

Ziegler-Natta Catalysis I. Mechanism of Polymerization of α -Olefins with Ziegler-Natta Catalysts*

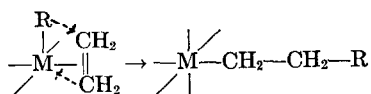
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A mechanism for the polymerization of olefins is proposed. An essentially octahedrally coordinated ion of a transition element with empty or nearly empty t_{2g} orbitals carrying in its coordination sphere one alkyl group and having one vacant octahedral position is supposed to be the active center. In this model the monomeric olefin is coordinated in the vacant position through a " π bond."

It is shown that theoretically one may expect the transition metal-to-carbon bond to become more susceptible to radical breaking at the very moment the π bond between metal ion and olefin is formed. Based on this theoretical argument, the proposed mechanism:



involves to a first approximation an electronic rearrangement and only small nuclear displacements. This mechanism may account for the low activation energy of the propagation step.

It further relates catalytic activity to the ionization potential for a d electron of the transition metal and the nature of the negative ions used in the transition metal compound.

It also provides a basis for the explanation of the formation of isotactic polymers when special solid catalyst systems are used.

I. INTRODUCTION

Ziegler's (1) discovery that ethylene could be polymerized at low pressure under the influence of a mixture of a transition metal compound and a metal alkyl derived from a strongly electropositive metal, opened a completely new field of catalysis. In particular Natta (2) and his co-workers have extended the possibilities of this peculiar reaction.

Several investigators have contributed to provide a suitable mechanism (3-11). With

* Part of this work has been reported in a preliminary publication: *Tetrahedron Letters* **17**, 12 (1960). Part of it was presented at the Coordination Conference, Detroit 1961: *Proc. 6th Intern. Conf. Coord. Chem. Detroit, 1961*, p. 241.

one exception (3), they agree that the monomer molecule is interposed between a metal atom and a carbon atom of an organometallic compound. There is, however, still disagreement concerning the nature of the active centers. According to most theories at least two metal ions bound in a complex are required; one to accommodate the monomer molecule, the other to carry the alkyl group. A further point of discussion is whether the growing polymer chain is attached to the transition metal or to the nontransition metal. The results of recent investigations strongly support the view that the growth reaction takes place at the transition metal ion (11-22).

In the literature on Ziegler-Natta catalysis little attention has been given to theoretical

concepts such as ligand-field theory and molecular orbital methods, in order to obtain a more detailed picture of the specific role of the transition element.

In the present paper we will try to approach Ziegler-Natta catalysis using the concept of π bonding between olefins and transition elements. The basic ideas will be discussed in the following section. Next a reaction mechanism will be proposed which may account for the driving force of the propagation reaction and the specificity of particular transition metal compounds.

II. π BONDING OF OLEFINS WITH TRANSITION ELEMENTS

The complex formation between an olefin and a transition metal compound was discovered more than a hundred years ago by Zeise (23). A proposal for the structure and the character of the bonds of these compounds was given by Chatt and Duncanson (24). Their ideas are demonstrated in Fig. 1. The C=C double bond is perpen-

carried out by Alderman, Owston, and Rowe (27) for *trans*- [Pt(C₂H₄){NH(CH₃)₂}Cl₂]. They find a C—C distance of 1.47 Å as compared to 1.34 in the free olefin molecule and a distance between Pt and the center of the C—C bond of 2.09 Å. The long C—C distance in the complex comes very close to what may be expected for a single bond between two trigonally hybridized C atoms (1.48 Å).

Unfortunately the standard deviation for the C—C distance is quite large, owing to the presence of the heavy Pt atom.

Also the downward shift of about 150 cm⁻¹ of the infrared absorption band in the C—C stretching region which is observed on complex formation (24, 28, 29) should be considered with some care. This frequency shift does not necessarily reflect the actual change in C—C bond strength since the normal coordinate belonging to the frequency in question may be a different mixture of C—C stretching and hydrogen motions in the free olefin and in the complex.

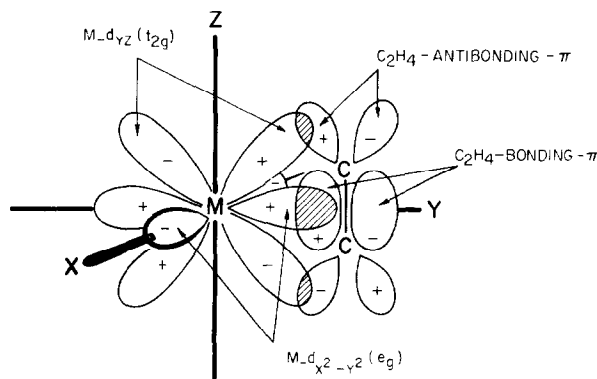


FIG. 1. Schematic picture showing spatial arrangement of the relevant orbitals in a π bond between a transition metal and C₂H₄.

dicular to one of the free valencies of the metal atom. Between metal and olefin a kind of double bond is formed, one of its components having σ and the other π symmetry.

The proposed structure was confirmed for Zeise's compounds [C₂H₄PtCl₂]₂ and K[C₂H₄PtCl₃] by Wunderlich and Mellor (25), and for [PdCl₂C₂H₄]₂ by Dempsey and Baenziger (26). The most complete structure determination has recently been

The results of both techniques, however, are compatible with a somewhat longer and weaker bond between the two carbon atoms. Otherwise the hydrocarbon seems to be only very slightly distorted, as may be deduced from proton magnetic resonance data (30).

The structure of these stable compounds may now be considered as well established and the original molecular orbital picture of the double bond between metal and olefin (24) seems an appropriate description

The relevant orbitals* in such a π bond are given below in order of increasing energy:

$$\psi_1 = ad_{x^2-y^2} + [(1 - a^2)/2]^{1/2}(p_A + p_B)$$

$$\psi_2 = bd_{yz} + [(1 - b^2)/2]^{1/2}(p_A - p_B)$$

$$\psi_3 = (1 - a^2)^{1/2}d_{x^2-y^2} - (a/\sqrt{2})(p_A + p_B)$$

$$\psi_4 = (1 - b^2)^{1/2}d_{yz} - (b/\sqrt{2})(p_A - p_B)$$

[Two of these, ψ_1 and ψ_2 , are bonding (cf. Fig. 2). This molecular orbital energy

For transition elements with no or only a few d electrons, ψ_2 will be empty or only half-filled. Therefore no great stabilization due to double-bonding may be expected. However, the rearrangement of the energy level scheme resulting from coordination of an olefin to such a transition element will still apply.

When we accept as a logical first step in Ziegler-Natta catalysis the coordination of

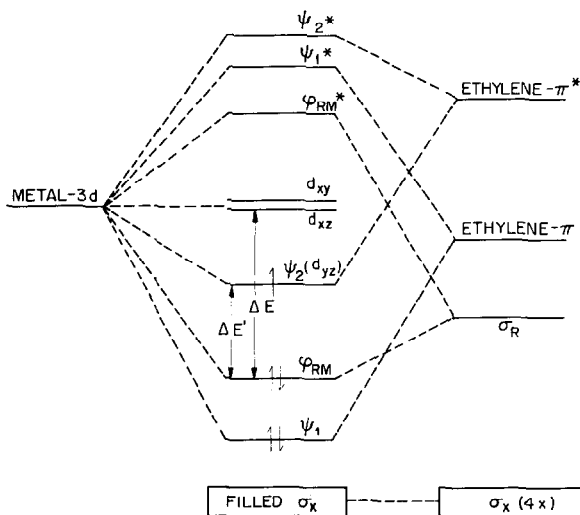


Fig. 2. Tentative molecular orbital energy diagram for the octahedral complex $\text{RTiCl}_4(\text{C}_2\text{H}_4)$. For reasons of simplicity, $4s$ and $4p$ orbitals are not taken into account and the $\text{Ti}-\text{Cl}$ bond is supposed to be 100% ionic.

diagram by no means pretends to be quantitative; it is based on the generally adopted ideas on the relative positions of metal and ligand orbitals, as will be outlined briefly in the discussion.

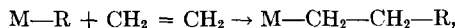
The metals known to form complexes with olefins are found among those having filled d orbitals. Here the stabilizing effect is the possibility of back-donation to the ligand of electrons originally in one of the d_{xy} , d_{xz} , and d_{yz} orbitals, by combination with an empty antibonding orbital of the olefin (in our example of Fig. 2: ψ_2).

* For convenience the formulae have been given for the case where bonds with the other ligands are 100% ionic. Since, as a rule, they are not, $d_{x^2-y^2}$ and d_{yz} ought to be replaced by linear combinations with ligand orbitals having the same symmetry. As a further simplification, interaction of the metal $4s$ and $4p$ orbitals has been omitted.

a monomer molecule to a transition metal-alkyl compound (13, 14, 20, 21), we may assume that this will be through a π complex, a suggestion made earlier by Fischer (31). The resulting rearrangement among the energy levels will prove to be an important feature in the discussion of catalytic activity.

III. MECHANISM OF THE PROPAGATION REACTION

The propagation step in Ziegler-Natta polymerizations, which is now generally taken to be the interposition of an olefin molecule between a metal atom and an alkyl group:



requires, as pointed out by several authors (13, 14, 20, 21), a transition metal-alkyl bond and the possibility to coordinate

the monomer to the transition element. The simplest configuration meeting these requirements is shown in Fig. 3, which repre-

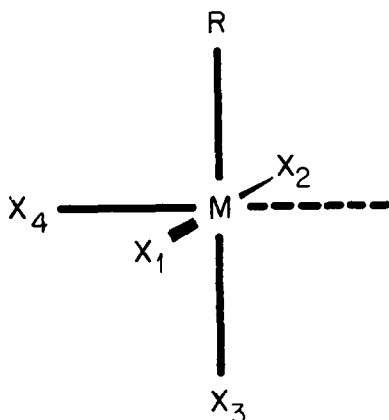
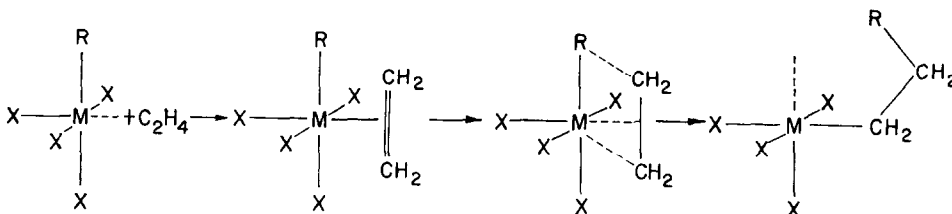


FIG. 3. Configuration supposed to be the active center in a Ziegler-Natta catalyst. M = transition metal ion; R = alkyl (growing polymer chain); X_1 - X_4 are anions.

sents an essentially octahedrally coordinated transition metal ion of which one of the octahedral positions is vacant while another is substituted by an alkyl group. In many



of the currently used catalysts, X_1 to X_4 are halogen ions.

Such a situation is most easily visualized at the surface of halogenides with layer structures, which are components of the most satisfactory catalyst systems [for example, α - TiCl_3 + $\text{Al}(\text{C}_2\text{H}_5)_3$]. Then X_1 , X_2 , X_3 , and X_4 are anions of the lattice of the solid compound (32).

In solution the composition and structure of the active complexes are not very well known. The transition element is probably part of a larger complex system with other metal compounds (13, 19). When X_1 to X_4 are regarded as bridging groups, the configuration as shown in Fig. 3 is also a feasible one in homogeneous systems.

When an olefin like ethylene is coordinated to, for instance, a Cl_4TiR complex in the way described in Section II, the following situation arises in the molecular orbital scheme: The metal d_{yz} orbital which originally had an energy comparable to that of the d_{xy} and d_{zx} orbitals now becomes combined with the π^* orbital of ethylene and forms the molecular orbital ψ_2 , which is considerably lower in energy. Thereby the energy gap between this orbital and the filled orbital

$$\varphi_{\text{RM}} = \alpha d_{yz} + (1 - \alpha^2)^{1/2} (sp^3)_R$$

representing the bond between alkyl group and Ti, is appreciably reduced. Since it is now easier to promote by thermal excitation an electron from the φ_{RM} orbital into the next vacant or partly vacant one, the RM bond will be more susceptible to breaking into radicals. This concept, which relates the strength of metal-to-carbon bonds with the energy gap between the highest filled and the lowest empty or half-filled orbital, was proposed by Chatt and Shaw (33) in order to explain the inherent instability of alkyls of transition metals.

We may now write the reaction mechanism as shown. The olefin is coordinated

to the transition metal ion at the vacant octahedral position through π bonding. The distance ΔE between the filled metal alkyl bonding orbital and the group of empty metal orbitals is hereby reduced to $\Delta E'$ (Fig. 2). Since we know that the catalyst system can be stored for a practically indefinite time ΔE apparently is a large enough energy gap to maintain the metal-alkyl bond in the absence of unsaturated hydrocarbons. However, when $\Delta E'$ is smaller than the critical energy gap in the Chatt and Shaw model the alkyl group will be expelled as a radical which attaches itself in a concerted process to the nearest C atom of the olefin while at the same time the other side of the olefin connects itself to the metal.

In this way the activation energy for a rearrangement in which the alkyl group moves from the transition metal towards the nearest C atom of the olefin is reduced.

After this first step the transition metal ion under consideration still has its alkyl group (two C atoms longer) and its vacant position, which, however, have changed places. When the reaction repeats itself, the alkyl group returns to its original position. This simple picture will be valid if the vacancy and the position of the alkyl group are equivalent as, for example, in homogeneous systems. However, in heterogeneous systems they may be nonequivalent (32). Then a modification of the picture will be required which will be shown to be the key to the explanation of stereoregular polymerization (42).

IV. DISCUSSION

A comparison of the present theory with a number of the existing ones shows that there are two main features:

(a) Specific use is made of a transition element in essentially octahedral surroundings. This is obvious in all those cases where a solid catalyst with a layer structure (e.g. α -TiCl₃) is used. In homogeneous systems, when complexes of lower-valency transition elements with nontransition metal compounds are probably the active species, it seems a much more realistic picture than the drawings of a central Ti atom with four valencies in a plane which are often encountered in the existing literature on the mechanism of Ziegler-Natta catalysis.

(b) The growing polymer chain remains attached in either of two octahedral positions of the same metal ion, whereas in the theories based on binuclear complexes it moves between two metal ions.

When these concepts are used together with the theoretical ones outlined in Secs. II and III the proposed mechanism permits explanation of a number of facts not covered by the existing ones.

1. The Driving Force

An explanation for the driving force of the propagation reaction is provided, which is well in keeping with the known kinetics.

Natta's investigations (2) of the polymerization of C₃H₆ with an α -TiCl₃-Al(C₂H₅)₃ system as a catalyst show that the rate of propagation is proportional to the total amount of α -TiCl₃ and the pressure of the olefin and is independent of the Al alkyl concentration.

The strict proportionality with the pressure of the olefin indicates that on the average the active sites are empty. The kinetics may then be explained in either of two ways:

(a) The adsorption of olefin at the active centers is the rate-determining step and the activation energy is that of the adsorption.

(b) The rearrangement of the alkyl group is the rate-determining step. In this case many olefin molecules move in and out of the vacancy at the active center before one of them finally reacts and is incorporated in the polymer chain.

The little change in the character of the olefin on complex formation with a transition element (see Sec. II) makes it improbable that the adsorption of monomer on the active site is the rate-determining step, which means that the situation is very probably that pictured under (b). For such a mechanism the experimental activation energy (2) of 10 kcal/mole will for the greater part be caused by the energy barrier of the rearrangement of the alkyl group. At first sight the activation energy seems low for such a complicated rearrangement. In the present mechanism, however, the nuclei are only slightly displaced in the propagation step.

Figure 4 demonstrates that the relative positions of alkyl group and olefin molecule are very favorable for such a process. When the center of the olefin is placed at the same distance as the negative ions, it is seen that the van der Waals radii are at least touching each other. The alkyl group approaches from the correct angle. When the parameters used in Fig. 4 (34) are adopted, the distance between alkyl and the nearest carbon atom must only contract from about 3.3 Å to 1.54 Å.

The process is to a first approximation an electronic rearrangement: An initial electron jump from the bond between metal and alkyl into the depressed ψ_2 level, followed by the formation of a new bond between an alkyl

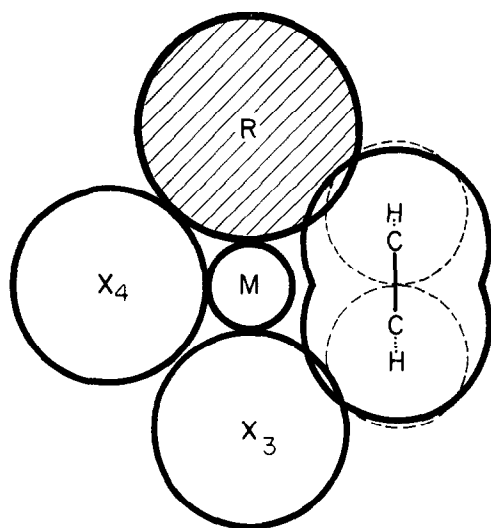


FIG. 4. Diagram of transition state; drawn to scale radii are used which may be considered representative: $R = 2.0 \text{ \AA}$, $X_3 = X_4 = 1.8 \text{ \AA}$, $M = 0.75 \text{ \AA}$, C (in C_2H_4) $= 1.7 \text{ \AA}$. Distance $M \rightarrow C = C = MX$.

radical and the nearest C atom of the olefin. At the moment of the migration of the alkyl radical the olefin already contains, at least partly, an extra electron in its antibonding orbital.

As mentioned earlier the experiments by Natta and co-workers (2) show that the polymerization rate is independent of the Al alkyl concentration.

In our mechanism the Al alkyl indeed plays no essential role in the propagation step. Nevertheless, its presence is very important and in many instances indispensable, as it plays a role in alkylating the transition element, in chain transfer, and as a scavenger. All the mechanisms of termination and chain transfer proposed by Natta (2) remain equally valid in our mechanism.

2. The Specificity of the Transition Metal Compound

The theoretical arguments indicate that the process of interposition of olefins is a subtle one. The isolated transition metal-alkyl bonds must be sufficiently stable in the absence of coordinated olefin, which requires an electronegativity of the metal ion that is not too high. This same bond

must become sufficiently destabilized when an olefin molecule is coordinated in the vacant position.

From the orbital energy diagram in the complex $RTiCl_4$ -ethylene (Fig. 2) it is apparent that the catalytic activity of the transition metal compound does not depend on the presence of an electron in $\psi_2(d_{yz})$, d_{xz} and d_{xy} . However, no two electrons are allowed to be present in ψ_2 . This means that metal ions with from 0 up to 3 unpaired d electrons may be operative. It further follows from Fig. 2 that the specific action of the transition element is possible when the energy of the metal $3d$ level is between the bonding and antibonding levels of ethylene.

Without complicated computations only a rough first approximation to the relative positions of these levels is possible in the following way:

We compare the states $Ti^0(d^2s^2)E^+(\pi)$, $Ti^+(ds^2)E^0(\pi^2)$ and $Ti^+(ds^2)E^0(\pi\pi^*)$, respectively, with the ionized state $Ti^+(ds^2)E^+(\pi)$ and make the assumption that the relative positions of these states at the equilibrium distances in the complex (without further interaction) are the same as at infinite distance. The results are summarized in Fig. 5.

The ethylene π level [$Ti^+(ds^2)E^0(\pi^2)$] is thus found at about $-85\,000 \text{ cm}^{-1}$ which is minus the ionization potential of C_2H_4 (35). Experimentally the forbidden transition between $^1A_{1g}$ and $^3B_{1u}$ of the ethylene molecule is probably represented by the weak bands found between $30\,000$ and $40\,000 \text{ cm}^{-1}$, while calculation estimates it to fall between $36\,000$ and $48\,000 \text{ cm}^{-1}$ (36). Accordingly we have taken the $Ti^+(ds^2)E^0(\pi\pi^*)$ at a distance of $40\,000 \text{ cm}^{-1}$ above $Ti^+(ds^2)E^0(\pi^2)$. In order to estimate the energy of the metal $3d$ level we compare as mentioned before $Ti^0(d^2s^2)E^+(\pi)$ with $Ti^+(ds^2)E^+(\pi)$. The energy difference between these two states may be approximated by taking the first ionization potential for a d electron out of a configuration d^ns^2 .

Our choice of a neutral ethylene interacting with a Ti complex carrying a single positive charge on Ti is based on Pauling's electroneutrality principle. This principle

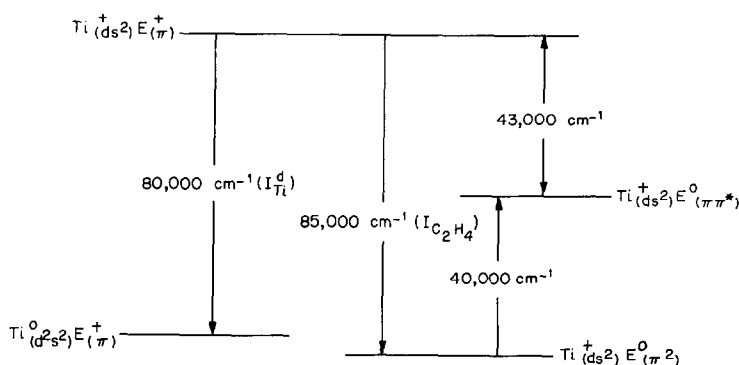
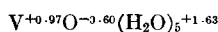


FIG. 5. Relative positions of a few states involved in the Ti-ethylene interaction.

was quite recently put on a firmer basis by Dunn (37), who concluded from spectral and magnetic properties of transition metal compounds that a metal ion of higher valency will not acquire a larger effective positive charge than something in between +1 and +2. In the self-consistent field calculation of the $\text{VO}(\text{H}_2\text{O})_6^{2+}$ ion by Ballhausen *et al.* (38) this is nicely confirmed. Although vanadium in this compound is formally tetravalent a population-density analysis gives:



Having adopted the arbitrary, but in view of the above quite reasonable, charge of +1 on the titanium ion the metal 3d level is in our diagram at $-80\,000\text{ cm}^{-1}$ and we see that according to this very simple approximation the relative order of levels in Fig. 2 seems justified.

It is interesting to compare other elements with titanium. The values for the $d^ns^2 \rightarrow d^{n-1}s^2$ ionizations in Table 1 are derived from C. E. Moore (39).

Unfortunately not all the required configurations are known from atomic spectra. It is, however, significant that CaCl_2 is not a catalyst; ScCl_3 is the first in the series which is active and for which the d orbital level is in between that for π and π^* of ethylene. TiCl_3 is the best in the series with a d orbital level of $-80\,000\text{ cm}^{-1}$, very close to the π level of ethylene. CrCl_3 with a d orbital level of $-100\,000\text{ cm}^{-1}$ is known to be a very poor catalyst. The same trend is apparent in the second and third series with

TABLE I
3d IONIZATION ENERGIES FOR THE ELEMENTS
OF THE FIRST HALVES OF THE
THREE TRANSITION SERIES

Element	Transition	I in (cm^{-1})
Ca	$ds \rightarrow s$	29,000
Sc	$ds^2 \rightarrow s^2$	65,000
Ti	$d^2s^2 \rightarrow ds^2$	80,000
V	$d^3s^2 \rightarrow d^2s^2$	Not known
Cr	$d^4s^2 \rightarrow d^3s^2$	100,000
Mn	$d^5s^2 \rightarrow d^4s^2$	115,000
Sr	$ds \rightarrow s$	18,000
Yt	$ds^2 \rightarrow s^2$	53,000
Zr	$d^2s^2 \rightarrow ds^2$	70,000
Nb	$d^3s^2 \rightarrow d^2s^2$	Not known
Mo	$d^4s^2 \rightarrow d^3s^2$	Not known
Ba	$ds \rightarrow s$	33,000
La	$ds^2 \rightarrow s^2$	52,000
Hf	$d^2s^2 \rightarrow ds^2$	57,000
Ta	$d^3s^2 \rightarrow d^2s^2$	71,000
W	$d^4s^2 \rightarrow d^3s^2$	Not known

the most favorable values in the fourth and fifth columns of the periodic system.

In the above correlation it was arbitrarily assumed that the metal ion would have an effective charge of +1. The precise value is of course dependent on the other ligands. So it should be pointed out that in an absolute sense the values of Table 1 are not to be taken literally, the approximations being too crude. It merely serves the purpose of indicating in what way it is possible with the proposed mechanism to explain the specificity of the metal ion and its valency and

the influence of the negative ions in the transition metal compound used.

In this context it is noteworthy that chromium in a chloride lattice is a poor catalyst because its d orbital level is too low. This d orbital level could be raised, for instance, by coordination with oxygen instead of chlorine. By doing so one arrives at the Phillips catalyst for the polymerization of ethylene, which according to ESR investigations contains $[\text{Cr}(\text{V})\text{O}]^{3+}$ ions in the surface of an alumina lattice as the active sites (40, 41).

The present approach, which tries to explain the phenomena of catalysis in terms of well-defined complexes between the reactants and one particular metal ion in the catalyst, pays much attention to a possible link between homogeneous and heterogeneous catalysis. Polymerizations with Ziegler-Natta systems appear to be particularly useful to demonstrate the potentialities of this approach.

It is another instance (43) where a detailed consideration of the complex between reactant and active site on an atomic scale proves to be superior to the approach which discusses catalytic properties in terms of the electron energy bands of the solid compound (the so-called electronic factor concept). In other fields of heterogeneous catalysis, where the relation to a homogeneous analogon is not so obvious, the present viewpoint may in the future be equally successful.

NOTE ADDED IN PROOF

In a private discussion at Pisa, Prof. E. Scrocco suggested that in Fig. 2 φ_{RM} might be lower than ψ_1 . In view of the relatively stable TiR bond and the low coverage of the surface in the adsorption equilibrium of ethylene this is indeed the more probable situation. However, it does not alter the main argument in the discussion of the mechanism.

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