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ON THE REACTION MECHANISM OF THE ETHYLENE POLYMERIZATION WITH HETEROGENEOUS ZIEGLER-NATTA CATALYSTS

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IN many of the current theories on the mechanism of Ziegler-Natta polymerizations two metal ions bound in a complex are supposed to be required; one to accommodate the monomer molecule, the other carrying the alkyl group. In this way Bier [1] and Gumboldt et al.[2] need two aluminium ions, Natta,[3] Uelzmann [4] and Patat and Sinn [5] use a titanium and an aluminium ion while de Bruyn [6] assumes the reaction to occur at a partly alkylated surface of $TiCl_3$ between two neighbouring titanium ions.

We start from the supposition that the essential reaction occurs at one Ti-ion on account of the general feeling that the presence of unfilled d-orbitals in transition elements, which are responsible for a number of

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[1] G. Bier, Kunststoffe 48, 354 (1958).

[2] A. Gumboldt and H. Schmidt, Chem. Ztg. 83, 636 (1959).

[3] G. Natta, J. Inorg. & Nuclear Chem. 8, 589 (1958).

[4] H. Uelzmann, J. Polymer Sci. 32, 457 (1958).

[5] F. Patat and H. Sinn, Angew. Chem. 70, 496 (1958).

[6] P.H. de Bruyn, Chem. Weekblad 56, 161 (1960).

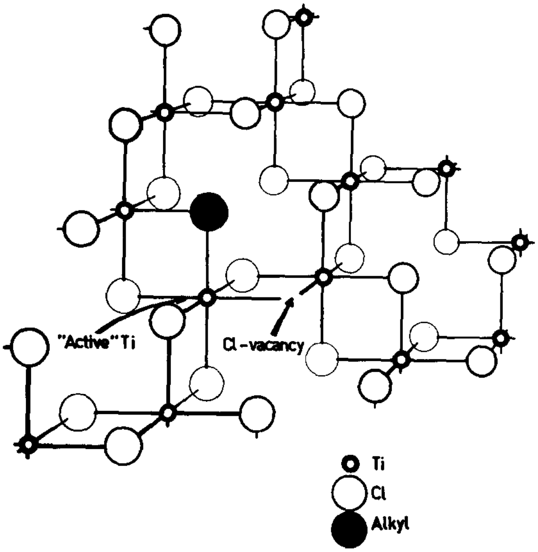
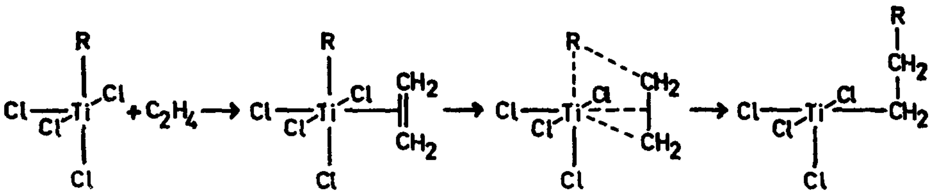


Fig. 1 Schematic drawing of α-$TiCl_3$ lattice with "active center" on the surface

characteristic physical properties, will also be responsible for their catalytic activity. An active center is thus defined as a Ti-ion in the surface layer of a $TiCl_3$ lattice of which one surface Cl-atom is replaced by an alkyl group R while an adjacent Cl-atom has been completely removed in order to accommodate the monomer molecule. This situation is shown in Fig. 1 and is supposed to be the result of the reaction of solid $TiCl_3$ with Al-alkyls. The role of the Al-alkyl is thus primarily an alkylating and reducing one.

The polymerization reaction may now proceed as follows:



After this step the active center retains a Ti-alkyl bond and a vacancy which have, however, mutually changed place. The process may now repeat itself by insertion of the next monomer molecule into the new Cl-vacancy.

Since in the transition state both alkyl group and reacting monomer molecule are attached to the same Ti-ion, only very slight displacements of the nuclei are involved in the propagation step which may be mainly described as an electronic rearrangement.

During the reaction the Al-alkyl may be important as chain-transfer agent and further in termination reactions, in reestablishing lost active centers and as a scavenger, but it is not essential for the propagation. This idea that the essential reaction occurs at one alkylated Ti-ion has already been put forward by Ludlum[7] and has been suggested by Ziegler.[8] The assumption is strongly supported by recent polymerization experiments of Beermann and Bestian.[9]

In conjunction with a few theoretical arguments hitherto not explicitly taken into account the proposed mechanism permits to explain a number of facts not covered by the existing ones.

a) It provides a better insight into the driving force of the reaction. Chatt and Duncanson[10] in 1953 proposed the π-type of bonding between transition metals and olefins. Since this hypothesis was confirmed by

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[7] D.B. Ludlum, A.W. Anderson and C.E. Ashby, J.Am.Chem.Soc. **80**, 1380 (1958).

[8] K. Ziegler, Int. Conf. on Coord. Chem. London 1959, The Chem. Soc. Spec. Publ. **13**, 1 (1959).

[9] C. Beermann and H. Bestian, Angew. Chem. **71**, 618 (1959).

[10] J. Chatt and L.A. Duncanson, J. Chem. Soc. 2939 (1953).

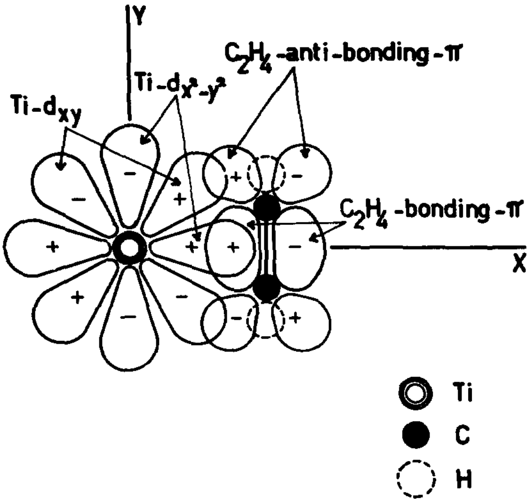

Fig. 2 The π-bond between Ti and C_2H_4.
Electron densities of the orbitals are schematically indicated

X-ray analysis for one of the more stable Pt-olefin complexes,[11] we must assume that also between Ti-ions and ethylene a π-bond is formed. Such a bond is shown in Fig. 2. Its characteristic features are the position of the ethylene molecule perpendicular to the free valency of the metal ion, which allows the π-electrons of the olefin to be used in the σ-bond formation with the $d_{x^2-y^2}$-orbital of the metal, and the possibility of overlap of the d_{xy}-orbital of the metal with the antibonding orbital of the olefin. The latter kind of interaction has an important influence on the energy level scheme of the system, particularly on the situation of the metal d-orbitals of t_{2g}-type. In the combination Ti-ethylene this results in a

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[11] P.R.H. Alderman, P.G. Owston and J.M. Row, *Acta Cryst.* **13**, 149 (1960).

decrease of the distance between the highest filled bonding orbital and the empty or nearly empty t_{2g}-level. Chatt and Shaw [12] have made it plausible that a small energy difference between filled and empty levels facilitates radical breaking of the σ-bonds of the system as a result of an easy promotion of electrons from the bonding levels to the suppressed t_{2g}-orbital. It therefore appears that the formation of the π-bond between titanium and ethylene is accompanied by a weakening of the already very labile titanium-alkyl bond, thus facilitating the migration of the alkyl group.

We assume that this is the way in which a transition element ion with empty or nearly empty d-orbitals functions as a catalyst in olefin polymerizations.

b) From the above considerations it will be clear that in order to show the desired catalytic effect the empty d-orbitals of the metal must be large enough to overlap sufficiently with the antibonding orbitals of the olefin. Therefore only ions with a comparatively low effective nuclear charge are expected to be good catalysts. This is approximately equivalent to Natta's statement [13] that metals with an ionization potential of the first electron smaller than 7 eV are particularly suited. The unique position of Ti may thus be explained from the size of the t_{2g}-orbitals in close-packed Cl-lattices and may possibly be related to the antiferromagnetic properties of α-$TiCl_3$.

c) The third and perhaps most striking consequence of the mechanism presented is the natural explanation for the formation of isotactic material when propylene is polymerized under the influence of α-$TiCl_3$ and Al-alkyls. This aspect will be treated in a separate letter.[14]

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[12] J. Chatt and B.L. Shaw, J. Chem. Soc. 705 (1959).

[13] G. Natta, Angew. Chem. 68, 393 (1956).

[14] P. Cossee, Tetrahedron Letters No. 17, 17 (1960).