CHAPTER-I. GENERAL INTRODUCTION

Polymers are chemical species having covalent structure, many time greater in extent than that occurring in simple compounds, which accounts for the characteristic physico-chemical properties such as high viscosity, long range elasticity, high strength, resistance (in certain cases) to aerial and themal decompositions etc. As early as 1920, Staudinger was the first person to realize polymers in terms of their unique structural characteristics and laid down the foundation for the systematic investigation of these substances in the light of their intra-molecular structural and chemical features. He refuted the prevailing concept of cyclic structure assigned to polymers and defined polymerization as the phenomenon of linking of simple molecules by covalent bondings.

At this early stage of the development of the macromolecular chemistry came Mark who, conducting parallel researches with Staudinger made some significant contributions in correlating the physical properties with the

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shape and structure of the polymers. In 1929, Carothers started a series of brilliant investigations, in which he established Staudinger's concept of covalent bonding through the syntheses of newer polymers with the help of established organic reactions. A further advancement to the studies in this field was made by Kuhn who initiated the statistical approach in the polymer problems like the distribution of molecular weight in the syntheses and degradations of polymeric substances and the prediction of their constitutions, reactions and physico-chemical properties.

Since then gradual improvements in our basic understanding of polymerization processes as a whole and new technological developments have been achieved by the pioneering researches by Morton (Alfin catalyst-1947), Ziegler (Ziegler catalyst systems - 1949), research groups in Standard Oil Company of Indiana (Activated Ni and Co catalysts - 1953, supported MoO_3 catalyst - 1954) and Phillips Oil Company (Activated Chromia catalyst or Marlex catalyst - 1954) and Natta (Characterization of Ziegler catalysts for stereo-regular polymerization - 1955).

It is for utilizing the efficiency of various kinds of solids as polymerization catalysts and thus for bringing about the stereospecificity in the polymer produced that the contributions of the above researchers have special bearing in the progress of polymer science. The hetero-catalytic processes over these catalyst systems are conducted either in fixed or in fluid beds. The catalysis proceeds through the adsorption of monomer on the solid surface present in the form of fine powder. For effective catalysis, two factors are of primary importance, firstly, the extent of adsorption

which is governed by the dipolar characteristics of the adsorbate, surface electronic properties of the adsorbent and the very chemical nature of the surface complex formed by the interaction of the adsorbent and the adsorbate, and secondly, and more importantly, the reactivity of the active surface complex so produced. In heterogeneous or quasi-heterogeneous polymerization reactions, however, it is the nature and reactivity of the surface complex which play the predominant role in determining the structure of the resulting polymer. The formation of high molecular weight stereo-regular polymers, as with Ziegler-Natta catalyst system or with activated metal oxide catalysts, is the result of definite interaction between the monomer and the catalyst and the desired orientation of the resulting complex upon the surface of the catalyst. The nature of the surface complex or the active species which is responsible for polymer propagation could be modified by proper choice of the catalyst system, incorporation of a co-catalyst or by the various methods of pretreatments. While the pretreatments of catalyst modify the adsorption characteristics of the monomer, the incorporation of co-catalyst modifies the nature of the active complex towards the desired structural orientation.

It is tempting to pursue the nature of the monomer-catalyst interactions which require a detailed knowledge of the chemical and hence the electronic characteristics of the interacting system. It is generally accepted that the π-electons available at the vinylic double bond in the monomer are involved in such interactions. In this respect, the solid catalysts may be classified into three groups - (i) catalysts containing metal atomsin certain oxidation states capable of forming co-ordinate bonding with the olefinic π-electrons. Such metals are, for example, B, Ti, V, Mo, Ni, Co etc., in

their lower valence states. Initiation over these catalysts are either ionic or free-radical in nature occurringeither through the transfer of π-electron from olefin to the metal ion, as in the case of Ziegler catalysts, with the formation of an ionic active centre or through the formation of co-valent bond with the olefin, as is observed with peroxided or simple metal alkylate catalysts, followed by free-radical generation. (ii) catalysts containing metal ion of very low electronegativity like aryl-alkali and alkyl-alkali catalysts in which active propagating carbanion results through the electron donation by the metal to the monomer, and (iii) the catalysts containing metal ion of very high electronegativity like supported chromia and molybdena catalysts, Ziegler catalysts and the Vandenberg catalysts which always correspond to a cationic mechanism of initiation.

From the available information and the discussions made so far, it can be surmised that for establishing the performance characteristics of a particular catalyst and the exact mechanism of polymerization involved thereon, it required a detailed insight to the physico-chemical properties of the particular monomer-catalyst system.

Bearing this in mind, a brief survey on the physico-chemical properties of N-vinylcarbazole, the monomer and V_2O_5, the catalyst has been presented in the following parts of this chapter.

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I-1. N-Vinylcarbazole as Monomer :

N-Vinylcarbazole (NVC) is a white crystalline solid melting at $64^{0}C$. It is obtained by vinylation of carbazole, an important component of the anthracene fraction of coal tar. It is soluble in most of the common organic solvents like benzene, toluene, xylenes, cyclo-hexane, aliphatic alcohols, esters and acetone. The poly-NVC is, however, soluble only in aromatic hydrocarbon solvents, which provides a way for its separation from monomeric NVC by precipitation with alcohols.

As early as 1934, Reppe[1] first realized the use of NVC as a monomer of practical importance. Since then, a number of workers tried to explore the technological promise of poly-NVC. Actually, in the following years, BASF-Germany could market poly-NVC, in the trade-name 'Luvican', — a material capable of furnishing attractive, yet protective, surface coating. In recent years, however, the cationic NVC-polymerization has attracted attention of a number of workers because of its controversial but unique polymerization characteristics.

Before going for a discussion on the polymerization characteristics of NVC, it is desired to give a brief account of its chemical and electronic features. Since NVC is a substituted carbazole, it shows basic properties arising out of the lone electron-pair on the ring nitrogen atom. The basicity is, however, not very pronounced because of the involvement of this lone-pair of electronsin delocalization throughout the ring system. Presence of vinylic substituent at the nitrogen atom gives rise to further reinforcement of the same. This could be visualized from the resonating structures of NVC as represented below.

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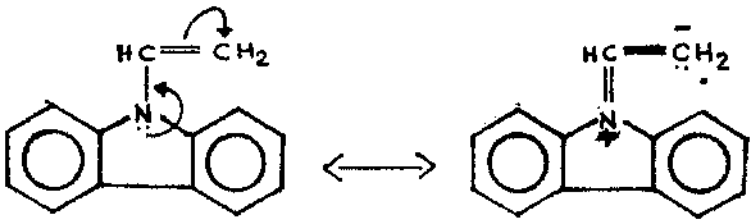
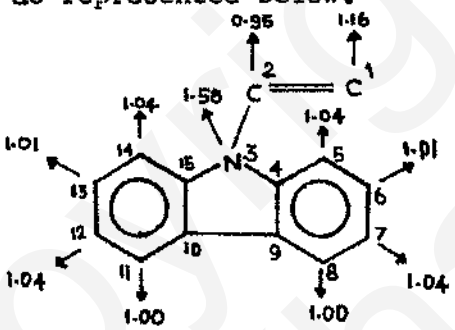


Rembaum et al.[2] have calculated the π-electron density of N-vinylcarbazole as represented below.



The benzene rings of the carbazole group contribute to this high electron density on the vinylic end carbon atom.

On the basis of the above facts, it is possible to verify the validity of different hypotheses, put forward to explain the polymerization characteristics of NVC with different initiator systems.

NVC undergoes polymerization by cationic, free-radical, thermal and radiation induced initiation. No report is available for its anionic polymerization, although Rembaum et al.[2] have indicated the possibility of

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initiating styrene polymerization by the anion radical of NVC produced by the interaction of NVC and metallic sodium in tetrahydrofuran. According to them, the nucleophilic attack on the vinylic double bond in NVC is not energetically favoured due to increased electron density around the vinylic double bond.

A number of workers have reported the polymerization of NVC by free-radical mechanism[3-15]. The initiators include the metal salts[9-13], generally sulphates, chlorides or complex salts, halogens[15], and organic peroxides[14]. Free-radical initiation by thermal treatment has also been reported by Ellinger[8].

The constant e.s.r. signal observed in the metal cation-[12,13] and halogen-[15] initiated polymerizations and the retardation exhibited by oxygen and strong-ligands[11] (which stabilize the higher oxidation states of metal cation through efficient co-ordinate bonding and lower the electron-acceptibility of the metal cation) like chloride, amines and ethers in the metal cation-NVC system and by anthracene in the thermal polymerization of NVC[8], are some of the solid supports in favour of the free-radical nature of the propagating species.

It is generally held that in the metal salt initiated polymerization of NVC, the metal cations act as redox catalysts. Initiation occurs through the reduction of the metal ion to the next lower valence state by one-electron transfer from monomer to the metal ion. As a result, a cation radical of NVC is formed which can propagate to give poly-NVC. The inherent π-acidity of the metal cation is believed to be responsible for the initiation of polymerization. Obviously, such a free-radical mechanism of initiation

holds good only with the metal salts in which the metal can exist in variable oxidation states.

No detailed study on the thermal and radiation induced polymerization of NVC has so far been made. Although Restaino et al.[16] and Chapiro et al.[17] have reported the possibility of NVC polymerization by high-energy radiation, exact nature of interaction involved therein is still unknown. It has been observed, however, that the effect of high-energy radiation is most pronounced in presence of an initiator. Thus Ellinger[18] found that the rate of polymerization of NVC in toluene at 30°C by dioxan-maleic anhydride mixture, irradiated with u.v. light, in presence of air is much faster than that initiated by dioxan-maleic anhydride alone. In this light, it may be surmised that the mechanism of initiation in such radiation induced processes is essentially the same as that in presence of an initiator only. The radiation provides only the necessary energy to facilitate the expulsion of electron from NVC molecule to produce a radical ion so that the initiation starts at a faster rate.

In recent years, the cationic polymerization of NVC with special reference to the elucidation of the exact mechanism of initiation has drawn the attraction of a number of workers. The initiators include the so called organic electron acceptors like halanils, chloro- and cyano-quinones, and nitro, chloro- and cyano- alkenes and alkanes, the Ziegler catalysts, simple metal salts and boron and aluminium halides. From the available reports the following general features of cationic NVC-polymerization may be summarized.

(i) Polymerization is initiated by an electron acceptor with the development of characteristic colour. The intensity of colour and the

frequency of spectral absorption depend on the electrophilicity of the acceptor and the medium of reaction[15,18-24].

(ii) Polymerization is not affected by oxygen which is known to be a free-radical scavenger[25].

(iii) Polymerization is inhibited by organic bases such as aniline, N, N-dimethylaniline, trimethylamine, N-methyl quinolinium salts[20] as well as by water and alcohols[19,20,24,26,27].

(iv) The rate of polymerization is faster in a solvent of high than in one of low dielectric constant. For example, the polymerization by p-chloranil at 40^0C is seventeen times faster in acetonitrile than in toluene[23].

(v) Initiators donot add up in the resulting poly-NVC as evidenced by the spectral studies and the end-group analyses[21].

(vi) The molecular weight of the poly-NVC is notably independent of the electron accepting power and the concentration of the initiators[18,24].

The generalizations, enumerated above, clearly suggest the cationic nature of the propagating species in NVC polymerization and are consistent with the electron density diagram of NVC calculated by Rembaum *et al.* (loc. cit.).

However, there exists a lot of controversy regarding the mechanism of homogeneous initiation of NVC polymerization by electron acceptors.

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Scott and co-workers[20] firmly believe that the polymerization in such systems proceeds by a cationic mechanism through the formation of a wurster ion. The identity of the u.v. spectra of the particular wurster ion and the colouration produced during polymerization, is claimed by Scott to be a strong support to their contention. The British[24] and Japanese[28] schools of workers, however, from their studies on the poly-NVC — initiator interaction and detailed kinetic investigation maintain that the wurster ion formation alone is insufficient to account for the polymerization characteristics of NVC. Formation as well as participation of wurster ion is, however, limited at the onset of the polymerization.

It is worthwhile to assess the possibility of wurster ion formation from the knowledge of the physico-chemical properties of NVC. There exist several reasonings rigid enough to support the wurster ion formation. These are

(i) Several organic amines are known to form cation radicals with electron acceptors. These cation radicals possess characteristic colour, often observed in NVC-electron acceptor interactions during polymerization[29,30].

and, (ii) A constant e.s.r signal is observed during the polymerization of NVC by halogens[15] - an indication that radical ion with lone electron is present in the system.

However, evidences are there, which go against the possibility of wurster ion formation. These are

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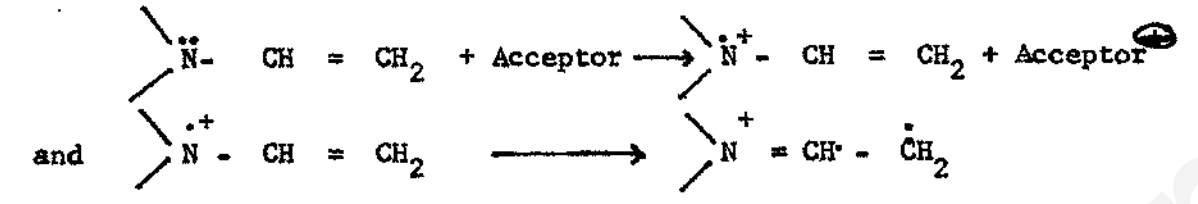
(i) Formation of wurster ion of NVC may be represented as



Such an interaction involves the transfer of an electron from the ring nitrogen atom to the acceptor; the ease of transfer increases with increased electron density on the ring nitrogen atom. A comparison of the electron densities on the nitrogen atoms in carbazole and N-vinylcarbazole points out to a lower electron density in case of NVC. This is due to the participation of the vinyl group in conjugation with the carbazole ring system. It is thus expected that carbazole should exhibit stronger interaction than NVC with the electron acceptors. But it is the reverse trend[21] which is usually observed. Thus the formation of wurster ion during initiation is open to criticism.

(ii) There is no evidence about the free-radical activity of the wurster cation of NVC in presence of an electron acceptor as is anticipated due to the presence of lone electron. Also no polymerization or copolymerization has been observed with styrene or acetonitrile (known to be susceptible to only the free-radical polymerization) when added in NVC polymerization system in presence of organic electron acceptors.

Moreover, oxygen which is known to inhibit free-radical polymerization, has been found not to retard, to any detectable extent, the polymerization of NVC by electron acceptors.

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(iii) It has been reported[31] that different colourations are developed when crystalline NVC is treated with different gaseous halogens. Thus with chlorine, bromine and iodine, the colourations are dark green, black and brown respectively. This indicates that the products of such interaction have absorptions at different wave lengths. If the colouration is due to the wurster ion of NVC, it should have produced a single colouration differing only in intensity. Clearly the colouration developed is not a necessary criterion for the wurster ion formation.

The absence of free-radical activity in NVC wurster cation, has been explained by Scott by the assumptions that the positive charge on the wurster cation is concentrated about the nitrogen atom and the separation of ionic and radical functions would involve quarternization of nitrogen atom and consequently a deactivation of the reactivity of the cationic function of the radical ion.

Steric hindrance must be expected to affect this separation of cationic and free-radical functions since the $>\overset{+}{N} = CH - \dot{C}H_2$ group would be planar with the aromatic ring system and hence would be subject to steric hindrance. Tsuji et al.[15], however, maintain that as the polymerization proceeds, the free-radical becomes delocalized over the carbazole ring system, which explains the constant e.s.r. signal observed in NVC-halogen polymerization system.

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On the basis of the above discussions, it is difficult to say anything conclusive regarding the formation of wurster ion. In all probability, it appears that NVC-electron acceptor interaction would in general lead to a charge-transfer complex and in certain cases where the interactions are very strong, complete one-electron transfer from monomer to initiator might result in a cation radical. Nomori et al.[23] from their observations in NVC-p-chloranil and NVC-tetranitromethane interactions arrived at the same conclusion. According to them, it was the charge-transfer complex, rather than the wurster ion, which was responsible for the initiation of polymerization and the colourations produced.

It has already been pointed out that the initiation of NVC polymerization by transition metal salts is free-radical in nature. Solomon et al.[32], however, report that the initiation by simple metal salt (in which metal can assume only one energetically favoured oxidation state) is definitely cationic in nature. Thus, with $Mg(ClO_4)_2$, they suggested a cationic mechanism which involved initiation by $MgClO_4^+$ ion.

Initiation of NVC polymerization by organic cation salts like tropylium fluoroborate, tropylium hexachloroantimonate, 2,4,6 - trimethyl pyridilium hexachloroantimonate and other salts of xanthylium and phenazonium cations[33] is also thought to follow a cationic mechanism. These initiators bear a marked contrast with the other initiators in that they, unlike other organic electron acceptors, add up at the end of the resulting polymer.

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Yet another important class of initiators includes some covalent oxyhalides, halides or sulphates of certain elements which are either nonmetals or metalloids. Such elements are P, As, Sb and Bi. Initiations with these catalysts are essentially cationic in nature as reported by Biswas and Chakraborty[34]. Detailed investigation with this class of catalysts in initiating the polymerization of NVC is in progress in this laboratory.

Report on the polymerization of NVC over Ziegler catalyst is very scanty. A Canadian patent[35] discloses the use of Ziegler catalyst for the polymerization of NVC to high molecular weight product. Solomon et al.[36] observed that NVC could be polymerized to stereospecific polymer over $TiCl_4$ - n-BuLi. They suggested interaction of monomer with both the catalyst and the co-catalyst, but failed to furnish any concrete evidence regarding the exact mechanism of initiation. Heller and co-workers[37] also studied the polymerization of NVC over $TiCl_4$ - AlR_3 and $TiCl_4$ - n-BuLi. They observed that $TiCl_4$ or $TiCl_3$ alone was capable of catalyzing the polymerization of NVC. In presence of co-catalyst like n-BuLi the conversion was high but the stereospecificity was low. This observation contradicted the one made by Solomon et al. as stated earlier.

No systematic investigation has so far been made on the kinetics of polymerization of NVC by electron acceptors. The main reasons are the lack of reproducibility in the kinetic measurements and very complex nature of initiation as well as the termination processes involved therein.

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Several contradictory reports are, however, available on the dependence of rate and the degree of polymerization on the monomer and the initiator concentrations. With p-chloranil as initiator in toluene medium, Ellinger[21] observed an approximately second order dependence of rate on both monomer and initiator concentrations. But Pac and Plesch[24] found that with p-chloranil-nitrobenzene system the rate was a complex function of monomer concentration, the rate being maximum at 0.18-0.19 mole lit^{-1}. The results proved unduly irreproducible in respect of initiator concentration. While Ellinger reports the decrease of molecular weight of poly-NVC with increase in initiator concentration, Pac and Plesch observed an apparent constancy of molecular weight of the resulting poly-NVC.

I-2. Physico-Chemical Properties of Vanadium Pentoxide in Relation to the Electronic Theory of Contact Catalysis :

Vanadium pentoxide is an orange-yellow solid, melting at $650^{0}C$, in which vanadium is present (almost) in +5 oxidation state with d^{o} configuration. The vacant d-shell is responsible for the considerable π-acidity exhibited by V_2O_5. Partial satisfaction of the electron thirst of V^{+5} ions is made by back donation of electrons from the oxide ions in the matrix and this imparts a considerable co-valent character to the oxide.

In recent years, V_2O_5 has been recognized as an efficient oxidation catalyst with wide industrial applicability. This has led to the extensive investigation on their properties, in a bid to evolve some guiding principle regarding their preparation, pretreatment etc. In course of these studies, several important facts about the crystal structure, electronic properties and phase compositions of V_2O_5 have been brought to light. These features are outlined below, in brief.

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The salient structural features[38] of V_2O_5 are illustrated in Fig. 1,2,3. The orthorhombic crystalline form of this oxide presents so irregular an octahedral arrangement of oxygen ions around the central vanadium ion that the metal is usually regarded as penta-co-ordinated. This is a consequence of the characteristic ionic size of V^{+5} which favours both the tetrahedral and the octahedral arrangements of oxygen in the lattice. The crystal matrix consists of an infinite array of VO_4 tetrahedron, each of which has three corner oxygen ions common with the neighbouring units. Oxygen ions at the opposite vertices of the tetrahedron are not shared. For the three-dimensional build up, one of the three shared oxygen ions acts as a bridge to develop a'lattice sheet' while the other two are used in forming the zig-zag VO_4 'chains'.

Electronic properties of V_2O_5 have been extensively studied. Its n-type semiconductivity arises out of nonstoichiometry resulting either from 'a priory' anionic vacancy or through the artificial creation of lattice defects by the altervalent foreign ions. It is generally held that the anionic vacancies containing quasi-free electrons result from the elimination of oxygen from the lattice simply by heating. But according to Maidenovskaya[39] et al.,no significant defect in the V_2O_5 lattice can be created by thermal treatment. Since V_2O_5 has a low fusion temperature (650^0C) and hence a low Tamman temperature, the mobility of the defects becomes quite appreciable at moderate temperatures. According to Clark and Berret[40], heating even upto temperatures of 180° and 350^oC is quite conducive to bring about respectively the surface and bulk mobilities of the defects.

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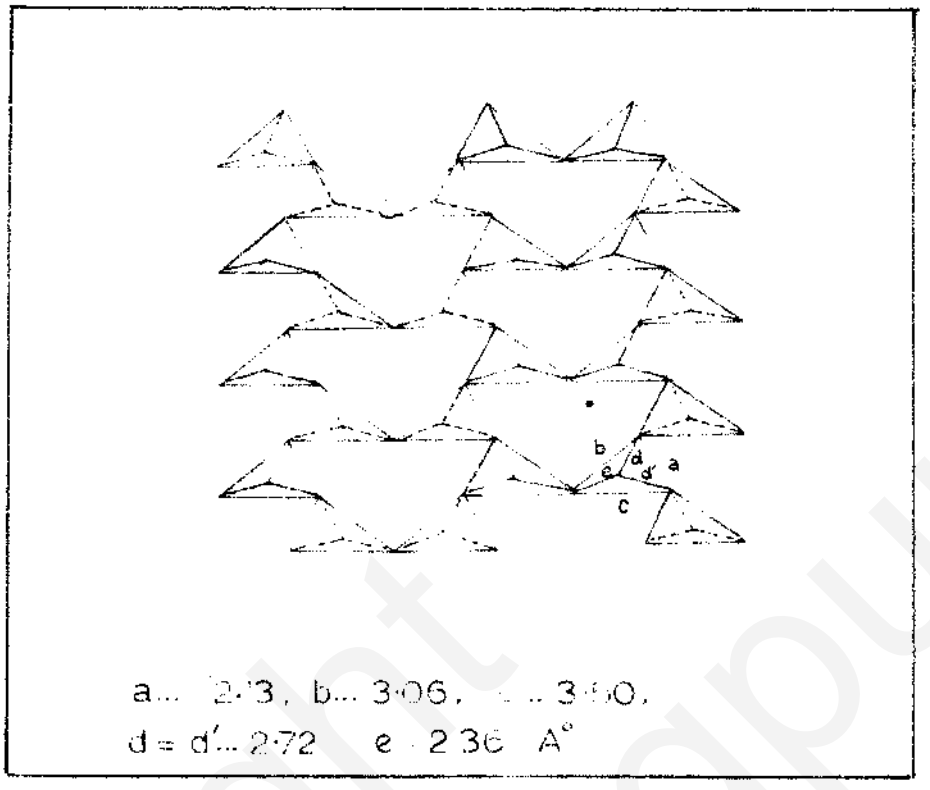

FIG. 1.. TWO DIMENSIONAL NET WORK OF DISTORTED VO_4 TETRAHEDRA IN VANADIUM PENTOXIDE

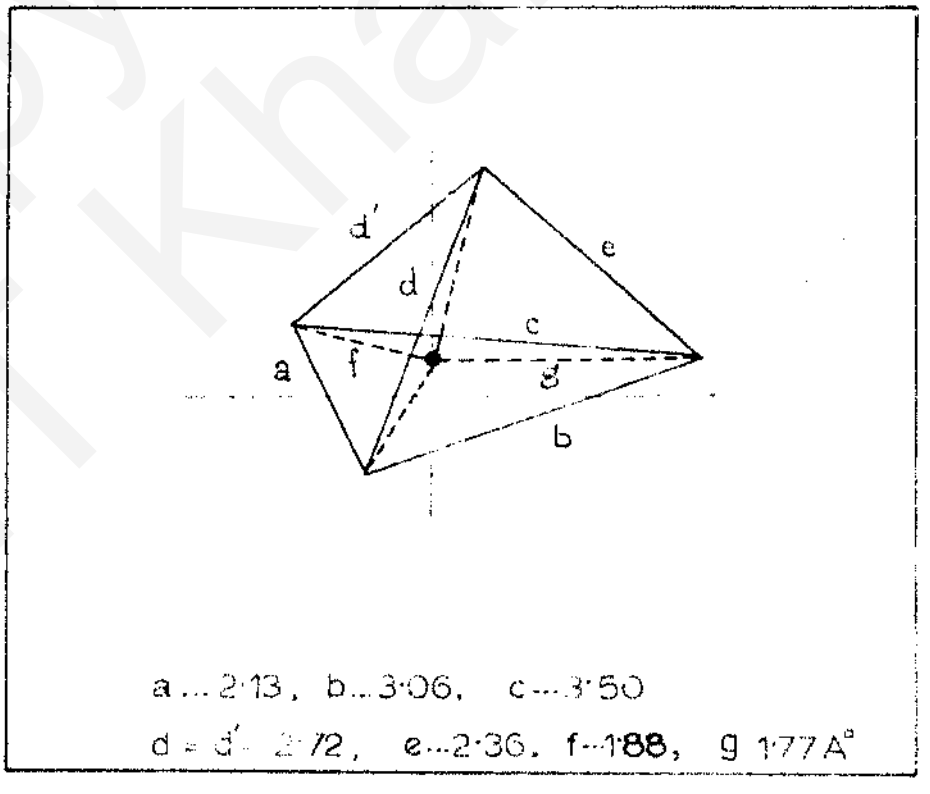

FIG. 2.. UNIT DISTORTED VO_4 TETRAHEDRON

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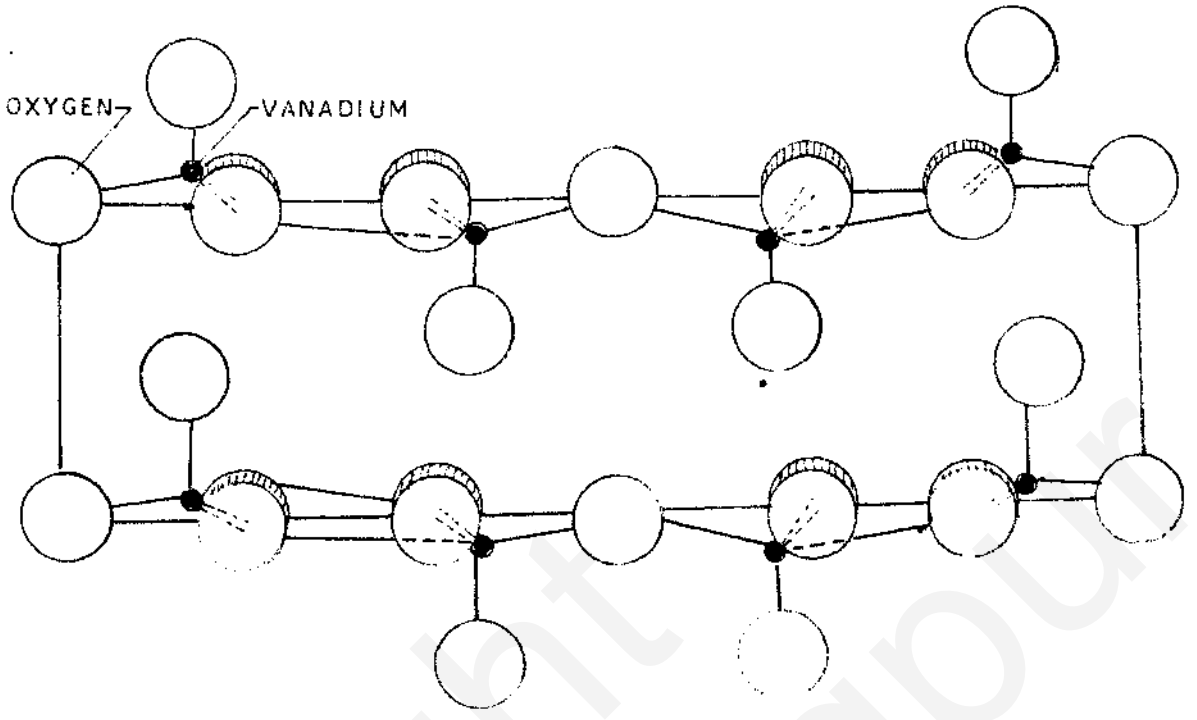

FIG. 3.. DIAGRAM OF V_2O_5 UNIT IN V_2O_5 CRYSTAL

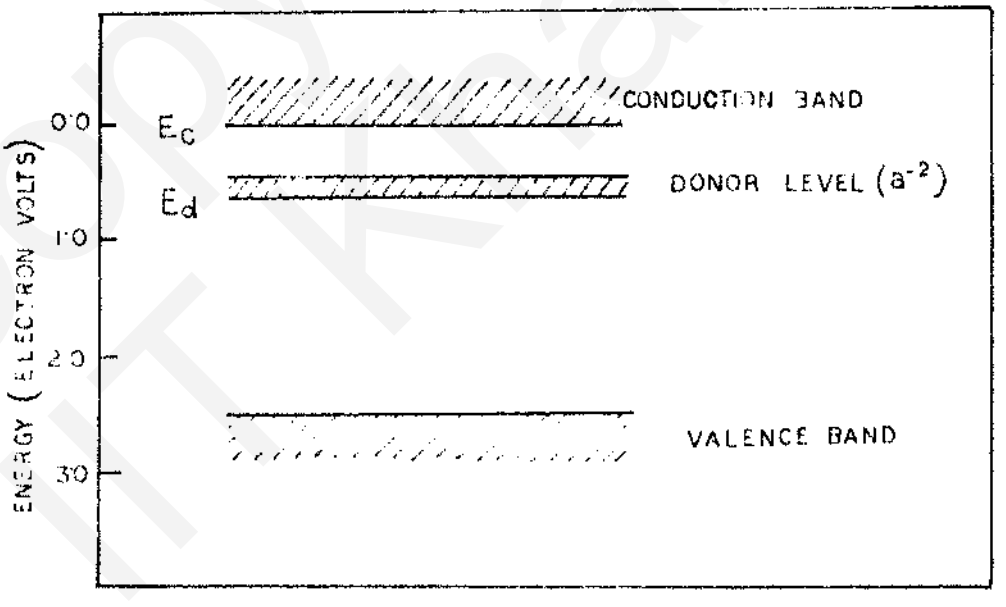

FIG. 4.. ENERGY LEVEL DIAGRAM OF V_2O_5

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Morin[41] has proposed the energy level diagram as shown in Fig.4. The anion vacancies in which the electrons are located in sufficient concentration serve as the donor level or band. The energy-gap between this level and the conduction level being only 0.42 ev, the quasi-free electrons can be easily excited to the latter state and thus they can take part in the catalyst-adatom interactions with facilities.

The excess of electrons resulting from the escape of oxygen from the lattice, besides being trapped in the anion vacancies, may also interact with V^{+5} to form V^{+4} ions. That such an interaction occurs to a small extent has recently been established by the determination of the magnetic susceptibility and e.p.r. spectrum of the V_2O_5 samples prepared by decomposing NH_4VO_3. This observation by Japanese group[42] refutes the earlier proposal of Petcherskaya et al.[43].

It is interesting to note that, the semiconductor catalysts, whether n-type (showing electrical conduction due to excess electrons) or p-type (having holes as the conducting agent), behave quite characteristically when they are allowed to interact with certain chemical species through some surface processes like adsorption, desorption etc. During cumulative or cationic sorption, in which electrons are transferred from compound to solid, the conductivity of n-type oxides would increase, while that of the p-type samples would decrease. For depletive (or anionic) chemisorption involving electron abstraction from the solid, the n- and p-type conductors respond in a manner quite opposite to the previous case.

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This correspondence-relation, alone or combined with the measurement of Hall Coefficient, has been widely used, perhaps much too often, to characterize the nature of electron-transition in catalysis.

Hauffe[44], Volkenstein[45], Weisz[46], Stone[47], Dowden[48], Parravano[49], Masse[50], Aigrain[51] and others have explained the electronic aspect of catalysis very critically through ingeneous experimental verifications and theoretical arguments. As a result, the electron-throry of catalysis and its variously refined and modified versions now provide some fairly successful dictates of the phenomenon of catalysis. It is to be noted here, that the tacit assumption concerning the equilibrium between the bulk and the surface, which is featured in the above theories, should not always be taken to be a foregone conclusion. This surmise may, of course, be reasonable at higher temperatures where the mobility of the defects could be fairly high.

The later refine ents of the electron-theory like the boundary-layer theory[52], and the charge-transfer concept[53] offer quantitative formulations about the gradual decrease in the adsorptive capacity of the catalysts with the progress of adsorption.

Even after these modificiations, a number of discrepancies between the experimental observations and theoretical predictions are there. This apparently indicates a very serious drawback of these theories, namely, the neglect to include the possibility of the actual physical exchange of certain species between the catalysts and the reactants in the fluid phase (liquid or gas).

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To make this concept more fruitful for describing the spatial and energy factors of adsorption and contact catalysis, recently sincere attempts are being made to combine the concepts of crystal-field[54] and the ligand-field[55] theories with the dictums of the electron-theory to throw light on the spatial and energetic requisites of the electronic and atomic exchange processes involved in heterogeneous catalysis. It is also suggested that for an accurate formulation of theory for the contact catalysis, the cation-cation exchange[56] forces operating on the surface should also be given due consideration.

Whatever may be the future shape and brief of this electronic concept of catalysis, in the majority of current investigations it is the nature and the relative variation of the magnitude of the bulk electrical conductivity of the semiconductor catalysts (due to adsorption, desorption or surface reactions) which are actually measured. It has been found that chemisorption of oxygen[60] reduces the conductivity of vanadium pentoxide, the process responsible for such decrease being

$$\tfrac{1}{2}\, O_2\ (\text{gas}) + 2\ e \rightleftharpoons O_\sigma^{-2}$$

(σ - surface and e-electron)

The gradual development of the double-layer in the gas-phase and the electron-depleted boundary-layer near the catalyst surface, limits the chemisorption of oxygen to a low value.

Chemisorption of adsorbates containing double or triple bonds (which provide higher electron (π) density at those bonds) like ethylene[57],

xylene[58] and naphthalene[59], increases the conductivity of an n-type conductor like V_2O_5. The situation on a p-type conductor is, however, very similar to that in case of the adsorption of oxygen on an n-type one. Gradual neutralization of the positive holes through the electron donation from the double or triple bond results in the formation of a double layer of positive charges in the fluid phase and in the boundary-layer of adsorption in the solid which restricts further adsorption of the adsorbate.

Such observations i.e. the change in the conductivity with adsorption, are utilized to visualize the electronic mechanism of the surface processes. The usefulness of thermo-electric potential[61], surface potential[62], AC-conductivity[63] etc. and also the significance of the measurements of the photo-initiated surface processes[64] have recently been appreciated and these aspects are gradually gaining ground in the catalytic research.

I-3. Vanadium Pentoxide as Polymerization Catalyst :

The use of vanadium compounds (mainly chlorides and sulphates) in combination with metal alkyl co-catalyst has been extensively made to explore the technological promise as well as the kinetic characteristics of those catalyst systems.

The investigation in this direction was initiated by Natta[65], who finally recommended the transition elements (which are most effective in initiating polymerization having work function less than 4 ev. and first ionization potential less than 7 ev. e.g. titanium, chromium, vanadium, and zirconium) as the best Ziegler catalysts. A series of

patents assigned to E.I. du Pont de Nemours and Co. and numerous other patents also refer to the use of vanadium compounds, generally chlorides, oxychlorides or sulphates, in which vanadium is present in oxidation state 2 or 3.

Although the Ziegler catalysts containing vanadium compounds have been largely investigated,very few reports are available on the use of vanadium pentoxide as polymerization catalyst. Furukawa et al.[66] examined the catalytic activity of a number of metal oxides towards the polymerization of acetaldehyde and found V_2O_5 to be completely inactive. Recently Smith and Zelmer[67] made use of V_2O_5, supported on SiO_2, in combination with $(i\text{-}Bu)_3Al$ for ethylene polymerization and studied the kinetics and mechanism of the reaction. To explain the results obtained with this system, they indicated the possibility of bimolecular termination with respect to active sites. Ozaki[68] also examined the catalytic activity of V_2O_5 (and also other oxides like CaO, BaO, Bi_2O_3, MnO_2, MgO, SnO, ZnO, TiO_2, Sb_2O_3, Cr_2O_3, MoO_3 and WO_3) in combination with diethylzinc for the polymerization of propylene oxide . V_2O_5 showed good activity, the best performance being shown by BaO system which produced a polymer with an intrinsic viscosity of 11.0. According to a number of U.S. and British patents[69-71], promoted vanadium pentoxideswere successfully used in the production of poly-propylene and poly-ethylene. The promoters used were some complex metal borohydrides, alkali or alkaline earth metal hydrides, alkali metal-aluminium hydrides, aluminium alkyls and aryls, aluminium

hydride and alkaline earth metal carbides and the catalytic activity was found to depend on the nature of the promoters employed and the pretreatment conditions.

Exact oxidation state of vanadium in the above mentioned catalysts is not known. It is, however, held that the active catalysts contain vanadium in +2 or +3 oxidation state. The reduction occurs either in situ during the introduction of the promoter as in case of alkali metal-aluminium hydrides and metal borohydrides, or during pretreatment preceeding actual catalysis.

Friedlander et al.[72] examined the promoting action of V_2O_5 in a number of commercial metal oxide catalysts for polymerization of mono, di, and the unsubstituted styrenes. The products, however, possessed no appreciable degree of crystallinity. This was explained by them to be due to the moderate Lewis acid character of V_2O_5. Bayer et al.[73], in a patent, described the use of V_2O_5 in combination with two co-catalysts, mono or di phenyl or octyl esters of phosphoric acid and ethyl or phenyl aluminium chloride. The catalyst was found to be highly active in polymerizing propylene, styrene, acrylonitrile, vinyl chloride, divinylbenzene and butadine. In another patent, assigned to Owens, Illinois Inc., Thomas[74] has made an unique claim as to the use of V_2O_5 in producing poly-siloxane through simultaneous hydrolysis and polymerization of organic tri-alkoxysilane under natural conditions.

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I-4. Polymerization by Other Oxide Catalysts :

Survey of literature shows that quite extensive investigations have been carried out on the polymerization initiated by oxide catalysts. Most of these investigations were on the chromia and molybdena catalysts in combination with different oxide supports and promoters. Of the different catalysts, mention should be first made of the Phillips chromia catalyst, developed by Phillips Petroleum Company and designated as 'Marlex Catalyst'[75], and the molybdena catalyst developed by Standard Oil Company of Indiana[76]. These two catalysts have been found highly active in polymerizing ethylene, propylene or a mixture of the two to a solid, crystalline polymer in high yield. In a number of patents, the use of different supports and promoters or co-catalysts has been described. The supports include, alumina, silica, silica-alumina, oxides of transition metals like Zr, Th, Hf etc. while the promoters or co-catalysts include the oxides of Cu, B, V, Ti, Mo, Fe, Co, Mn, Zn, Sr, W, Mg and Ba for chromia catalysts and alkali and alkaline earth metals, their hydrides, borohydrides and aluminohydrides, aluminium alkyls and aryls, the oxides of Fe, Ni, Co, etc. and the carbides of alkaline earth metals for molybdena catalysts. Besides chromia and molybdena catalysts, possibility of utilizing the oxides of other group Va and VI a metals like, niobium, tantalum, tungsten and uranium has also been tested. However their use has been kept limited within the laboratory for their comparatively lower activity, higher cost and rigorous pretreatment and polymerization conditions. All these catalysts need pre-reduction before they are subjected to actual catalysis. This can be achieved either by contacting the catalysts with the monomer or reducing it in a flow of hydrogen or in situ, during the incorporation of promoters like alkali or alkaline earth metals, their hydrides, borohydrides and aluminohydrides.

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Friedlander et al.[72] examined the efficiency of a number of activated commercial-type metal oxide catalysts containing Mo, Cr, Bi, Pt, Ni and Co and covering a broad range of acidity, surface area, and texture, for the polymerization of p-dimethylstyrene, α-methylstyrene and styrene. They obtained essentially amorphous polymer with styrene and semi-crystalline ones with α-methyl and p-dimethyl styrenes. The extent of polymerization as well as the relative stereospecificity of the polymers produced was found to be strictly dependent on the acidity of the catalyst.

Furukawa (loc. cit.), in a series of investigations, observed that acetaldehyde could be polymerized to high molecular weight polymer by adding it in vapor phase or in solution over γ-alumina, which was kept at dry-ice temperature. This led him to investigate the polymerizing activity of other oxides such as CrO_3, MoO_3, B_2O_3, P_2O_5, MgO, ThO_2, SiO_2 (gel), Al_2O_3/SiO_2 (13/87), CuO, TiO_2, ZrO_2, ZnO, Fe_2O_3, MnO_2, BaO, PtO_2, PdO, Ni_2O_3 and CaO. Of these, CrO_3 and MoO_3 gave polymers of high molecular weight but in much low yield. B_2O_3, P_2O_5 and MgO showed negligible activity producing a trace of soft, tacky polymers of lower molecular weight while the rest did not show any reactivity. It was reported by Gregg and Sing[77] that the activity of alumina samples was largely governed by the conditions of pretreatments. The catalyst samples, heated below 200^0C and above 1100^0C, possessed no polymerization activity and also showed no appreciable degree of adsorption of nitrogen over them. On the other hand, the samples heated between 300^0 and 1100^0C were found to be highly active on both the counts. Thus the higher catalytic efficiency of CrO_3 and MoO_3 and inactivity of other oxides

as observed by Furukawa et al., could be explained in the light of physico-chemical characteristics of the oxides which govern the adsorption of acetaldehyde and the nature of active species on the surface.

As early as 1923, Staudinger and his co-worker[78] carried out systematic studies on the polymerization of alkene oxides in which they made use of some oxides like ZnO, SrO, CaO, MgO, Fe_2O_3 and PbO besides Al_2O_3, SiO_2 and activated carbon. They found that Fe_2O_3, MgO, PbO, SiO_2, Al_2O_3 and activated carbon had no activity towards ethylene oxide polymerization while the others produced soft, waxy to hard tough polymer of molecular weight ranging from 50,000 to 100,000. Following the same line, Union Carbon and Carbide Company[79] of the U.S.A. developed a catalyst for commercial production of poly-ethylene oxide of very high molecular weight.

In addition to these simple oxides, a number of spinal type mixed oxides have been investigated. Foster and Whitman[80], in their patent, claimed that reduced phosphomolybdic acids, alone or promoted, were quite active for the production of high molecular weight linear poly-ethylene. The catalyst, formulated as $P_2Mo_{20-24}O_{3-51}$, was believed to contain Mo in oxidation state below +4. Alkali and alkaline earth metals and their hydrides or aluminohydrides acted as promoters. A similar catalyst,[81] represented by the formula $P_2Mo_{20-24}O_{31-60}$, and its reduced metal salt[82] $M_yP_2Mo_{20-26}O_{37-65}$ (M is a metal of groups, I-A, I-B, II-B, III-B, VII-A and the base metals of group VIII), have also been claimed to be highly effective in synthesizing high melting and high molecular weight poly-ethylene from CO and H_2.

I-5. Generalized Kinetic Scheme and Mechanism of Polymerization on Oxide Surface :

In polymerizations initiated by solid surfaces, the reaction proceeds through the adsorption of monomer followed by the formation of an active chain bound to surface. The propagation may then continue either according to Langmuir-Hinshelwood mechanism or by Rideal mechanism. The termination of the growing chain may occur either on the surface or in the solution.

Two different possibilities are encountered in the mechanism of polymerization - one, in presence of a co-catalyst as in the classical Ziegler-Natta-type catalyst and the other in absence of a co-catalyst as in the case of metal oxide catalyst. Interpretation of the kinetic data obtained with the Ziegler-Natta catalyst systems is complicated due to the involvement of the co-catalyst. Reich and Stivala[83] made a novel attempt to summarize the general kinetic characteristics of the polymerization results obtained with different Ziegler-Natta catalyst systems. They made some assumptions that (i) overall polymerization mechanism remained unaltered, regardless of the catalyst system or monomer used,(ii) the overall kinetics were guided by the predominance of one of the reaction steps over the others,(iii) polymerization proceeded on the solid catalyst surface of homogeneous activity. They also explained the role of the co-catalyst present in the Ziegler-Natta catalyst systems. According to them, a co-catalyst offers properly spaced dual active sites by getting itself adsorbed on the main catalytic components. These might then induce stereospecific polymerization by imparting preferred and regular orientation to the adsorbed monomer molecule.

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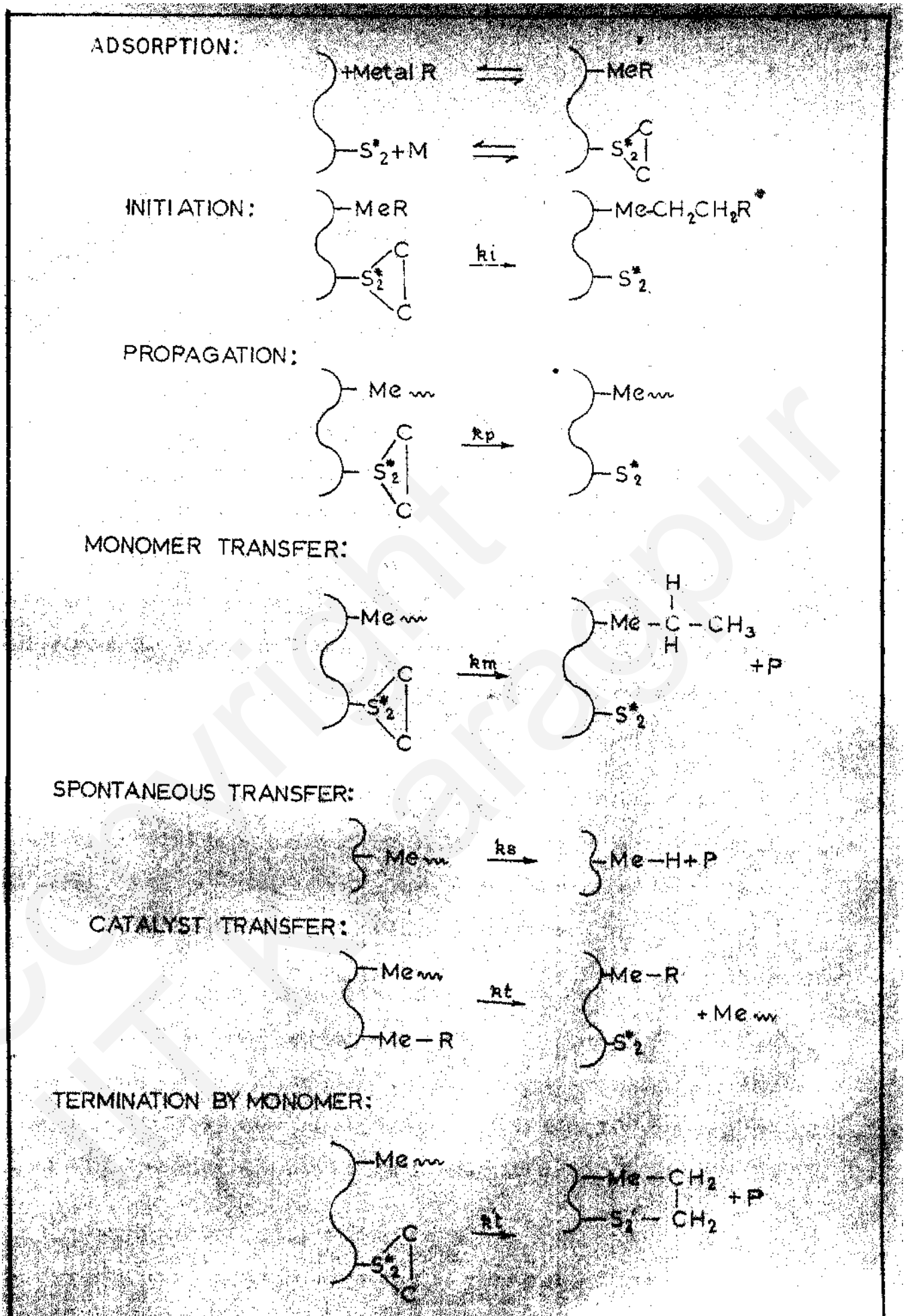

FIG.5. GENERALIZED KINETIC SCHEME ACCORDING TO REICH AND STIVALA

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On the basis of these concepts, the course of polymerization may be resolved in several steps as shown in Fig.5. Here S_2^* is an active dual site, S_2' is an inactive dual site and Me denotes the metal component of the co-catalyst.

In this kinetic scheme, Reich and Stivala assumed the co-catalyst and monomer adsorption equilibria to be strictly maintained throughout the reaction. The polymerization then proceeds through Langmuir-Hinshelwood mechanism, the equilibrium concentrations of the surface species being governed by simple Langmuir isotherm. The relative importance of the steps other than the adsorption processes in the overall kinetics is governed by the nature of the catalyst, co-catalyst and monomer and also by catalyst to co-catalyst ratio.

This kinetic scheme as presented by Reich and Stivala has been found to be valid in a number of cases. The results obtained by Ludlum, Anderson and Ashby[84], Gilchrist[85], Natta[86] and McGowan and Ford[87] were found to be in excellent agreement with this scheme.

However, the scheme is not valid in systemswith no co-catalyst because it does not take the initiation by catalyst itself into account. A generalized scheme for the polymerization over solid surface, applicable to both metal oxide and metal-alkyl-metal halide (Ziegler) catalyst systems, has been proposed by Friedlander[88] which is illustrated in Fig. 6 (a),& (b).

Though the ion-radial scheme proposed by Friedlander is unique in representation, it lacks supporting experimental evidences. Natta has

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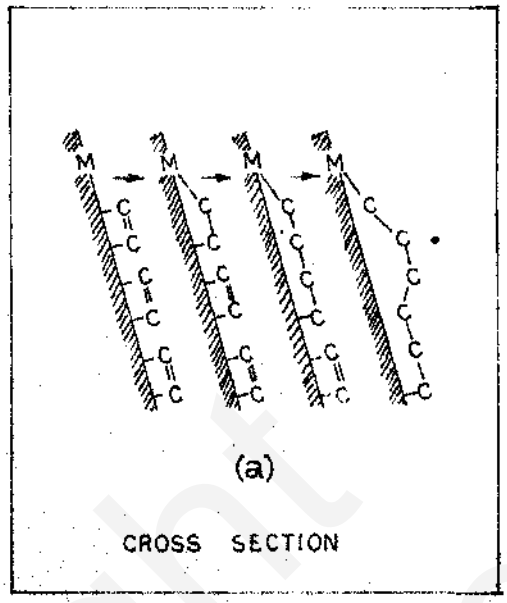

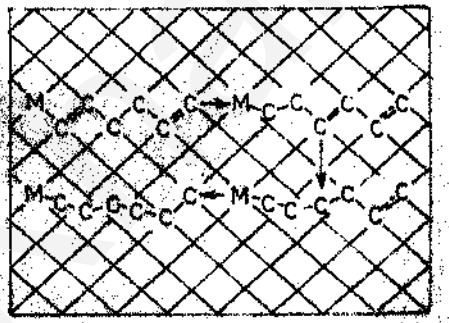

FIG. 6. REPLICA POLYMERIZATION MECHANISM ACCORDING TO FRIEDLANDER

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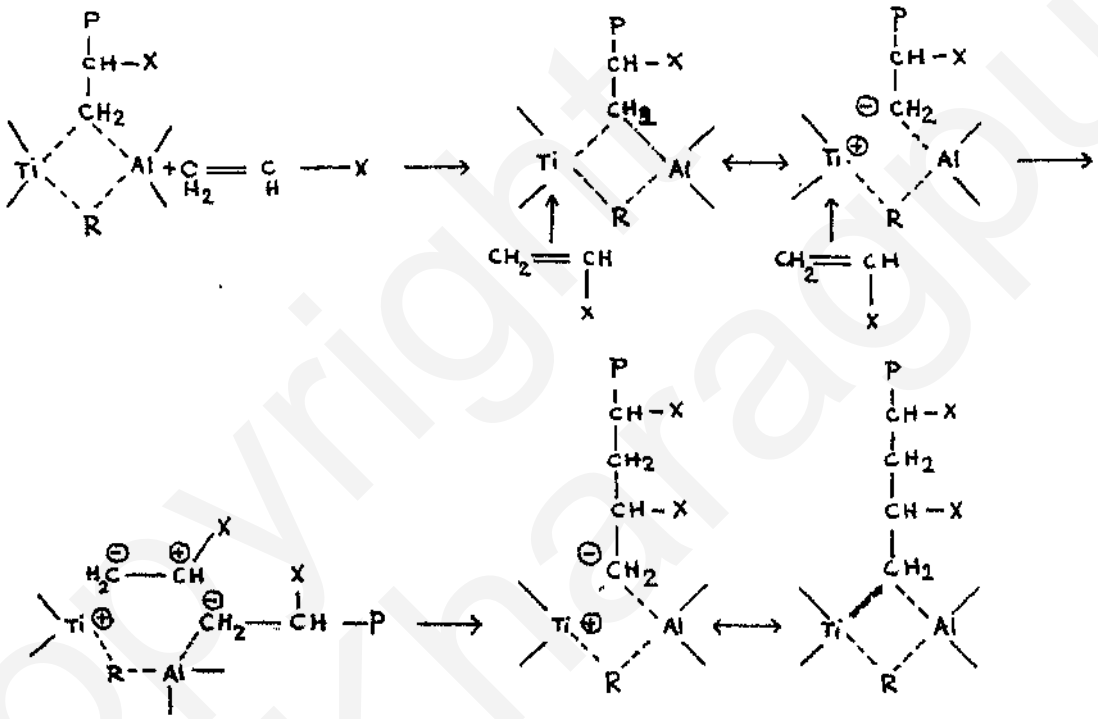
strongly criticized this mechanism and has rejected its applicability in Ziegler system of catalysts. On the basis of the experimental work, Natta[89] put forward a co-ordinate mechanism of polymerization on Ziegler catalysts. The mechanism is very similar to one proposed by Natat and Sinn[90] and may be represented as



Later, Friedlander[91] extended the co-ordinate mechanism to embrace hetero-catalytic polymerization in absence of any co-catalyst. In his scheme, the catalyst, acting as both electron donor and acceptor, initiates polymerization. The mechanism is schematically represented in Fig. 7.

In Ziegler catalyst systems, the propogating species and the catalyst form an ion-pair, held together by electrostatic forces. Such a situation is possible because of the presence of metal alkyl co-catalyst which supplies alkyl group to block the other end of the polarized monomer molecule.

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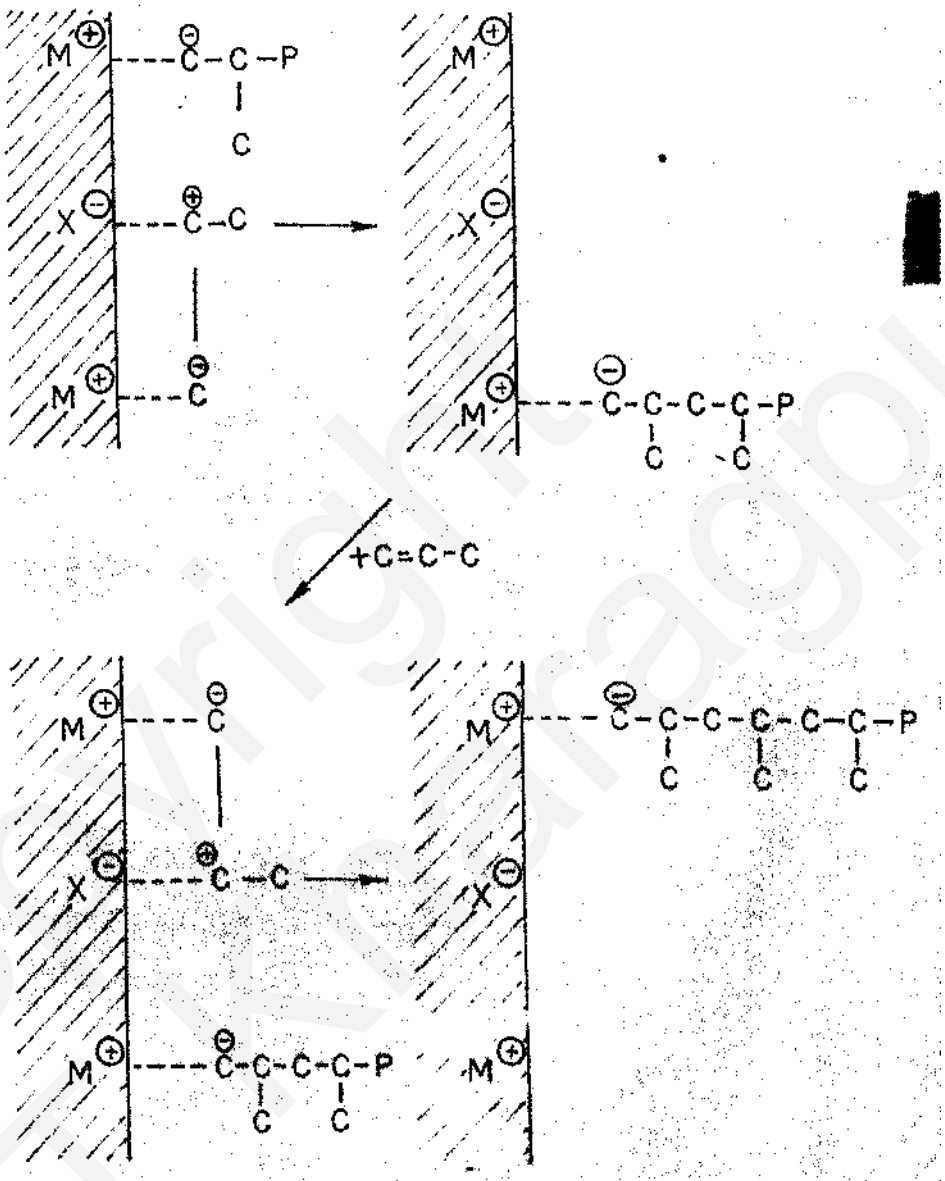

FIG. 7. SURFACE COORDINATE MECHANISM ACCORDING TO FRIEDLANDER

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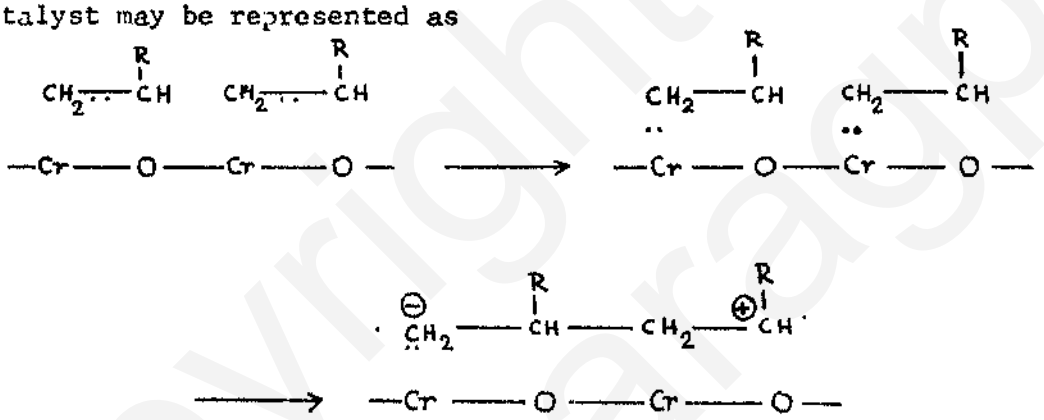
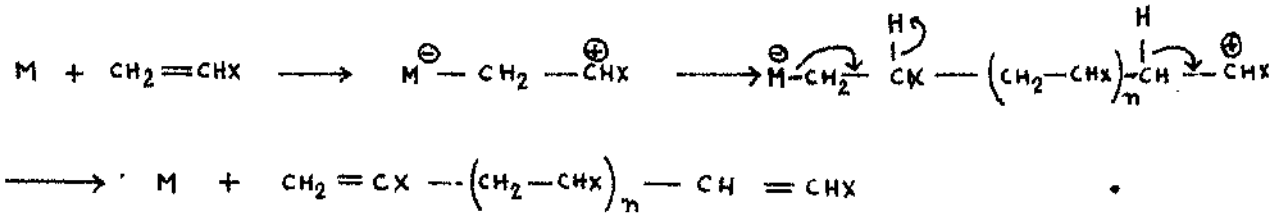
In absence of any co-catalyst, as in case of simple oxide catalysts such an initiation scheme is impossible; here the initiation of polymerization is believed to occur in different ways. One of the possibilities has been proposed by Eirich and Mark[92] who suggest that the inherent Lewis acidity of the metal ion causes polymerization of the vinylic double bond through partial or full transfer of electron to the catalyst. According to this postulation, the polymerization of olefin over chromia catalyst may be represented as



Curphey[93] suggests yet another mechanism of initiation in which complete transfer of an electron occurs from the vinylic double bond of the monomer to the catalyst. Propagation of the polymer chain continues along the surface of the catalyst with the positive charge at the end of the chain and termination occurs via the expulsion of proton and hydride ion from the β-carbon atoms at the chain ends.



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I-6. Scope of the Present Work:

All along the foregoing threadbare discussions, it has been intended to project the various upto-date briefs and aspects of heterogeneous polymerization catalysis with special reference to the mechanism of heterocatalytic cationic polymerization of vinylic monomers.

It is clear from the previous deliberations that a serious indecision still persists regarding the mechanism of the cationic polymerization of NVC. What seems more surprising is that there has been made hardly any serious attempt to study the kinetics of its polymerization over solid surfaces, which could have helped in providing a rational approach towards the satisfactory explanation of the prevailing falacies on its cationic polymerization.

So far as the heterocatalytic polymerization over solid surface is concerned, there is available very limited report, excepting a few with Ziegler catalyst systems, on the elucidation of the mechanism of polymerization in relation to the physico-chemical properties of the solid like the surface and bulk structures of atomic (or ionic) arrangements, the surface and the bulk acid-base characteristics, the electronic structure of individual ionic species in the solid, the nature and the extent of the inherent or induced semiconductivity exhibited by it and the nature of the physico-chemical interactions

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involved during the pretreatment of the same. Perhaps, the most neglected class of these compounds is the one comprising of the so called oxide catalysts like MoO_3, CrO_3, V_2O_5, CaO etc. although their activities have been critically studied and successfully utilized, even on the industrial level, in other types of reactions.

A fruitful contribution to the understanding of the exact mechanism of the cationic NVC-polymerization as well as the role of solid catalysts in relation to their physico-chemical properties can be made available from the study of the polymerization characteristics of NVC over a certain oxide catalyst. The choice of V_2O_5 as the polymerization catalyst is largely due to the fact that a more detailed and consistent information on the physico-chemical properties are available with this oxide. Also, the general inferences, which can be drawn about its role in bringing about the polymerization of NVC, may be extended to the other types of reactions, especially the heterogeneous catalytic oxidation processes, in which the role of V_2O_5 is not well-understood in terms of its n-type semiconductivity.

Finally, it is to be noted that the elucidation of the polymerization mechanism in the light of the extrinsic and intrinsic properties of the solids will be of immense help in selecting efficient catalysts for the polymerization of olefins.

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