Delta H - T\Delta S < 0$) and a less negative change of entropy. Ethylene alone can satisfy these requirements and can polymerize by the free radical mechanism only at extremely high pressures. Otherwise, it cannot polymerize without the aid of transition metal active centers and the help of a support which provides the conditions necessary for polymerization.[17]

Oxidation states of chromium active centers

But, why does chromium enter into the process and how does it help the ethylene molecules to polymerize? Let us consider the current explanation using the insertion mechanism.[1-3] Even the initiation reaction is not fully understood; it is believed that initially some alkylated chromium active centers are formed, *i.e.*, initial Cr−R species have to be formed. Whatever is the oxidation state of the active chromium centers, there is at least one empty d-orbital (□) on an alkylated chromium atom (□Cr–R). The chromium has a necessity to fill the empty orbital with electrons. According to the current explanation, propagation of the polymer chain consists of two steps. In the first one, an ethylene molecule (Et) is coordinated to a chromium atom supplying π-electrons to the empty orbital (Et···Cr–R). It seems that the chromium atom has filled the empty orbital. In the second step, however, it is proposed that the coordinated ethylene molecule escapes from the just filled chromium orbital and inserts itself into the Cr–R bond making the chromium orbital empty again (□Cr–Et Cr–R). It is believed that these two steps are repeated again and again, several thousands times. It is evident that the chromium active center is circumvented and deceived, again and again, several thousands times! Each time an ethylene molecule has fulfilled its tendency to polymerize, but the chromium active center has never filled the orbital! A similar insertion mechanism and quite similar open questions exist in the interpretation of the Phillips process, such as in the case of ZN polymerization of olefins.

In addition to the empty orbital, Cr atoms have a diversity of oxidation state. Various chromium compounds are used as precursors for the preparation of chromium active centers: oxides, acids, sulfates, acetates, *etc*. In the most cases, initially almost all Cr atoms of some precursor are in the same oxidation state, *i.e.*, Cr(III) or Cr(VI), sometimes Cr(II). After impregnation onto a support, the thermal treatment and activation in the presence of oxygen or an inert medium, and possible reduction by hydrogen or carbon monoxide, a diversity of Cr oxidation state is achieved. A typical Phillips catalyst with 1 wt. % Cr supported by silica, after calcination in dry air, shows the existence of mixed oxidation states: 70.4 %

Cr(VI) and 29.6 % Cr(III).[6] Further changes in the Cr oxidation states occur on addition of ethylene, *i.e.*, Cr(II), Cr(III), Cr(IV), Cr(V) and Cr(VI) oxidation states have been found.[4,6,7,18-29] Initially formaldehyde and ethylene oligomers are produced.[4,6,7] According to the proposed mechanism[7] (Fig. 1), some of the Cr(VI) atoms are transformed into the unstable transient Cr(IV), then reduced to Cr(II) species (steps 1 through 4, producing the species A, B, C, D and E). Starting from 70.4 % Cr(VI) and 29.6 % Cr(III), after ethylene addition, it was found that the fraction of Cr(VI) decreased to 47.8 %, while the fractions of Cr(III) and Cr(II) increased to 39.3 % and 12.9 %, respectively. It is believed that the increase of Cr(III) species is due to the interaction between Cr(II) and Cr(VI) species (step 5, producing F). It has been confirmed that surface Cr species in the oxidation states Cr(III) and Cr(V) showed no direct relationship with the polymerization activity and thus could be ruled out as the active Cr precursor.[25]
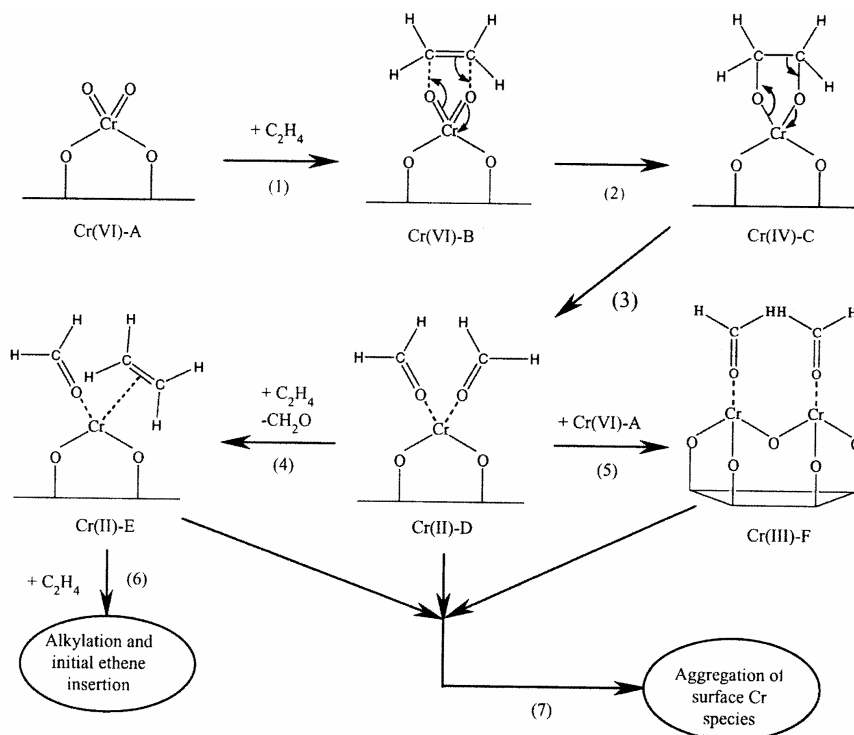

Fig. 1. Plausible mechanism of the reactions occurring on the CrO$_x$/SiO$_2$ catalyst engaged in the induction period through interaction with ethylene.[7]

In a case of Cr precursor treatment with CO, most of Cr atoms are reduced to the oxidation state Cr(II).[4,8,18-24] In the presence of ethylene, the oxidative addition of one, two or three ethylene molecules to Cr(II) species gradually converts them into various alkylated Cr(IV) species (Fig. 2).[4,26,28,29]
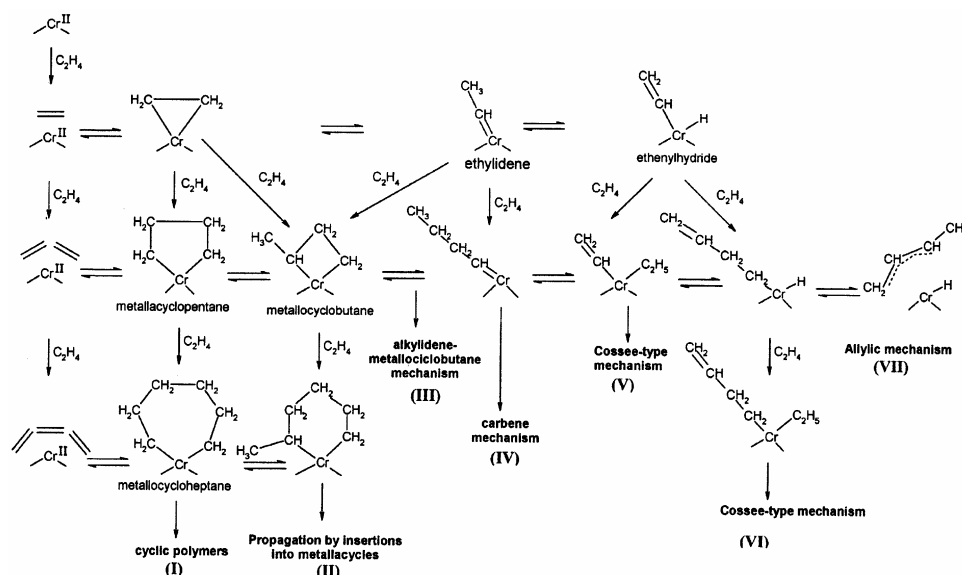
Fig. 2. Initiation mechanisms proposed for CO reduced Cr/SiO$_2$ precursors.[4]

Generally, starting from a relatively homogeneous oxidation state of Cr atoms in some precursor, a significant diversification of the oxidation state is achieved by the processes of impregnation, thermal treatment, activation and by the initial interaction with ethylene. The catalysts consist of Cr atoms which are heterogeneous in respect to their oxidation state. There is a tendency of chromium to re-homogenize its oxidation state and to stabilize itself to the oxidation state Cr(III). This happens by ethylene polymerization. The initially formed unstable Cr(II) and Cr(IV) species are transformed to the more stable Cr(III) species by simultaneous polymerization of ethylene to a macromolecular chain. Hence, during ethylene polymerization by Cr(II) precursors, the fraction of Cr(II) decreases while the fraction of Cr(III) increases.[4] Chromium active centers are deactivated, *i.e.*, stabilized, simultaneously with ethylene polymerization. Deactivation of the active centers and ethylene polymerization are mutually interdependent acts. Both of them are possible, however, only in the presence of some support (carrier).

Relaxation of silica surface strain by chromium and ethylene

"Usually the carrier does play an essential role, because without it such (chromium) compounds rarely exhibit any activity... In fact, neither (chromium) species is very active for ethylene polymerization until it has been supported on a carrier".[8] The catalyst support not only acts as a dispersing agent for the active Cr centers, but its properties have also a dramatic effect on the polymer characteristics. The most important factors are pore volume, pore size and surface area.

The crucial question is: Why a support enters into the process? During the thermal treatment and the calcination, silica dehydroxylation occurs, resulting in the formation of surface strained siloxane groups.[4] It has been explained that the hydroxyl and siloxane concentrations change with the thermal treatments and that they influence the silica surface strain. It has been noted that the grafting of Cr(II) ions decreases the silica surface strain. The role of surface strain in the Cr(II)/SiO$_2$ system activated at high temperature in influencing the activity is not completely clarified, even if the more recent information suggests that the effect is not negligible.[4] In any case, it is evident that Cr precursors reacting with hydroxyl groups help silica to reduce the strain.

The ethylene adsorption has a quite similar effect: "We have to consider that the adsorption of molecules is always associated with a surface relaxation phenomenon".[4] It was confirmed experimentally that the surface of the support and the pore volume were decreased significantly by ethylene adsorption.[30]

Importance of ethylene adsorption for polymerization

It is well know that ethylene and CO, as well as some other compounds are adsorbed on silica even in the absence of chromium or any other transition metal. Newalker *et al.*[31] reported the adsorption of light hydrocarbons on HMS type mesoporous silica (980 m^2 g^{-1}, the pore size distribution was centered at about 20 nm) at pressures up to 1000 mm Hg (at 30 and 50 °C, respectively): ethane 0.5055 and 0.3366 mmol g^{-1}; ethylene 0.7531 and 0.5091 mmol g^{-1}; propane 1.316 and 0.8214 mmol g^{-1}; propylene: 1.9819 and 1.3757 mmol g^{-1}; acetylene 1.4241 and 0.9429 mmol g^{-1}; carbon monoxide 0.0667 mmol g^{-1} at 30 °C; nitrogen 0.0484 mmol g^{-1} at 30 °C. Padin and Yang[32] reported the adsorption of ethylene at 1 atm and 70 °C: 0.53 mmol g^{-1} at silica (670 m^2 g^{-1}, pore volume 0.46 cm^3 g^{-1}), and 0.32 mmol g^{-1} at silica (398 m^2 g^{-1}). Ethylene adsorption on silica was up to 1.6 mmol g^{-1} at 0 °C and 800 mm Hg.[33] Data on ethylene adsorption on silica at temperatures 0, 25, 40, 142, 175 and 226 °C have also been reported.[33] (These empirical facts have been almost completely neglected by polymer scientists who have made efforts to identify the active sites in the Cr/SiO$_2$ system.)

Although chromium is fully attached at 300 °C during the thermal treatment of silica with a Cr precursor, the subsequent polymerizing activity of CrO$_x$/SiO$_2$ continues to increase right up to the point of silica sintering at a high temperature.[8] Silica sintering is a consequence of stress and strain relaxation. Sintering destroys the surface area and the porosity of the silica. Hence, the ability of silica to adsorb ethylene should decrease. Consequently, the polymerization activity increases with increasing calcination temperature up to a maximum at around 925 °C, and then declines.[8] (A similar result was obtained in the case of propylene adsorption and polymerization by classical supported ZN titanium catalysts.[34] The adsorptivities of various supports, without a titanium precursor, were determined

after calcination at different temperatures in the range of 100–1000 °C. It was found that the maximum values of adsorptivities were obtained after heat treatment of the support at 300–400 °C. Also, supports previously loaded with titanium precursor were calcinated separately in the same temperature range 100–1000 °C. So-prepared catalysts were used for propylene polymerization. It was found that supports calcinated at 300–400 °C exhibited the maximum polymerization activities. It was concluded that there was a parallelism of support adsorptivity and its catalytic activity, *i.e.*, the maximum adsorptivity of an unloaded support corresponded to a maximum polymerizability of a titanium loaded support.)[34]

But, why does ethylene adsorbs on silica? The answer is: silica helps ethylene to partially deliberate its free energy as heat of adsorption, the value of which decreases from 32 to 16 kJ mol^{-1} with increasing coverage.[31] A nuclear magnetic resonance study confirmed that there are deformations in the electronic and geometric structure of ethylene adsorbed on zeolite, as well as the orientation of ethylene molecule due to neighboring molecules.[35] More recent data confirmed that there are several chemisorbed species of ethylene adsorbed on all the studied surfaces.[36–39] Physically adsorbed and ordered di-σ-bonded ethylene with a molecular plane parallel to a platinum surface was formed at low coverage. With increasing coverage, chemisorbed π-bonded ethylene intrudes into di-π-bonded ethylene layer onto the surface. The π-bonded ethylene is concluded to have its molecular plane tilted while the C=C bond remains parallel to the surface of platinum and silver.[38] In other words, the π-electrons are partially localized on the C atoms, the double bond is extended thus enabling a higher mobility of the CH$_2$ groups, but the movement of the ethylene molecule as a whole is restricted. (Very similar changes were noticed in the case of propylene adsorption, *i.e.*, chemisorption of the first monolayer induces the rehybridization of the double bond in propylene towards a significant single character.[40] The C=C bond length of propylene in the gas phase is 0.133 nm, but that of chemisorbed propylene is 0.148 nm, thus approaching the single C–C bond length of 0.154 nm, with a concomitant significant reduction of the double bond character.[41] The extension of chemical bonds of adsorbed molecules is a typical phenomenon observed in adsorption processes).[36]

There is a great negative change of entropy if the free ethylene molecules have to be polymerized. This is the "limiting force" of the polymerization kinetics. The support also aids ethylene to partially solve this problem. Typically, a dependence of heat of adsorption with coverage is usually observed to display three regions, namely the adsorbent–adsorbate interaction, followed by the adsorbate–adsorbate interaction and finally by condensation.[31] Consequently, the entropy of adsorbed ethylene decreases with the coverage, (θ), approaching a minimum value when a monomer monolayer is completed, *i.e.*, at the coverage $\theta = 1$.[33] Low entropy means that the ethylene molecules are organized at the surface of

the support. Such organized molecules have less to lose if they should polymerize. Hence, the entropy of polymerization of organized monomers should have a small negative value and the "limiting force" could be overcome. The molecular distortion, the reduced mobility and the self-assembling of the ethylene molecules are prerequisites for ethylene polymerization and they are achieved with the help of the support.[17] (The same prerequisites can be achieved by compression of ethylene gas. In this case, polymerization by the free radical mechanism is possible, but only under low entropy conditions in which different supramolecular ethylene species are present.)[10,42−44]

The importance of monomer adsorption for its polymerization was recognized immediately after the discovery of ZN catalysts and was discussed extensively.[17,45,46] According to our knowledge, there was no thorough research of monomer adsorption on the surface of supports that are used in ZN and Phillips polymerizations in order to explain their mechanism, since very soon after their discovery, the insertion mechanism was proposed and generally accepted. On the other hand, there are many investigations on olefin (ethylene, propylene, butylene-1, butylene-2, 1,4-pentadiene) adsorption on the various supports (metals, metal oxides, silica, aluminum oxide, aluminosilicates, *etc*.) important for olefin hydrogenation, oxidation, isomerization and other reactions.[47]

Today, the surface science of adsorption has advanced and approached many rules, findings and statements.[36] They are also of a great value for the interprettation of olefin polymerization, since according to the CPM that will be presented here, it is necessary to have monomer molecules adsorbed on the surface of a support. When the surface of some support is exposed to adsorption of some molecules, a surface film of adsorbate is formed. Two types of interactions contribute to the formation of a surface film: 1) the interactions (electronical and geometrical) between the support and molecule of adsorbate and 2) the lateral interactions between the adsorbed molecules. The evolution of a film depends on the coverage and time. The structure of the film and the orientation of the adsorbed molecules depend on the type of the dominating interactions and on the surface area available to each adsorbing molecule. If the coverage is low and the available area per adsorbing molecule is large, a disordered two-dimensional gaseous phase is formed. Each molecule of adsorbate is oriented to the surface occupying a relatively high surface area. The gas possesses neither short-range nor long-range order and there is little interaction between the adsorbed molecules. As the coverage increases, the available area decreases and a phase transition occurs into a two-dimensional liquid-like phase. Liquids exhibit short-range but no a long-range order. Further adsorption reduces the available area of the support and transforms the adsorbate film into a solid-like phase. The molecules stand up straight toward the surface because thus they occupy a minimum space on the surface. The types of condensed adsorbed phases which can be formed de-

pend greatly on the intermolecular interactions adsorbate–adsorbent and within the film, *i.e.*, lateral interactions between the adsorbate molecules. The lateral interactions are responsible for the formation of a two-dimensional ordered solid phase. The degree of ordering depends on the coverage, exposure time and the strength of the intermolecular interactions. The adsorbate undergoes self-assembling, *i.e.*, phase transition from a disordered phase into an ordered phase. If the adsorbate is appropriate and if sufficient time is given, the system locks into a final structure which is well-ordered. The self-assembling is enhanced by the presence of some nucleation centers, *i.e.*, surface defects or some nucleating agents (*e.g.*, metal ions). Once the ordered phase is formed, it does not spontaneously revert to a disordered phase.

Thus, it can be realized how olefins are adsorbed on a support. The gradual formation of a monomer monolayer is realized by a simultaneous change in the orientation of the molecules and degree of order, as was demonstrated for many other substances.[36] The role of support is to deform the monomer molecules as well as to concentrate and to orient them properly, thus facilitating their polymerization.

THE CHARGE PERCOLATION MECHANISM (CPM)

Based on the theory of the polymerization of organized monomers proposed by Semenov, Kargin and Kabanov,[45,46] which was applied to explain free radical polymerization of compressed ethylene gas[10,42–44] and liquid methyl methacrylate,[48] and based on an analysis similar to that presented in the previous section, the charge percolation mechanism (CPM) was suggested and applied it to explain olefin polymerization in ZN systems.[9–13] Here the CPM is adopted to explain ethylene polymerization in the presence of the Cr/SiO_2 system.

Starting from Cr(VI) precursors, after immobilization on silica, thermal treatment and addition of ethylene (or CO), immobilized Cr(II) species are produced (Figs. 1 and 2). After the oxidative addition of ethylene to the Cr(II) species, the various Cr(IV) species are formed. Both species, *i.e.*, Cr(II) and Cr(IV), exist simultaneously on the support.

The species Cr(IV) and Cr(II) are unstable. There is a tendency to equalize their oxidation states to Cr(III) by charge transfer from Cr(II) to Cr(IV), but it cannot be done since they are immobilized and highly separated on the support. However, the monomer molecules can help. It is well known that ethylene molecules are gradually adsorbed on silica, producing a layer of adsorbate even in the absence of Cr or any other transition metal.[31–33] The immobilized Cr(II) to Cr(IV) species on the support are gradually surrounded by an adsorbed monomer film. A cluster of monomer, with overlapped π-bonds, connects two immobilized Cr species (Fig. 3, top). Once the bridge is completed (the moment of percolation), a charge transfer occurs. The terminal monomer molecules, adjacent to Cr(IV) and Cr(II), are inserted into their vacancies, making π-complexes with them, if the

shape and size of the monomer molecule are in accordance with the vacant spaces of the active centers. Thus, monomer molecules form a bridge consisting of a π-electron cloud between the Cr(IV) and Cr(II). The whole π-electron cloud in the monomer cluster will be pulled toward Cr(IV), since it has a more positive charge than Cr(II). Thus, the monomer cluster is excited, *i.e.*, the π-electrons are displaced toward Cr(IV), producing a partially negative charge toward Cr(IV) side. This displacement of π-electrons attracts a proton from the alkyl group of Cr(IV) to terminal monomer molecule, leaving an electron pair on the alkyl group. Simultaneously, a partially positive charge is formed on the terminal monomer molecule coordinated to Cr(II), a proton from the terminal monomer molecule is repelled to Cr(II). The electron pair on the left terminal monomer molecule enables the simultaneous polymerization of all monomer molecules belonging to the bridge between Cr(II) and Cr(IV). Both Cr species equalize their oxidation states simultaneously with the polymerization of monomer (Fig. 3, bottom). The polymer chain is removed from the support making its surface free for subsequent monomer adsorption. The whole process is repeated by the oxidation–reduction of some other Cr(II)–Cr(IV) ensembles immobilized on the support.
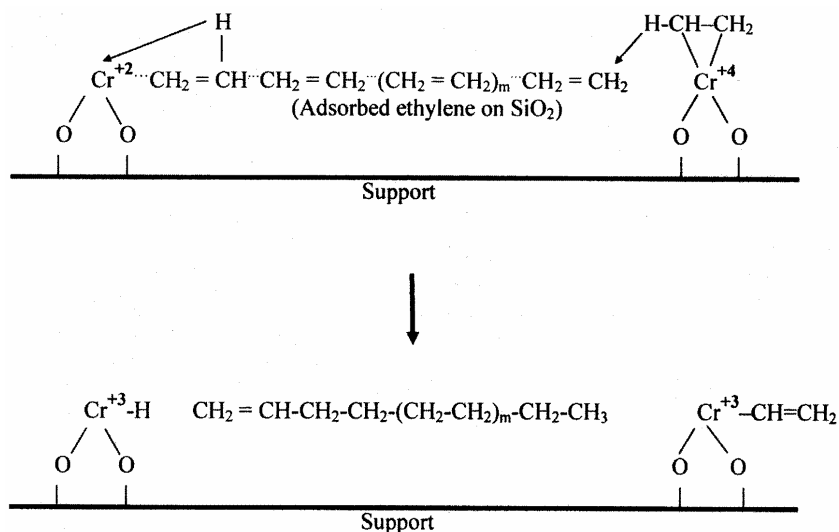

Fig. 3. An elementary step of the charge percolation mechanism.

Any of the Cr(II) and Cr(IV) species presented in Figs. 1 and 2 could be the active center. After charge percolation, various alkylated Cr(III) species could be formed, depending on the type of the alkyl group.

As the results of the process, unstable species Cr(II) and Cr(IV) are deactivated since they are transformed to the more stable green Cr(III) species, as was experimentally confirmed.[4,7,49,50] Monomer adsorption and its polymerization is a device for charge percolation between Cr(II) and Cr(IV), whereby the oxidation

state of the Cr atoms is homogenized. The polymerization is not possible without this kind of deactivation and this type of deactivation is not possible without the polymerization of the monomer. Both processes, *i.e.*, homogenization of the oxidation state of Cr and ethylene polymerization, are mutually interdependent acts, neither possible without the other.

The support plays a very important role. It offers the sites to bring both components together, by immobilization of Cr and by adsorption of monomer. Thanks to the support, it is possible that both reactions (the oxidation–reduction of Cr and the polymerization of monomer) are merged and performed at the same location, simultaneously, in a common process. Simultaneously, strain relaxation and fragmentation of the support occur due to the heat evolved in these processses. Furthermore, once both reactions are completed, a part of the support becomes free for subsequent monomer adsorption.

SIMILARITY OF THE CPM WITH SOME EXISTING EXPLANATIONS

Estimating the situation in the 1970s in his famous book "Ziegler–Natta Catalysts and Polymerizations" Boor stated: "Each worker has examined some aspect of the problem and has given his view of what is happening. The findings are similar to pieces of a puzzle which are coupled to form the whole picture; only here, some critical pieces are still missing".[51] In the previous section, it has been shown that the CPM gives the critical pieces asked for by Boor.

It seems that the CPM is something quite new and not known in current chemistry. This is not true.

A quite similar mechanism, however, was proposed very soon after the discovery of ZN and Phillips polymerizations. Friedlander and Oita[52] and Kargin and Kabanov[46] suggested that propagation occurs by the addition of adsorbed olefin molecules to an active center (Fig. 4). They also proposed that the polymer chains are detached from the support, thus making some adsorption sites free for subsequent monomer adsorption. They believed, however, that a polymer chain propagates by a radical or ion–radical mechanism. Since the presence of radicals was not confirmed, this mechanism was rejected, together with the proposal that the adsorbed monomer molecules were enchained.

It was proposed by Rebenstorf and Larsson[53] that the initiation reaction for the polymerization of ethylene could be the addition of one ethylene molecule to one dinuclear surface chromium complex by the formation of a $Cr–CH_2–CH_2–Cr$ bridge. More recent theoretical calculations showed that there was a slight bias toward $Cr(II)−Cr(IV)$ over the $Cr(III)−Cr(III)$ ensembles as active centers.[54] This is very similar to the proposal made by the CPM.

Similar electron transfer reactions between two transition metal atoms by a ligand bridge, which includes a transition metal oxidation–reduction and a chemical transformation of the ligand bridge, are described in inorganic chemistry as mutually interdependent acts.[55] In the case of olefin polymerization by the CPM, the bridging group is a monomer cluster between two Cr active centers.
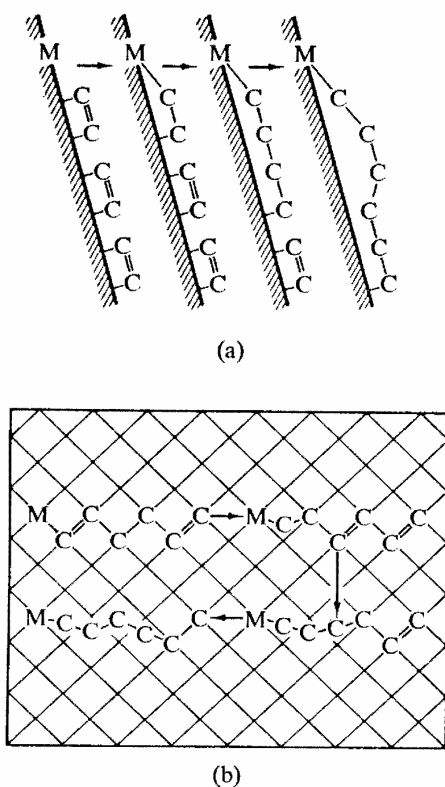
(a)

(b)

Fig. 4. Replica polymerization mechanism proposed by Friedlander and Oita[52] (a – cross section; b – surface view).

Also, the proposed CPM is quite similar to reactions catalyzed by enzymes, which are also highly entropy dependant. An enzyme usually contains an acid and some base residues. The high effectiveness of the action of an enzyme is often explained by the simultaneous action of these groups by the transfer of a proton from an acid group to a reacting substrate and a proton from the substrate to the base group ("push-pull" mechanism).[56] The mechanism of natural polymer synthesis, *i.e.*, proteins and DNA replication performed by enzymes are quite similar to the CPM of synthetic polymer synthesis by a supported transition metal complexes and a self-assembling adsorbed monomer.

CONCLUSIONS

The CPM includes three basic participants, *i.e.*, ethylene, chromium precursors and supports, in three mutually interdependent acts, *i.e.*, ethylene polymerization, chromium deactivation by oxidation–reduction and silica strain relaxation. The CPM is in good agreement with the experimental data on the polymerization of ethylene by supported CrO_x systems. It gives reasonable answers on all open questions mentioned in the introduction: (1) the active centers are Cr(II) and

Cr(IV) ensembles; (2) the mechanism of initiation includes the coordination of ethylene molecules with CrO_x species and the reduction of Cr(VI) to Cr(IV) and to Cr(II) (Fig. 1); (3) the polymerization is performed by the charge percolation mechanism proposed for supported CrO_x as well as for other Ziegler–Natta polymerizations by transition metals (Fig. 3); (4) the diversity of the Cr oxidation state (Figs. 1 and 2) and the tendency to stabilize them to Cr(III) is the "driving force" for polymerization.

The answers on the other open questions listed in the introduction, *i.e*., 5., 6. and 7., as well as more evidence of the validity of the CPM will be given in a subsequent article (Part VII of this work).[14]

ИЗВОД

МЕХАНИЗАМ ПОЛИМЕРИЗАЦИЈЕ ПЕРКОЛАЦИЈОМ НАЕЛЕКТРИСАЊА И СИМУЛАЦИЈА ЦИГЛЕР–НАТА ПОЛИМЕРИЗАЦИЈЕ. ДЕО 6. МЕХАНИЗАМ ПОЛИМЕРИЗАЦИЈЕ ЕТИЛЕНА ПОМОЋУ ОКСИДА ХРОМА НА НОСАЧУ

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Упркос обимним истраживањима у протеклих 50 година, остала су без одговора многа питања о полимеризацији етилена помоћу оксида хрома на носачу. Стога се у овом раду разматрају основне поставке ове полимеризације. Показано је да се и у овом случају могу наћи одговори помоћу механизма перколације наелектрисања, којег смо недавно предложили за полимеризацију олефина применом Циглер–Ната комплекса прелазних метала.

REFERENCES

1. P. Hogan, *J. Polym. Sci., Part A-1*, **8** (1970) 2637
2. E. J. Arlman, *J. Catal*. **3** (1964) 89
3. P. Cossee, *J. Catal.* **3** (1964) 80
4. E. Groppo, C. Lamberti, S. Bordiga, G. Spoto, A. Zecchina, *Chem. Rev.* **105** (2005) 115
5. B. M. Weckhuysen, R. A. Schoonheydt, *Catal. Today* **51** (1999) 215
6. B. Liu, M. Terano, *J. Mol. Catal. A: Chem*. **172** (2001) 172
7. B. Liu, H. Nakatani, M. Terano, *J. Mol. Catal. A: Chem*. **184** (2002) 387
8. M. P. McDaniel, *Adv. Catal.* **33** (1985) 47
9. D. Stoiljković, B. Pilić, S. Jovanović, D. Panić, in *Current Achievements on Heterogeneous Olefin Polymerization Catalysts*, M. Terano, Ed., Sankeisha Co., Nagoya, 2004, p.135
10. D. Stoiljković, B. Pilić, R. Radičević, I. Bakočević, S. Jovanović, D. Panić, Lj. Korugić–Karasz, *Hem. Ind*. **58** (2004) 479
11. B. Pilić, D. Stoiljković, I. Bakočević, S. Jovanović, D. Panić, Lj. Korugić–Karasz, in *New Polymeric Materials*, Lj. Korugić–Karasz, W. MacKnight and E. Martuscelli, Eds., ACS Symp. Series, New York, 2005, p. 215
12. B. Pilić, D. Stoiljković, I. Bakočević, S. Jovanović, D. Panić, Lj. Korugić–Karasz, *J. Serb. Chem. Soc.* **71** (2006) 357

13. B. Pilić, D. Stoiljković, I. Bakočević, S. Jovanović, D. Panić, Lj. Korugić–Karasz, *Mat. Sci. Forum* **518** (2006) 381

14. D. Stoiljković, B. Pilić, M. Bulajić, N. Đurasović, N. Ostrovski, *J. Serb. Chem. Soc.*, in press

15. H. Berthod, *Ann. Chim.* **6** (1961) 286

16. E. Hunter, in *Polythene*, A. Renfrew, P. Morgan, Eds., Iliffe and Sons Ltd., London, 1957, Chapter 3

17. N. G. Geylord, H. F. Mark, *Linear and Stereoregular Addition Polymers*, Interscience Publishers, New York, 1959, Chapter 3

18. A. B. Gaspar, J. L. F. Brito, L.C. Dieguez, *J. Mol. Catal. A: Chem.* **203** (2003) 251

19. A. B. Gaspar, R. L. Martins, L. C. Dieguez, *J. Mol. Catal. A: Chem.* **169** (2001) 105

20. A. B. Gaspar, L. C. Dieguez, *Appl. Catal.: A. General* **227** (2002) 241

21. P. Hogan, in *Polyethylenes*, The Plastics and Rubber Institute, London, 1983, Chapter B3.1

22. E. Groppo, C. Prestipino, F. Cesano, F. Bonino, S. Bordiga, C. Lamberti, P. C. Rhune, J. W. Niemantsverdriet, A. Zecchina, *J. Catal.* **230** (2005) 98

23. B. M. Weckhuysen, A. A. Verbreckmoes, A. R. De Baets, A. Schoonheydt, *J. Catal.* **166** (1997) 160

24. A. B. Gaspar, L. C. Diegiez, *J. Mol. Catal. A: Chem.* **219** (2004) 357

25. B. Liu, P. Šindelár, Y. Fang, K. Hasebe, M. Terano, *J. Mol. Catal. A: Chem.* **238** (2006) 142

26. S. Scott, J. A. N. Ajjou, *Chem. Eng. Sci.* **56** (2001) 4155

27. E. Groppo, C. Lamberti, G. Spoto, S. Bordiga, G. Magnacca, A. Zecchina, *J. Catal.* **236** (2005) 233

28. E. Groppo, C. Lamberti, S. Bordiga, G. Spoto, A. Zecchina, *J. Catal.* **240** (2006) 172

29. F. Aubriet, J.–F. Muller, C. Poleunis, P. Bertrand, P. Di Groce, P. Grange, *J. Am. Soc. Mass Spectrom.* **17** (2006) 406

30. M. A. Landau, V. V. Shchekin, *Neftekhimiya* **3** (1963) 713

31. B. L. Newalkar, N. V. Choudary, U. T. Turaga, R. P. Vijayalakshmi, P. Kumar, S. Komarneni, T. S. G. Bhat, *Micropor. Mesopor. Mater.* **65** (2003) 267

32. J. Padin, T. Yang, *Chem. Eng. Sci.* **55** (2000) 2607

33. K. L. Mentell, in *Ethylene and Its Industrial Derivates*, S. A. Miller, Ed., E. Benn, London, 1969, Chapter 7

34. A. Simon, A. Grobler in *Makro Mainz – 26*[th] *Int. Symp. Macromol.*, I. Lüderwald and R. Weiss, Eds., Vol. I, IUPAC, Mainz, 1979, ch. A2–39

35. G. M. Muha, D. J. C. Yates, *J. Chem. Phys.* **49** (1968) 5073

36. K. W. Kolasinski, *Surface Science – Foundation of Catalysis and Nanoscience*, John Wiley and Sons, Chichester, 2002, p. 270

37. U. Müller, U. Schmiemann, A. Dülberg, H. Baltruschat, *Surf. Sci.* **335** (1995) 333

38. J. Kubota, S. Ichihara, J. N. Kondo, C. Hirose, *Surf. Sci.* **357–358** (1996) 634

39. L. Clemen, R. M. Wallace, P. A. Taylor, M. J. Dresses, W. J. Choyke, W. H. Weinberg, J. T. Yates, *Surf. Sci.* **268** (1992) 205

40. F. Zaera, D. Chrysostomou, *Surf. Sci.* **457** (2000) 71

41. A. Valcárcel, J. M. Ricart, A. Clotet, A. Markovits, C. Minot, F. Illas, *Surf. Sci.* **519** (2002) 150

42. D. Stoiljković, S. Jovanović, *J. Polym. Sci: Polym. Chem. Ed.* **19** (1981) 741

43. D. Stoiljković, S. Jovanović, *Angew. Makromol. Chem.* **106** (1982) 195

44. D. Stoiljković, S. Jovanović, *Acta Polymerica* **39** (1988) 670

45. N. N. Semenov, *Khim. Tekhnol. Polimerov* **7–8** (1960) 196

46. V. A. Kargin, V. A. Kabanov, *Zh. Vses. Khim. Ob.* **9** (1964) 602

47. H. P. Leftin, M. C. Hobson, in *Advances in Catalysis*, D. D. Eley, H. Pines, P. B. Weisz, Eds., Vol. 14, Academic Press, New York and London, 1963–1964, p. 115

48. R. Radičević, Lj. Korugić, D. Stoiljković, S. Jovanović, *J. Serb. Chem. Soc.* **60** (1995) 347

49. J. P. Hogan, *J. Polym. Sci. A-1* **8** (1979) 2637
50. O. M. Bade, R. Blom, M. Dahli, A. Karlsson, *J. Catal.* **173** (1998) 460
51. J. Boor, *Ziegler–Natta Catalysts and Polymerizations*, Academic Press, New York, 1979
52. H. N. Friedlander, K. Oita, *Ind. Eng. Chem.* **49** (1957) 1885
53. B. Rebenstorf, R. Larsson, *J. Mol. Catal.* **11** (1981) 247
54. O. Espelid, K.J. Borve, *J. Catal.* **206** (2002) 331
55. F. A. Cotton, G. Wilkinson, *Advances Inorganic Chemistry, 5th ed.*, John Wiley and Sons, New York, 1988, p. 1311
56. G. M. Panchenkov, V. P. Lebedev, *Chemical Kinetics and Catalysis*, Mir Publishers, Moscow, 1976, p. 542.