

coordination with the olefin molecule due to transfer of n -electrons to the d -orbitals of the chromium atom, but strengthens again after insertion of the monomer molecule into the chain. The alternative strengthening and weakening of the Cr^{3+} -C bond thus results in the polymerisation reaction, and is only made possible by the donor-acceptor capacity of the chromium atoms (Miessarov, 1970). The Cr^{5+} atoms in the active complex are stable against reduction by the monomer and solvent due to a decrease in the positive loading thereof which is caused by the redistribution of electron density between Cr^{3+} and Cr^{6+} (Miessarov, 1970).

- Beck and Lunsford (1981) have stated that the active coordination site is in a valence state between Cr^{6+} and Cr^{2+} . To support this statement, Shelef (1969) found that the reduced Cr/SiO_2 catalyst is not homogeneous with relation to the chromium oxidation state, but contains a distribution of different oxidation states and phases. Cr^{5+} was excluded as the active site on the basis of a negative correlation with catalytic activity and Cr^{2+} was excluded due to the fact that extensive reduction to Cr^{2+} resulted in an inactive catalyst (Beck & Lunsford, 1981).
- During the reduction reaction the intermediate formation of Cr^{5+} and Cr^{3+} takes place, and involves the rate determining reduction of Cr^{5+} to Cr^{4+} viz (Beck & Lunsford, 1981; Ellison *et al.*, 1985):



There is a chemical equilibrium between Cr^{3+} and Cr^{6+} and the kinetic expression for the reaction is:

$$\text{Cr}^{5+} = [\text{Cr}^{3+}]^{1/3} [\text{Cr}^{6+}]^{2/3} \quad (2.9)$$

From the above data it is thus very clear that there is a great deal of uncertainty concerning the nature of the active chromium species in the polymerisation reaction. The most recent thoughts seem to indicate that Cr^{2+} and/or Cr^{3+} species are responsible for the observed catalytic activity (Przhevalskaya *et al.*, 1975; Beck & Lunsford, 1981; Rebenstorf & Larsson, 1981 & 1983; Ermakov *et al.*, 1971; Scarano *et al.*, 1994; Groeneveld *et al.*, 1983 a, 1983 b; Fubini *et al.*, 1980; Ghiotti *et al.*, 1983; Zecchina *et al.*, 1975; Krauss *et al.*, 1987).

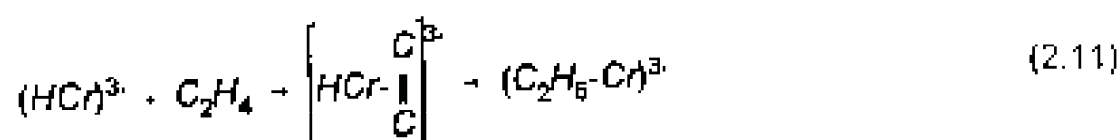
2.3.3.2. Initiation, propagation and termination

The reaction mechanism involved in the Cr/SiO_2 catalysed polymerisation of 1-alkenes has been divided into three different steps, namely initiation, propagation and termination.

i). Chain initiation

The Phillips catalyst differs from the Ziegler-Natta catalyst in the sense that it does not need an activator or co-catalyst to initiate the reaction (Tail, 1989).

Groeneveld *et al.*, (1983 a, 1983 b) found from their experimental results that an active polymerisation site consists of a Cr^{2+} cation with a silanol group in its immediate vicinity. The mechanism suggested for the initiation reaction is the following:

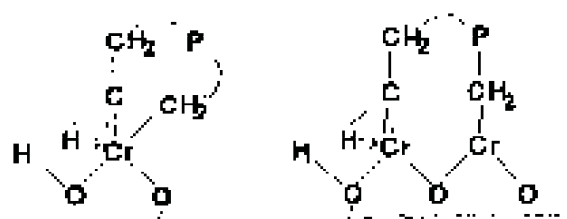


Adsorption of the ethylene onto the active chromium species takes place via σ - π backbonding. The adsorbed ethylene molecule then combines (insertion reaction) with

a bound hydrogen atom to form an ethyl group that is attached to the Cr ion (Groeneveld *et al.*, 1983 a, 1983 b; Witt, 1974). Subsequent propagation proceeds via a mechanism similar to the accepted Ziegler-Natta mechanism (see Section ii).

On the other hand, Rebenstorf and Larsson (1981) have suggested that the initiation reaction for the chromium/silica catalyst involves one ethylene molecule adding to a dinuclear surface complex via formation of a $M-CH_2-CH_2-M$ bridge. The polymerisation can occur on either Cr^{2+} and Cr^{3+} sites. The polymerisation reaction can be initiated at any active site, but the reaction can only continue on the external sites due to blocking of the internal sites by the growing polymer chain (Arلمان & Cossee, 1964; Groeneveld *et al.*, 1983 b).

According to Ghiotti *et al.*, (1988) the slow step in the initiation of ethylene polymerisation concerns the formation of a cyclic structure involving the ethylene which is coupled to the chromium by means of a carbene type bond. Two possible structures can be formed, namely a metallo-cyclic compound with only one chromium atom involved or a poly-methylene chain which has been coupled to two chromium ions:



ii). Chain propagation

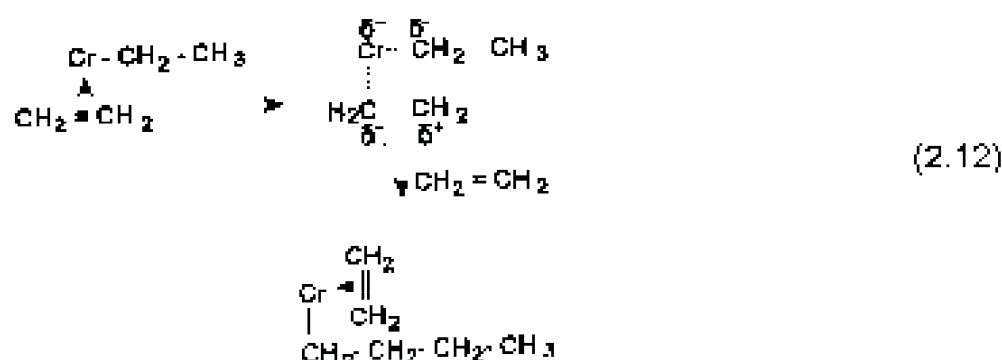
The propagation mechanism suggested by Arلمان and Cossee (1964) for Ziegler-Natta catalysts is most commonly accepted as the mechanism involved in the chain propagation of the polymerisation and oligomerisation reactions catalysed by the

$\text{CrO}_3/\text{SiO}_2$ catalyst.

The propagation mechanism consists of two steps, namely:

- i) Adsorption of the olefin on a vacant ligand position on the chromium active centre *via* σ - π backbonding
- ii) Insertion of the olefin between the alkyl group and the Cr atom *via* the cis-insertion mechanism of Arlman and Cossee (1964) for Ziegler-Natta catalysts (Young & Lovell, 1991; Groeneveld *et al.*, 1983 b; Ermakov *et al.*, 1971). The reaction proceeds *via* a polar cyclic transition state which entails simultaneous bond breaking and bond formation. It is also known as the *cis*-migration mechanism (Henrici-Olivé & Olivé, 1977; Cossee, 1964; Arlman & Cossee, 1964; Tait, 1989; Hogan, 1970; Groeneveld *et al.*, 1983 b). The metal has a positive polarisation on the M-R bond (Wilt, 1974; Hogan, 1970).

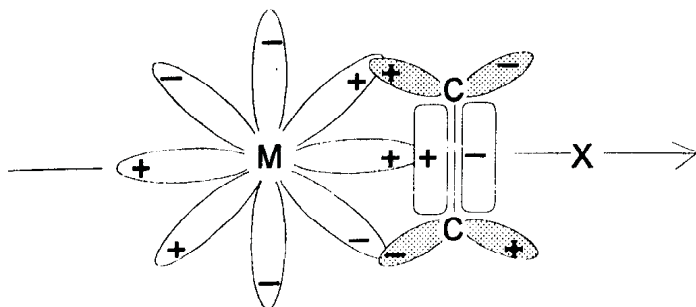
The polymer chain propagation mechanism *via* a polar cyclic transition state is shown schematically below (Wilt, 1974; Hogan, 1970; Cossee, 1964):



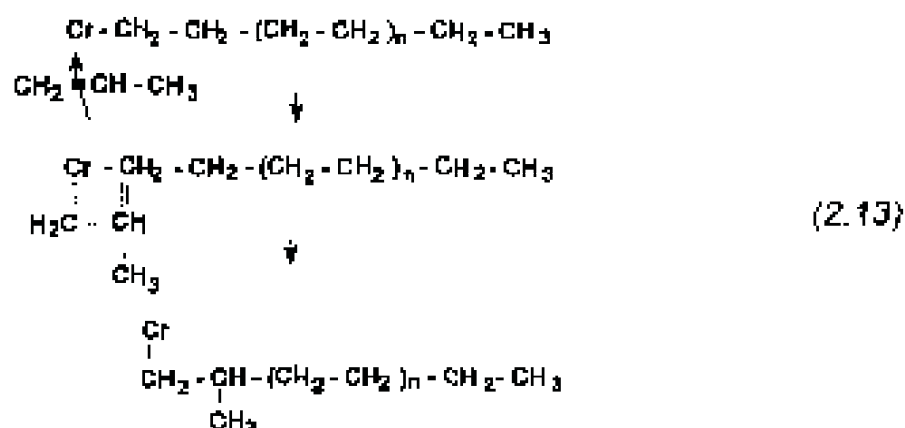
On migration of the alkyl group the σ orbital of the carbon atom overlaps with the metal d_{xy} orbital (Henrici-Olivé & Olivé, 1977; Tait, 1989). The overlap of the alkyl bonding orbital with the metal d_{xy} orbital leads to a transfer of electron density from the carbon atom to the metal (Henrici-Olivé & Olivé, 1977). The electron density on the metal is then transferred to the olefin *via* the antibonding π^* orbital of the olefin (Figure 2.1). The alkyl group of the M-R bond interacts *via* a concerted mechanism with the nearest

carbon atom of the bonded alkene and results in migration of the carbon atom to the π -alkene ligand (Pasquon *et al.*, 1989; Gavens *et al.*, 1982; Tait, 1989). In the cyclic transition state the negatively charged carbon atom of the $M^{\delta+}-C^{\delta-}$ bond binds to the unsaturated carbon with the smallest number of hydrogen atoms - a Markownikoff mechanism. The metal atom hence attacks the less substituted carbon of the double bond (Henrici Olivé & Olivé, 1977).

Figure 2.1 : Orbital overlap between the metal d_{xy} orbital and the alkyl σ bonding orbital



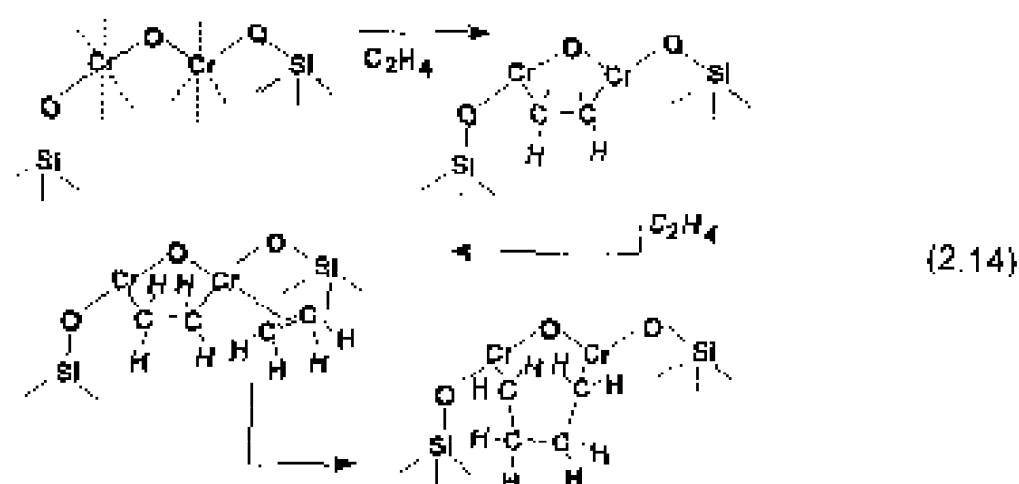
As an olefin molecule is inserted into the chain, the next olefin is associated and polarised at the chromium centre (Witt, 1974). For propylene the olefin carbon atom to which the methyl group is attached, is more positive in character due to the electron withdrawal effect of the methyl group (Witt, 1974). Branching occurs as a result of this effect. The addition of an α -olefin to the growing chain and subsequent formation of branched vinyl unsaturation can be represented as follows (Hogan, 1970):



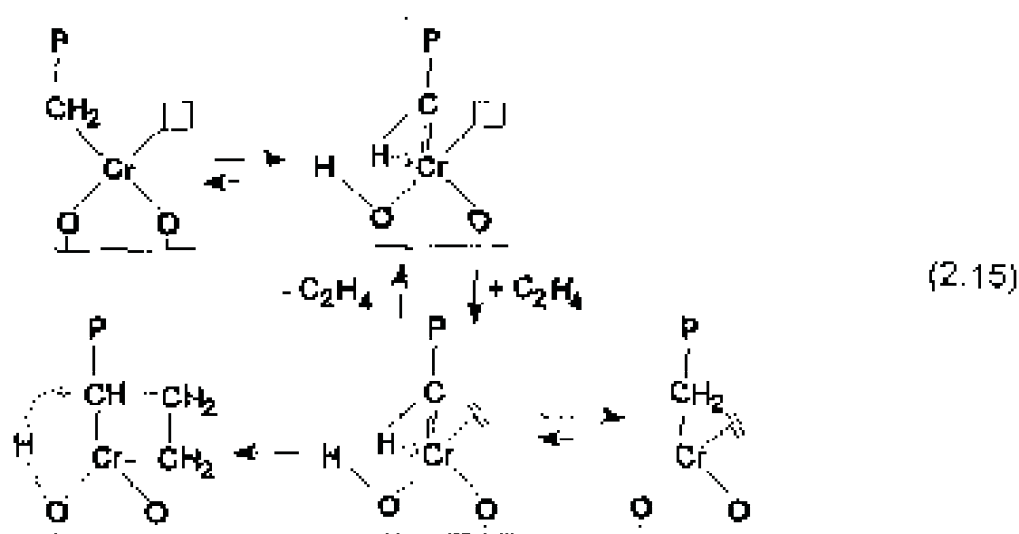
Kazanski and Turkevich (1967) have suggested that the active Cr^{5+} is situated within the square plane of a square pyramidal structure. To enable insertion of ethylene, the chromium migrates to the apex of this structure and causes a stretching of the chromium-carbon bond distance. After insertion of the ethylene molecule the chromium moves away from the apex to its original configuration to accept another ethylene molecule.

Van Reijen and Cossee (1966) suggested that polymerisation occurs on a penta-coordinated complex similar to the mechanism suggested by Arlman and Cossee (1964). The penta-coordinated complex is formed during the initiation step by the reaction of an olefin with a *tetrahedral* complex of oxygen atoms which exists around Cr^{5+} at that specific stage of the reaction (Van Reijen & Cossee, 1966).

A related mechanism which entails the addition of the olefin to a dinuclear surface complex is represented below (Rebenstorf & Larsson, 1981). The initiation step differs from the other mechanisms normally suggested since it involves the insertion of an ethylene molecule between the two metal atoms of a dinuclear complex. The propagation proceeds by means of the Cossee mechanism (Rebenstorf & Larsson, 1981).

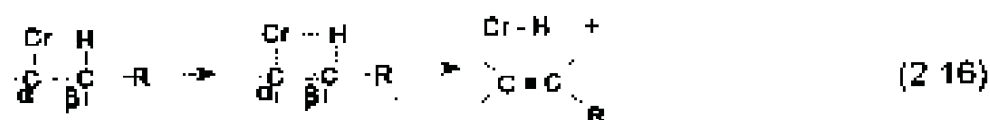


A carbene mechanism for the propagation step involving one Cr ion and only one end site of the cyclic polymer is shown below (Ghiotti et al., 1988). Of significance is the formation of the α -agostic hydrogen bond to chromium.

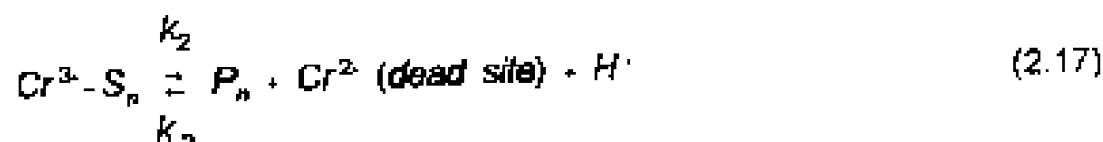


iii). Termination

Termination of the growing chain proceeds by means of a β hydrogen elimination to form an unsaturated molecule and a hydrogen atom which is attached to the chromium ion (Hogan, 1970; McDaniel & Johnson, 1987; McDaniel, 1985; Skupinska, 1991):



According to Groeneveld *et al.* (1983 b) the above termination process can be represented by the following reaction:



with P_n an olefinic, dead polymer molecule covering a potential site and S_n a polymeric alkyl group.

2.3.4. Factors that affect the oligomerisation/polymerisation activity of the $\text{CrO}_3/\text{SiO}_2$ catalyst

The basis of the Phillips catalyst relates to the impregnation of SiO_2 with chromic acid to obtain a $\text{CrO}_3/\text{SiO}_2$ catalyst which can be calcined in air at a high temperature and then reduced with CO, H_2 or any other reducing agent to obtain the chromium in the active form (Scarano *et al.*, 1994; Zecchina *et al.*, 1994; Hogan, 1970; Tait 1989; Witt, 1974; Whiteley *et al.*, 1992; Hogan & Kitchen, 1965; Krauss & Westphal, 1977). The various steps in obtaining an active oligomerisation/polymerisation catalyst and the effect of these variables and other variables on the catalyst activity will be discussed in the following pages.

2.3.4.1. The support

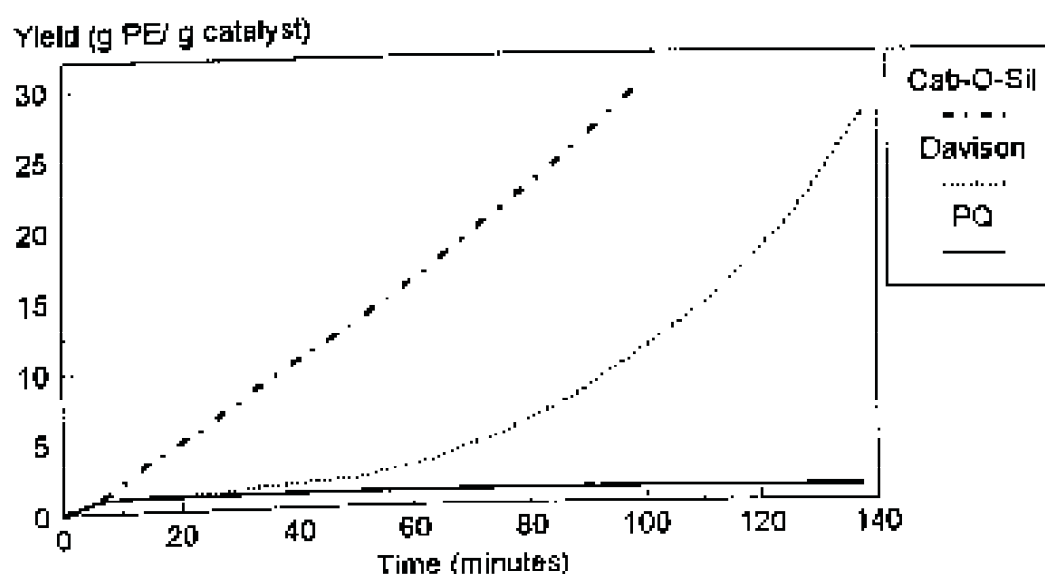
*Chromium oxides do not have the ability to accomplish polymerisation in the absence of a support since a specific interaction between the support and the chromium is necessary for polymerisation activity (Witt, 1974). The support determines the specific surface and mechanical strength of the catalyst. It also prevents sintering of the catalyst at high temperatures and facilitates the transfer of heat released during the oligomerisation/polymerisation reaction (Kazanskii & Pecherskaya, 1968). Since the support is not always completely inert, it often also affects the activity and selectivity of the catalyst. The properties of the physical support which determine the catalyst activity are the surface area, ability to fragment, fragment sizes, fragment porosity and transport limitations (McDaniel, 1985; Follestad *et al.*, 1990). For chromium oxide catalysts the number of propagation centers and the propagation rate constant is influenced by the nature of the support (Ermakov *et al.*, 1971). The structure of the active center in which a chromium atom is connected to the cation of the support ($\text{Si}^{4+}/\text{Al}^{3+}$) through an oxygen atom actually determines the influence the support has on the propagation reaction (Ermakov *et al.*, 1971). The chromium oxide species bind to the oxide support by means of an esterification reaction with the surface hydroxyl groups (Hardcastle & Wachs, 1988; Fubini *et al.*, 1980; Witt, 1974; Krauss *et al.*, 1976; Weckhuysen *et al.*, 1996). If an insufficient number of hydroxyl groups are available on the silica Cr_2O_3 is formed due to decomposition of the unbound Cr^{6+} (Hardcastle & Wachs, 1988).*

A requirement of the support material that has been noted in the literature for the Phillips catalysed oligomerisation reaction is that the support must have a large surface area and a large pore volume. Pore diameters of between 60 and 300 Å have been recommended (Petrine & Wu, 1991; Wu & Chu, 1994; Wu, 1989 a, 1989 b, 1991; Hogan & Kitchen, 1965). The catalyst activity is increased by large pore-openings on the support since the reactants and products must be able to diffuse to and from the catalyst sites (Buchanan & Wu, 1994; Petrine & Wu, 1991; Wu, 1989 a & b; Wu &

Chu, 1994; Wu, 1991). The support normally used is silica (Pelrine & Wu, 1991; Wu, 1992).

In a study of the effect of a support on the polymerisation activity of the Cr on silica catalyst, Dalla Lana *et al.*, (1993) compared a non-porous silica, namely Cab-O-Sil, (BET surface area = $163 \text{ m}^2.\text{g}^{-1}$; pore volume = $0 \text{ cm}^3.\text{g}^{-1}$) and two porous silicas namely Davison (BET surface area = $277 \text{ m}^2.\text{g}^{-1}$; pore volume = $1.57 \text{ cm}^3.\text{g}^{-1}$) and PQ (BET surface area = $330 \text{ m}^2.\text{g}^{-1}$; pore volume = $1.5 \text{ cm}^3.\text{g}^{-1}$) by loading 5% Cr on each and testing the polymerisation activity of the various samples. The difference in activity between the three types of silica supports can be seen in Figure 2.2.

Figure 2.2: Polymer yield as a function of time with various supports (Dalla Lana *et al.*, 1993)



After the first 5 minutes of the polymerisation reaction the conversion is suppressed in the case of the two porous catalysts due to blockage of the pores by the growing polymer chains (Dalla Lana *et al.*, 1993; Follestad *et al.*, 1990; Corner, 1988). Fragmentation of the Davison catalyst takes place due to a pressure build-up within the pores caused by the polymer and this leads to the exposure of further active sites

(Follestad *et al.*, 1990; Conner, 1988). Insufficient initial fragmentation is thus the determining factor for the slow rate which is observed during the initiation period of the Davison catalyst (Follestad *et al.*, 1990; Conner, 1988). Since fragmentation of the PQ support does not take place, the activity cannot be regained once the pores have been blocked by product and thus no increase in the product yield is observed with time. The external surface chromium active sites of the PQ support are probably negligible when compared to the active sites within the pores. The non-porous support on the other hand has smaller particles with a larger external surface which results in an active catalyst. The pore size distribution is thus of critical importance (Dalla Lana *et al.*, 1993). According to McDaniel (1985) the activity of the catalyst increases with an increase in the pore volume of the support. Micropores are blocked and deactivated due to the formed poly-ethylene, while larger pores weaken the structure of the support and promote breaking and fragmentation (Dalla Lana *et al.*, 1993; Groeneveld *et al.*, 1983 a).

According to McDaniel (1985) and Weckhysen *et al.*, (1996) an increase in the average pore diameter of the silica support also results in a decrease in the molecular weight of the product, while Hogan and Kitchen (1965) found the opposite to be true. In small pores branching of the oligomer/polymer chains also becomes more likely, since the active sites of the catalyst are closer together (McDaniel, 1985). The molecular mass of the oligomerisation/polymerisation product and activity of the catalyst is inversely proportional to the hydroxyl population of the support medium (Welch & McDaniel, 1983).

Holm and Clark (1968) have indicated that the chromium oxide - support oxide interaction decreases the reducibility of the chromium. For a $\text{CrO}_3\text{-Al}_2\text{O}_3$ catalyst this interaction is the weakest, while the interaction is the strongest for a $\text{CrO}_3\text{-SiO}_2$ catalyst (Holm & Clark, 1968). Fouad *et al.*, (1994) found in contradiction to the above that the chromium-support interaction is much weaker in the case of silica, when compared to alumina. According to Miessarov (1970) the high degree of reducibility (strong oxidizing

capability) of CrO_3 on silica gel and alumina silicates can be attributed to the acidic properties of these supports (Miessarov, 1970). The coordination between CrO_3 and the protons of the silica gel hydroxyl groups lowers the electron density of the chromium atom and increases the reducibility thereof (Miessarov, 1970). The hexavalent chromium atoms can only be reduced to the lower valence states if the oxygen atoms coupled to them are removed simultaneously. Reduction of the first chromium layer in oxide catalysts is difficult to achieve due to strong coordination of this layer with the hydroxyl protons of the silica atoms (Miessarov, 1970). The use of an effective support with chromium oxide catalysts thus increases the reducibility of the CrO_3 and promotes donor-acceptor properties of the chromium atoms (Miessarov, 1970).

Due to the fact that aluminium oxide forms a type of aluminium chromate compound with CrO_3 , it does not conform to the requirements of an effective support, such as silica or alumina silicate (Miessarov, 1970). Alumina catalysts also contain 50% - 100% more hydroxyl groups than silica after calcination at normal calcination temperatures (McDaniel, 1985). In spite of the fact that more sites are available for attachment to Cr ions, the effect does not lead to a higher activity since the larger number of OH groups affect the polymerisation reaction in a negative manner (McDaniel, 1985). It was found that the $\text{Cr}^{2+}:\text{Cr}^{3+}$ ratio increases with the silica content of the support: silica rich surfaces mainly contain Cr^{2+} ions while Cr^{3+} predominates on alumina supports (Weckhuysen *et al.*, 1996).

Aluminium phosphate is in many respects very similar to silica, since both are iso-electronic and iso-structural and the phase-diagrams of the two are almost identical (McDaniel, 1985). On AlPO_4 the P-OH and Al-OH groups present cause the support to be more acidic in character and the P=O species cause a decrease in the hydroxyl population of AlPO_4 (McDaniel, 1985; McDaniel & Johnson, 1987). Cr/AlPO_4 is thus a slightly more active catalyst than Cr/SiO_2 , and results in the formation of high molecular mass polymers and a broader molecular weight distribution (McDaniel & Johnson, 1987).

2.3.4.2. Impregnation and drying

Impregnation of the Cr onto the support takes place from a solution of the metal salt in water or organic solvents such as ethanol, methanol or acetic acid (Buchanan & Wu, 1994; Pelrine & Wu, 1991; Wilt, 1974; Whiteley *et al.*, 1992; Pelrine *et al.*, 1992, 1993; Hierl & Krauss, 1975; Wu, 1989 a, 1989 b, 1991, 1992; Wu & Chu, 1994). When the solution comes into contact with the porous support (350 m².g⁻¹ surface area), the liquid diffuses into the pores under the influence of strong capillary forces of 640 atmospheres (Maatman & Prater, 1957). The CrO₃ is not simply distributed onto the support surface, but a definite surface phase is formed.

According to Krauss and Westphal (1977) the following reactions take place during the impregnation and activation of a monochromale species on silica:



It was found that the CrO₃ dispersion on the support changes with an increase in the drying temperature of the catalyst (Liu *et al.*, 1988). An increase in the drying temperature from 101°C to 170°C resulted in an increase in the dispersion threshold from 0.27 to 0.38 g CrO₃. g⁻¹ SiO₂ with a specific SiO₂ surface of 364 m².g⁻¹. The results of Liu *et al.* (1988) indicate that CrO₃ is not dispersed as a monolayer, and that the increase in dispersion threshold with temperature might be due to the polymerisation of CrO₃.

2.3.4.3. *The chromium oxide loading*

Hill and Ohlmann (1989) found that there are four types of unstable Cr^{6+} -oxide species in addition to the stable Cr^{6+} -surface compounds. The number of unstable Cr^{6+} species increases with an increasing chromium content. During temperature programmed heating in N_2 the existence of such unstable species is indicated by 3 peaks respectively at 670, 750 and 920 K which correspond to the release of oxygen by the decomposition of the unstable Cr^{6+} to give finally Cr_2O_3 and oxygen (Hill & Ohlmann, 1989).

The reaction rate for the polymerisation of ethylene over a Cr/SiO_2 catalyst increases with the chromium loading up to a loading of approximately 1.5%. Thereafter it decreases with a further increase in the loading (Kazanski & Turkevich, 1967; Groeneveld *et al.*, 1983 a). At a low loading (< 1%) all the chromium atoms are initially active, while at the higher loadings only the fraction of chromium atoms along the periphery of the particle are active (Groeneveld *et al.*, 1983 a; McDaniel, 1985). At a chromium loading $\leq$ 0.5% the activity of the catalyst is directly proportional to the chromium content and a high degree of dispersion is present after catalyst reduction (Zecchina *et al.*, 1975 a). Zecchina *et al.*, (1975 a) found that a chromium loading of 0.5 % produced the most active catalyst.

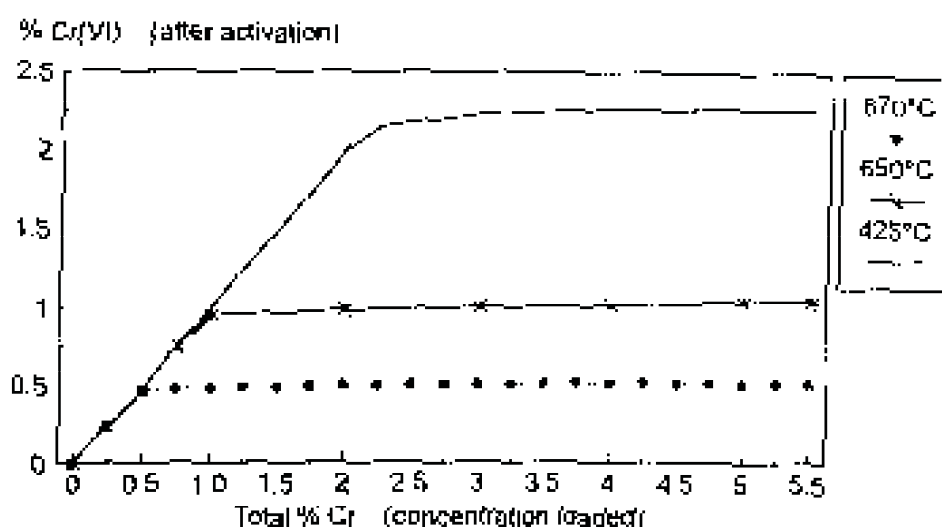
With chromium loadings between 0.2 and 5.0 mass % the chromium species are mainly present on the surface as clusters of Cr-O tetrahedra (Ellison *et al.*, 1985). At higher loadings (> 5% Cr) a Cr_2O_7 -type molecular structure is present within large clumps of chromium containing material (Ellison *et al.*, 1988, Charcosset *et al.*, 1967; Weckhuysen *et al.*, 1996). The Cr_2O_7 structure contains 4 oxygen atoms which surround each chromium atom and form a complex with distorted T_d symmetry. One oxygen atom is shared by two tetrahedra to form a Cr_2O_7 molecular group. Only a fraction of the chromium is thus present in thin layers of one to three chromium atoms deep which can undergo a stabilisation reaction with the support medium (Ellison *et al.*,

1985; Groeneveld *et al.*, 1983 a). With a loading of 11.8% Cr only 57% of the total chromium is stabilised as Cr^{6+} during the activation step in air at 540°C while the rest is decomposed to Cr_2O_3 (Hogan, 1970). The agglomeration of the chromium oxide to form huge inactive oxide structures is probably the reason for the inactivity obtained with chromium loadings higher than 10% (Charcosset *et al.*, 1967).

A decrease in the chromium loading results in a decrease in the reducibility of the catalyst (Ellison *et al.*, 1985; Holm & Clark, 1968). This stabilising effect at a lower chromium loading can be attributed to an interaction between the support and the chromium. The reducibility of the catalyst increases with an increase in the CrO_3 concentration due to a decrease in the thermal stability of the CrO_3 (Miessero, 1970). On the grounds of the relative polarising ability of the M-O bonds, this effect is the smallest for CrO_3 and the strongest for WO_3 (Ellison *et al.*, 1985). In contrast to the last mentioned, Zecchina *et al.*, (1975 a) found that samples with a high chromium concentration in general offer more resistance against complete reduction, and that a number of oxidation-reduction cycles are necessary to bring about complete reduction.

The maximum concentration of chromium that can be stabilised on the support under specific conditions is known as the saturation coverage (McDaniel, 1982 c; Weckhuysen *et al.*, 1996). In Figure 2.3 the chromium saturation coverage was plotted as a function of the chromium loading.

Figure 2.3: Cr^{5+} saturation coverage as a function of the chromium loading (McDaniel, 1982 c)



Chromium loadings higher than the saturation coverage result in decomposition of the excess CrO_3 to crystalline Cr_2O_3 during calcination (McDaniel, 1982 c, 1985; Zecchina *et al.*, 1975 a). As the chromium loading is increased from 1% to 5% a definite change in the catalyst colour from orange to green can be observed which is an indication of an increase in the Cr_2O_3 content (Hogan, 1970). If the total concentration of chromium loaded onto the support is lower than the saturation coverage, all the chromium will be stabilised during the calcination step. An increase in the chromium loading up to 5% is accompanied by a linear decrease in the number of surface hydroxyl groups. Thereafter the OH content does not correlate with a further increase in the chromium loading (Zecchina *et al.*, 1975 a). At chromium loadings higher than 5% the surplus chromium is not bonded to the surface, although 40% of the silica surface is still vacant.

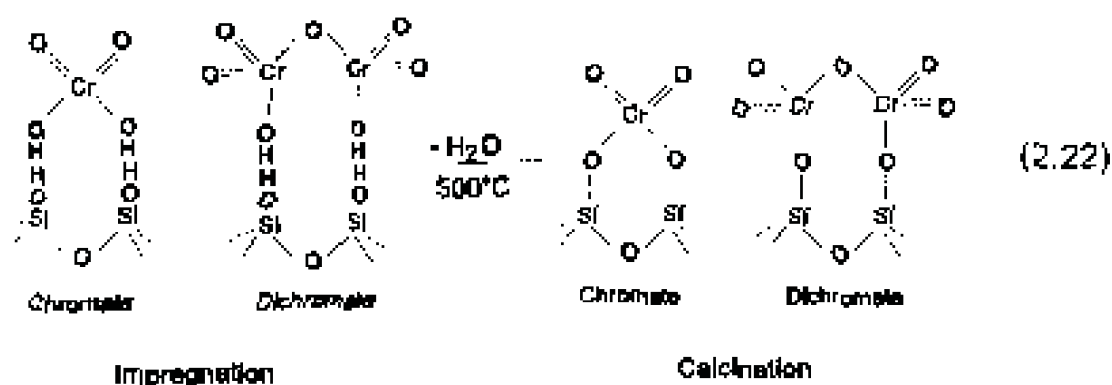
Witt (1974) found that an increase in the chromium concentration resulted in a decrease in the molecular mass of the polymer product. This decrease corresponded to the effective monomer concentration around the catalyst site. This concentration increased as the chromium concentration decreased, which allowed for the growth of longer polymer chains.

2.3.4.4. Calcination

After drying, calcination is performed at temperatures between 200°C and 900°C to obtain the tetrahedral Cr^{6+} state and to fix the chromium onto the surface takes place (Pasquon & Giannini, 1984; Kostrov *et al.*, 1976; Pelrine *et al.*, 1993; Fouad *et al.*, 1994; Buchanan & Wu, 1992; Pelrine & Wu, 1991; Wu, 1989 a, 1989 b, 1991, 1992; Wu & Chu, 1994; Fubini *et al.*, 1980; Merryfield *et al.*, 1982; McDaniel, 1985; Van Reijan & Cossee, 1966; Hogan & Kitchen, 1965; Ghiotti *et al.*, 1979). During the calcination/oxidation process the catalyst becomes bright orange in colour (Groeneveld *et al.*, 1979).

Chromium oxides that have been impregnated on silica will not be active unless they have been heated in air to at least 200°C (Witt, 1974). The reason for this is that the chromium trioxide must be heated above its melting point ($\pm 197^\circ\text{C}$) to enable an esterification reaction with nearby silanol groups on the silica with the resultant formation of Cr-O-Si surface species (Witt, 1974; Fubini *et al.*, 1980; Hogan, 1970; Groeneveld *et al.*, 1979; McDaniel, 1985; Fouad *et al.*, 1994). The last mentioned process takes place at a temperature less than 350°C. The anchoring of the chromates and/or dichromates onto the surface results in a decrease in the symmetry of the Cr^{6+} species and the formation of highly covalent bonds with the silica (Fubini *et al.*, 1980; Best *et al.*, 1977). After the Cr^{6+} species have been anchored to the surface, they are thus stable. The pre-treatment of the catalyst thus determines the final properties of the catalyst (Zecchina *et al.*, 1975 a). According to Hill *et al.*, (1980) the composition of the species which form during the reaction between the chromium and the silica atoms is not known. The lower valence states of the chromium (CrO_2 and Cr_2O_3) are formed by the decomposition of Cr^{6+} that has not been anchored onto the silica support at temperatures between 350°C and 400°C (Fubini *et al.*, 1980; Fouad *et al.*, 1994; Hill *et al.*, 1980). The lower valence states can be reoxidised fully at 550°C (for CrO_2) and 700°C (for Cr_2O_3) (Fubini *et al.*, 1980; Hill & Öhlmann, 1990). Some researchers

are convinced that the CrO_3 binds as a chromate species on the silica when it is impregnated onto the support from an aqueous solution (Hogan, 1970; McDaniel, 1981, 1982 a, 1982 b, 1985; Hierl & Krauss, 1975). At the lower chromium loadings chromate is believed to be predominantly present, while an increase in the chromium loading results in increasing amounts of dichromate species at a high calcination temperature (McDaniel, 1981, 1982 a, 1982 b). Some rearrangement of the chromate species to dichromate species thus occurs at high temperatures and is accompanied by a colour change from yellow to orange in some cases (McDaniel, 1985; Hogan, 1970). Other scientists believe that the chromium is impregnated as a dichromate species onto the silica since the chromate structure is subjected to a degree of strain while the dichromate species fits in well with the silica structure (Zecchina *et al.*, 1975 a; Groeneveld *et al.*, 1979; Rebenstorf & Larsson, 1981; Richter & Öhlmann, 1985):



After calcination the Cr^{6+} catalyst is sensitive to moisture (Whiteley *et al.*, 1992; Hogan, 1985). On exposure to moisture, the orange Cr^{6+} calcined catalyst changes to yellow/brown and loses oligomerisation/polymerisation activity (McDaniel, 1985). Another calcination step restores the activity. During the oxidation of Cr^{3+} to Cr^{6+} not all the Cr^{3+} species are oxidised since Cr_2O_3 will only take up oxygen at temperatures

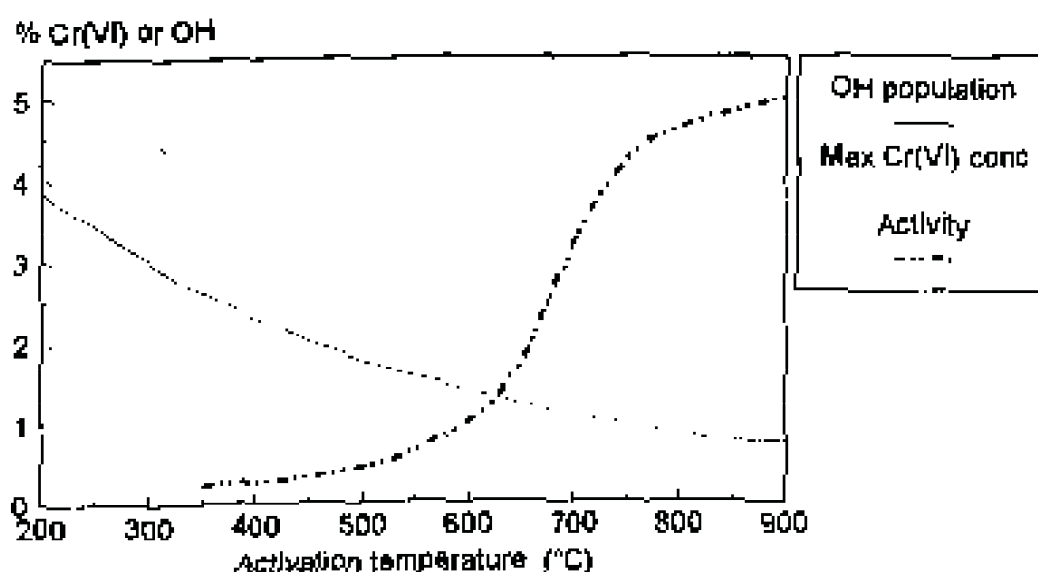
higher than 700°C (Hill & Öhlmann, 1990). In systems where Cr^{3+} and Cr^{6+} are present as a mixed valence species the catalyst has a brown colour while Cr^{3+} clusters give the catalyst a green colour (Ellison *et al.*, 1985).

2.3.4.5. The calcination temperature

High temperatures of calcination of the Phillips catalyst result in a decrease in the catalyst reducibility due to better distribution of the chromium on the support and thus better interaction with the support (Holm & Clark, 1968). The catalytic properties are thus greatly determined by the interaction between the metal oxide and the support oxide. The catalyst activity increases with an increase in the activation temperature from 400°C to 815°C (Hogan & Banks, 1958; Merryfield *et al.*, 1982).

McDaniel (1982 c) did an investigation of the maximum amount of Cr^{6+} that can be stabilised on the silica (saturation coverage) at different temperatures of calcination of the Cr/SiO_2 (Figure 2.4)

Figure 2.4: Cr^{6+}/OH concentration as a function of the activation temperature (McDaniel, 1982 c)



An increase in the activation temperature results in a decrease in the hydroxyl population of unimpregnated silica due to condensation of the OH groups. The maximum Cr^{6+} population that can be stabilised on the support thus decreases with an increase in the temperature (McDaniel, 1982 c; Krauss & Westphal, 1977). In contrast to the expectation that a decrease in the catalyst activity will take place with an increase in the activation temperature (due to lower Cr^{6+} coverage at higher temperatures) an increase in the catalyst activity has been observed (McDaniel *et al.*, 1982; Welch & McDaniel, 1983; Wilt, 1974; Ermakov *et al.*, 1971; Merryfield *et al.*, 1982). The explanation for this phenomenon is that the activity of the catalyst is little affected by the Cr^{6+} density (McDaniel *et al.*, 1982 c). The activation temperature is of much greater importance, irrespective of the concentration of chromium loading since the hydroxyl population on the silica may affect the polymerisation in a negative manner due to coordination with the active centres. (Merryfield *et al.*, 1982, McDaniel, 1982 c; McDaniel & Johnson, 1987). The increase in catalyst activity is thus caused by an increase in the propagation rate constant at a higher activation temperature (Ermakov *et al.*, 1971; Hogan & Banks, 1958; Merryfield *et al.*, 1982). Hogan (1970) confirmed that a very small fraction of the total chromium is active during the polymerisation, and that the calcination temperature is of critical importance to obtain this fraction in the active state. The activity of the catalyst increases with the calcination temperature up to a maximum of 925°C; thereafter the activity decreases due to sintering of the silica (McDaniel, 1985). The more dehydrated the catalyst, the lower the molecular weight of the polymer product up to a maximum calcination temperature of 925°C (McDaniel, 1985). The molecular mass of the product decreases due to an increase in the rate of the chain transfer reaction in the presence of the active species produced at a higher calcination temperature (McDaniel & Johnson, 1982, 1987; Clark *et al.*, 1956; Hogan & Banks, 1958; Ermakov *et al.*, 1971; Weckhuysen *et al.*, 1996).

At high activation temperatures (700°C - 800°C) the $-\text{Si}-\text{OH}$ groups of the catalyst react to form $-\text{Si}-\text{O}-\text{Si}-$ bonds with an accompanying release of water. The reoxidation of Cr^{2+} to Cr^{6+} during the reduction process can thus not take place due to the absence of $\text{Si}-$

OH groups and Cr^{2+} is thus mainly formed during the reduction step (Krauss *et al.*, 1975).

When titanium oxide is used as a support the surface chromium(VI)oxide species are not stable towards elevated calcination temperatures, and they are converted to a lower chromium oxide oxidation state (Hardcastle & Wachs, 1988). In the case of a silica-oxide support, the surface Cr^{6+} oxidation state is stabilised at elevated calcination temperatures (Hardcastle & Wachs, 1988). At a high activation energy the mobility of CrO_3 is increased, and the reaction :



is accelerated (Hogan, 1970). Above a calcination temperature of 500°C the structure is very similar to that of $\alpha\text{-Cr}_2\text{O}_3$ (Ellison *et al.*, 1985).

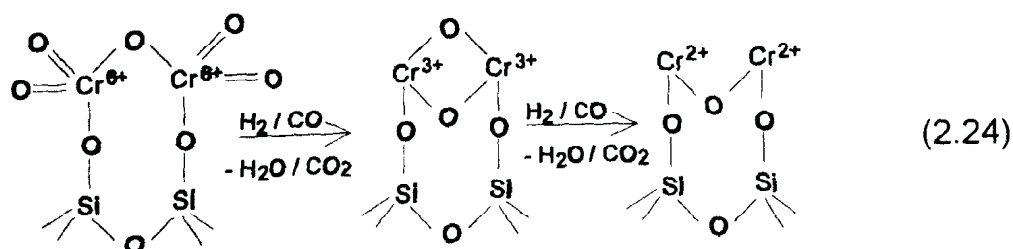
2.3.4.6. Time of calcination

An increased calcination time causes only a slight decrease in the saturation coverage of the chromium on the silica support (McDaniel, 1982 c). After 24 hours calcination at 425°C in oxygen a decrease takes place from 2.25 Cr^{6+} per nm^2 (with 2 hours calcination) to 1.88 Cr^{6+} per nm^2 .

2.3.4.7. Reduction to the active state

Reduction of the catalyst can be brought about by the use of reducing agents such as CO , H_2 , CS_2 , CH_3SCH_3 , SHCH_3 or metal alkyl containing compounds such as R_3Al , R_3B or R_3Mg (Petrine & Wu, 1991; Buchanan & Wu, 1994; Whiteley *et al.*, 1992; McDaniel, 1985; Wu, 1989 a, 1989 b, 1992; Ghiotti *et al.*, 1979). Various opinions exist concerning the nature of the active species that are formed during this reduction step (see section 2.3.3.1). During the reduction of the $\text{CrO}_3/\text{SiO}_2$ catalyst the colour changes

from bright orange to blue-green (Pelrine & Wu, 1991; Pelrine *et al.*, 1993; Groeneveld *et al.*, 1979). Prolonged reduction causes the catalyst to change to a blue colour (Groeneveld *et al.*, 1979). The ideal quantity of CO to be added to ensure complete reduction of the Cr^{6+} is twice the stoichiometric amount (Pelrine & Wu, 1991; Pelrine *et al.*, 1993). The reduction reaction is highly exothermic and coordinatively unsaturated Cr ions in a low valence state are formed (Zecchina *et al.*, 1975 a; Fubini *et al.*, 1980). The surface reaction of the dichromate species that takes place during the reduction at 500°C can be represented as follows (Groeneveld *et al.*, 1979):



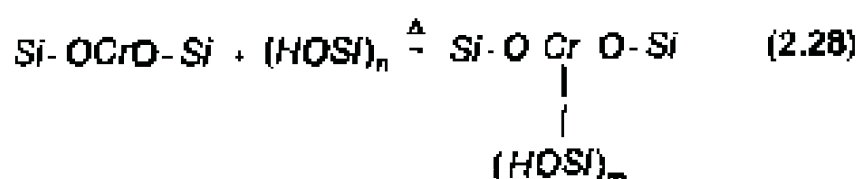
The reduction of the $\text{CrO}_3/\text{SiO}_2$ catalyst (i.e. CO oxidation) proceeds *via* a Langmuir-Hinshelwood reaction pathway which requires that both reactants adsorb onto the catalyst surface prior to the reaction (Ruddick & Badayal, 1997):



During the reduction of the Cr^{6+} ion to the Cr^{2+} state reoxidation to the Cr^{3+} state can take place by reaction with silanol groups on the support (Groeneveld *et al.*, 1979). The reaction has been detected by TPR experiments in which a constant consumption of H_2/CO occurs at temperatures higher than the primary reduction peak (Hill & Öhlmann, 1990). By the effective removal of water that has been formed with H_2 as reducing agent the oxidation reactions are prevented and large quantities of Cr^{2+} are thus formed (Hogan, 1970; Groeneveld *et al.*, 1979).

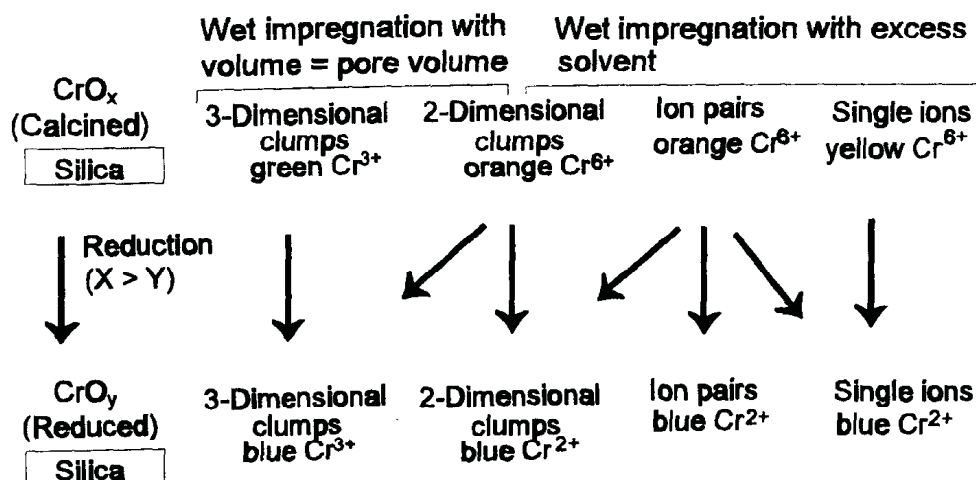
Literature review

According to Krauss and Westphal (1977) the following reactions take place during the reduction of monochromate species on silica:



Exposure of the CO treated catalyst to air causes reoxidation of reduced Cr to Cr^{6+} and is accompanied by a bright chemiluminescence due to the formation of oxygen atoms (O^*) on coordinatively unsaturated Cr^{2+} sites (Hogan, 1970; Carruthers & Sing, 1967; Weckhuysen *et al.*, 1996; Hill & Öhlmann, 1990; Ruddick & Badayal, 1997). The formation of different catalyst species after impregnation, oxidation and reduction is shown in Figure 2.5 (Groeneveld *et al.*, 1979).

Figure 2.5: Formation of different catalyst species during catalyst preparation
(Groeneveld *et al.*, 1979)



2.3.4.8. The reducing agent

Hogan (1970) compared the reduction of a 2.5% CrO_3 on silica catalyst with CO and H_2 as reducing agents and found that the reduction rate with CO is much faster and progresses much further than with H_2 . The standard energy of reduction with CO at 310 K is -106 kJ.mol^{-1} , while in the case of reduction with H_2 it has a value of -24 kJ.mol^{-1} (Fubini *et al.*, 1980). The water gas shift reaction equilibrium shows that H_2 is slightly less effective in its reducing capability than CO (Groeneveld *et al.*, 1979):



The Gibbs-function has a value of

$$\Delta G_t^0 = -30 + 0.042(T-298) \text{ kJ.mol}^{-1} \quad (2.30)$$

in the above water gas shift reaction equilibrium (Groeneveld *et al.*, 1979; Atkins, 1986).

It has been observed that the H_2 -treated catalyst turned a grey-green colour while the CO treated catalyst became a blue colour. During H_2 reduction the water formed oxidized the Cr^{2+} to Cr^{3+} or caused hydrolyses of the Cr-O-Si bond which eventually resulted in the formation of Cr_2O_3 (Zecchina *et al.*, 1975 a; Beck & Lunsford, 1981; Groeneveld *et al.*, 1979; Witt, 1974; Welch & McDaniel, 1983; Hogan, 1970). CO treatment only resulted in the formation of CO_2 which caused no decomposition of the Cr-O-Si surface species (Hogan, 1970; Beck & Lunsford, 1981; Zecchina *et al.*, 1975 a; Hill & Ohlmann, 1990). The dehydroxylation mechanism which occurred during the reduction with CO is probably related to the above mentioned water gas shift reaction (Welch & McDaniel, 1983). The most effective reducing agents are those which enhance dehydroxylation of the support (Welch & McDaniel, 1983). Such agents are specifically CO and the organic sulfides (Welch & McDaniel, 1983).

CO is a two-electron reducing agent, and an even number of electrons is involved if a dichromate species is reduced to two Cr^{3+} ions from the Cr^{6+} form. Only in the case of surface chromate species is the Cr^{2+} reduced form possible since the reduction of Cr^{6+} to Cr^{3+} requires an uneven number of electrons (Zecchina *et al.*, 1975 a).

The use of ethylene as reducing agent appears effective only if the reduction is carried out at a temperature lower than $300^\circ C$ (Rebenstorf & Larsson, 1983). At higher temperatures the ethylene is oxidised to CO_2 and H_2O . At temperatures under $300^\circ C$ the ethylene is probably converted to formaldehyde, and a reaction similar to the oxidation of CO to CO_2 during CO reduction, takes place. A similar Cr^{2+} dinuclear surface complex is thus probably formed (Rebenstorf & Larsson, 1983). When ethylene is added to the Cr^{6+} catalyst, an initial initiation period is present before the polymerisation reaction commences. This induction time (i.e. reduction time) of the Cr^{6+} to Cr^{2+} and/or Cr^{3+} decreases with an increase in the calcination temperature, reactor temperature and ethylene concentration (Merryfield *et al.*, 1982; McDaniel, 1985).

The reduction of the chromium oxide catalyst with various reducing agents (SO_2 , NH_3 ,

HCN) results in a change in the propagation reaction rate constant since the surface chromium complexes which are formed differ due to the presence of different ligands generated from the reducing gas (Ermakov *et al.*, 1971).

2.3.4.3. The reduction temperature

The activity of the Cr/SiO_2 catalyst increases with an increase in the reduction temperature up to 350°C ; thereafter the activity slowly decreases with a further increase in temperature (Zecchina *et al.*, 1975; Merryfield *et al.*, 1982; Ruddick & Badayal, 1997). The higher reduction temperatures result in a rearrangement of the chromium ions into a higher coordination state and yield an accompanying decrease in the activity of the catalyst (Zecchina *et al.*, 1975 a). A change in the Cr^{2+} coordinative unsaturation thus results in deactivation of the catalyst (Welch & McDaniel, 1983; McDaniel, 1985; Merryfield *et al.*, 1982). Holm and Clark (1968) and Ermakov *et al.*, (1971) also found that reduction at temperatures higher than 300°C caused a decrease in the polymerisation activity of the catalyst.

Welch and McDaniel (1983) have suggested the use of a drastic reduction-oxidation cycle to improve the activity of the Phillips catalyst. During the reduction step with CO at high temperatures of 700°C to 900°C the support is chemically dehydroxylated. Breaking of the chromium - support bond results in the destruction of the Cr^{2+} high molecular mass centres and the formation of CrO and Cr_2O_3 aggregates (Welch & McDaniel, 1983). The reduction step is followed by a reoxidation step which results in the breaking of the aggregates, and redistribution of the individual Cr^{6+} atoms over the surface. Due to dehydration of the surface during the reduction step, the new bonds are mainly formed with siloxanes or other oxide bridges and are more active Cr^{2+} species than those previously produced. The process finally produces the same end product as that obtained by the anhydrous impregnation of chromium on a calcined support (Welch & McDaniel, 1983).

2.3.4.10. *The influence of the reduction time*

An increase in the time of reduction (at 350°C) of the Phillips catalyst with CO is accompanied by a sharp increase in the total amount of CO₂ formed up to an optimum reduction time of 2 minutes. At this time a maximum activity is obtained due to complete conversion to the Cr²⁺ state (Groeneveld *et al.*, 1983 a). In spite of the fact that the catalyst activity decreases with further exposure to CO, the amount of CO₂ produced still increases slowly with a further increase in the reduction time. The further CO₂ production which takes place, even after complete reduction of the catalyst, is caused by the intermediate reoxidation of Cr²⁺ ions by surface hydroxyl groups according to the equation (Groeneveld *et al.*, 1983 a):



The formed Cr³⁺ species are then reduced by CO once again with the resultant formation of CO₂. According to Beck & Lunsford (1981) the optimum reduction time with CO at 400°C is 8 minutes, while a reduction time of 120 minutes results in a catalyst with no measurable activity.

Hogan and Banks (1958) found that the temperature and time of reduction are interrelated, with longer times being required at lower temperatures and shorter times at higher temperatures.

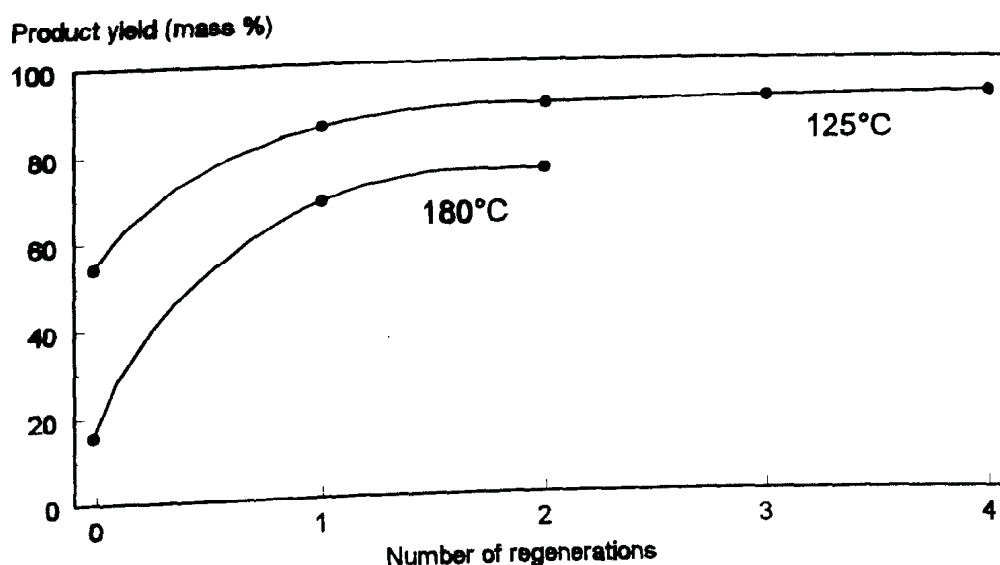
2.3.4.11. *Regeneration of the spent catalyst*

When use is made of a fixed bed reactor for the oligomerisation/polymerisation reaction, there is a need for the deactivated catalyst to be reactivated by means of regeneration within the reactor. Pelrine and Wu (1991) developed an effective process for the regeneration of the catalyst which resulted in no loss of either the product yield or characteristics of the product. This entailed:

- Thermal treatment of the deactivated catalyst under an inert gas to remove unreacted olefin and oligomer product.
- Oxidation of the catalyst at a high temperature to remove carbon deposits and to obtain the chromium in the Cr^{6+} state.
- Reduction of the catalyst at a low temperature to obtain it in the active form.

The regenerated catalyst may remain active for up to 4 months (Pelrine & Wu, 1991). The effect of an increasing number of regenerations on the catalyst activity can be seen in Figure 2.6. The activity of the catalyst improves significantly after the first cycle of regeneration (Pelrine & Wu, 1991).

Figure 2.6: Product yield as a function of the number of regenerations (Pelrine & Wu, 1991)



During oxidation of the reduced Cr/silica catalyst a loss of water takes place which indicates the presence of hydroxyl groups in the reduced species (Hill & Öhlmann, 1990).

2.3.4.12. The oligomerisation/polymerisation temperature

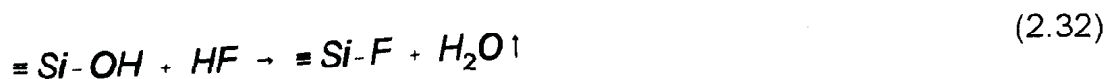
Kazanski and Turkevich (1967) found that the polymerisation rate for ethylene over a Cr/SiO₂ catalyst reached a maximum at about 100°C; thereafter it decreased to zero at a temperature of 250°C. The viscosity and molecular mass of the oligomerisation/polymerisation product decreases with an increase in the temperature (Pelrine & Wu, 1991; Clark *et al.*, 1956; Hill *et al.*, 1980; McDaniel & Johnson, 1982). Faster deactivation of the chromium on silica catalyst occurs if the oligomerisation reaction of 1-alkenes is performed at higher temperatures (> 120°C) (Pelrine & Wu, 1991).

In the case of the polymerisation reaction it was found that the polymerisation of higher olefins in a fixed bed reactor takes place at a lower optimum temperature than the polymerisation of ethylene (Clark *et al.*, 1956).

2.3.4.13. The addition of modifiers or co-catalysts to the Cr/SiO₂ catalyst

i). Fluoride

The addition of fluoride to the catalyst system results in the substitution of the surface hydroxyl groups according to the reaction (McDaniel, 1982 c, 1985):



The result of the fluorination reaction is in many cases an increase in the catalyst activity, and a decrease in the molecular mass distribution of the polymer product. An increase in the fluorine content results in a decrease in the quantity of Cr⁶⁺ that can be stabilised onto the surface. Due to the mobility of the fluoride ion even a small concentration (0.3 mass %) has a great effect on this reaction (McDaniel, 1982 c, 1985).

ii) Aluminium

The presence of aluminium often results in an increase in the polymer molecular mass (McDaniel, 1982 c). The impregnation of the silica with 2.0 mass % Al by means of an aqueous aluminium nitrate solution results in a higher OH concentration at calcination temperatures of 400°C and 600°C with no change at 890°C. The Cr^{6+} concentration after impregnation with aluminium is thus higher after heat treatment at 400°C and 600°C (McDaniel, 1982 c).

Aluminium and fluoride thus influence the saturation coverage by determining the total number of sites available for occupation by chromium (McDaniel, 1982 c).

iii) Titanium

Titanium is often added to a chromium/silica catalyst system to reduce the molecular mass distribution of the product, but it has no effect on the saturation coverage of the Cr^{6+} (McDaniel, 1982 c). The addition of a small amount of titanium on the support of the Cr/silica catalyst results in an increased activity due to an increase in the reducibility of Cr^{6+} and an increase in the termination rate of the polymerisation reaction (McDaniel *et al.*, 1983; McDaniel, 1985; Ellison & Overton, 1994). The titanium acts as a promoter by direct coupling to the chromium to form Ti-O-Cr bonds which influence the electronic environment around the chromium active centre. This has been detected by XPS (a decrease in the XPS bonding energy of the Cr^{6+}) (McDaniel, 1985; McDaniel *et al.*, 1983). The simplest method of adding titanium is by means of a reaction between the silica surface and a titanium ester (McDaniel, 1985). Sintering is normally promoted by the presence of titanium if the titanium has been coprecipitated with the silica gel, but this can be prevented by adding the titanium as a surface layer (McDaniel 1985).