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Chapter 1

The oligomerisation of 1-alkenes to high viscosity oils

1.1. INTRODUCTION

The polymerisation of a large variety of unsaturated hydrocarbons is promoted by supported chromium oxide catalysts (Clark *et al.*, 1956). The same chromium oxide catalyst, also known as the Phillips catalyst, has also been found to have the ability to *oligomerise* α-olefins (Wu, 1992, 1991, 1989 a, 1989 b; Pelrine & Wu, 1991; Wu & Chu, 1994; Pelrine, 1992; Pelrine *et al.*, 1992, 1993). Due to the recent availability of high purity industrial α-olefinic streams it was decided to test the oligomerisation of these industrial (and other) α-olefins in the presence of Phillips type catalysts. The oligomer product required would be a high viscosity lubricating oil with many possible applications (Buchanan & Wu, 1994; Wu, 1989 a, 1989 b). The motivation behind the development of such synthetic lube oils would be to obtain products of which the viscosity is useful over a wide temperature range (have a high viscosity index) and of which the lubricity, thermal and oxidative stability, and pour point is equal to or even better than that of mineral oils (Pelrine & Wu, 1991). Some of the applications of such products would be their use in (Industrial Lubrication and Tribology, 1994):

- two-stroke oils: produce low smoke, clean burning, low deposits and good lubricity
- compressor lubes: low toxicity, inertness and good electrical properties
- metal working lubes: non-staining, low toxicity, clean depolymerisation
- gear oils: shear stable, VI improver, tackiness additive
- greases: adhesiveness, inert, hydrophobic
- wire rope protectives: inertness, adhesiveness, corrosion prevention and lubricity

Other potential applications which are outside of the automotive crankcase application field include use in brake fluids, compressor oil, electrical insulating oils, grease bases, hydraulic fluids, lubrication of food contact equipment, marine engine lubrication, personnal care products, refrigeration lubrication and turbine oils (Shubkin *et al.*, 1993). Friction is reduced with the use of synthetic lubricants and the effectivity of engines can thus be improved over a wide range of working conditions (Pelrine & Wu, 1991). Poly-acrylates have been used as viscosity index improvers until now. These products undergo degradation at the high temperatures and shear rates employed in high effectivity engines (Buchanan & Wu, 1994). The use of a more stable viscosity index improver such as a 1-alkene oligomerisation product will thus have many possible advantages. The improved lubricant properties of these products is the result of a limited degree of branching in the long-chain oligomers (Pelrine & Wu, 1991).

1.2. MOTIVATION FOR THIS STUDY

The Phillips CrO_3/SiO_2 catalyst has been proven in various patents to have the ability of oligomerising 1-alkenes to a high viscosity lube oil (Wu, 1989 a, 1989 b, 1991, 1992; Pelrine & Wu, 1991; Wu & Chu, 1994; Pelrine, 1992; Pelrine *et al.*, 1992, 1993; Buchanan & Wu, 1994). In spite of this fact, no in-depth study has been done on the effect of a variation of the oligomerisation conditions on the catalyst activity and selectivity and on the product characteristics. Further, the identity of the various isomers formed in the oligomerisation reaction had not been analysed in earlier literature reports. The approach followed in this thesis concerns both "one-factor-at-a-time" experiments, where the effect of a variation of only one variable is studied at a time, as well as a statistical design approach where the effect of a variation of more than one variable at a time is studied. These approaches permit analysis of optimisation of typical reaction conditions. The CrO_3/SiO_2 catalyst will also be compared to other potential oligomerisation catalysts.

1.3. OVERVIEW

In Chapter 2 a review is given on oligomerisation and polymerisation processes in general. Emphasis is placed on catalysis by a supported chromium catalyst. A literature survey of Cr/SiO_2 for use as both an oligomerisation and a polymerisation catalyst has been undertaken. It is expected that common features are to be found in both reactions. Indeed, there is very little discussion of the use of Cr/SiO_2 as an oligomerisation catalyst in the literature and most of the discussion will hence revolve around what is known about the polymerisation reaction. Various reaction mechanisms suggested for the reaction will be presented to illustrate the fact that the nature of the active species involved as well as the precise reaction mechanism is still uncertain. The effect of different variables on the chromium catalysed reaction will also be discussed. The data in this chapter provide background information which will be compared to the experimental results of this study.

Since some oligomerisation experiments were planned with molecular sieve catalysts, it was appropriate to include a literature chapter on molecular sieves (Chapter 3). The characteristics of molecular sieves, their preparation and properties will be discussed in general. Attention will also be given to the literature data which is available on the oligomerisation of 1-alkenes in the presence of molecular sieve catalysts.

The experimental chapter (Chapter 4) describes the methods that were used in the preparation of the catalysts and the equipment employed and procedures followed in testing the oligomerisation activity of these catalysts. The characterisation data of the 1-hexene feed used in the oligomerisation experiments are also included. The methods used for characterisation of the catalysts and the oligomer products are also listed.

Preliminary studies (Chapter 5) to develop a suitable catalyst to be used in further experiments of this investigation were undertaken. An in-depth characterisation of the active catalyst(s), before and after deactivation is given. From the research done in this

chapter the necessary characterisation data was obtained to select a catalyst with which further experimentation in this thesis was continued. The formation of Cr_2O_3 was found to be the reason for catalyst deactivation.

In Chapter 6 the effect of different variables on the oligomerisation reaction and the product obtained was studied. Since only one variable was varied at a time, the approach used in this chapter can be classified as a "one-factor-at-a-time" approach. The variables investigated were the number of catalyst regenerations, reaction temperature, chromium loading, reducing agent, oxygenates in the feed, reduction temperature, catalyst activation conditions, pressure, LHSV and gas composition. Where possible, emphasis was placed on the effect of the reaction conditions on the carbon distribution of the product and the viscosity of the product.

Since the variables do not necessarily have an independent effect on the oligomerisation reaction, the need was identified to perform statistical optimisation experiments (Chapter 7). In such experiments more than one variable is varied at a time, and the response is monitored as a function of these different variables. Two statistical designs were performed. The first concerned optimisation of the reduction conditions (reduction temperature and time) while the second concerned optimisation of the oligomerisation conditions (temperature, LHSV, pressure). From the data obtained, response surface three dimensional graphs were plotted. These graphs allowed for the determination of the outcome at any given set of variable values. Various responses were studied such as conversion, C_{18} selectivity, viscosity index, cycle time and activity as a function of the variables that were varied.

An in-depth GC-MS and NMR analysis was performed on representative samples of the total oligomer product as well as distilled fractions containing large quantities of dimer and trimer products (Chapter 8). From this data attempts were made to compare the actual products obtained with theoretical predictions and with literature data. Attempts were made to identify the various dimeric isomers in the oligomeric product mixture.

Mechanistic evaluations were also made.

Oligomerisation of other industrial α-olefins (1-pentene, 1-decene, C_5/C_6 mixtures) as well as commercially available similar products (1-hexene and 1-decene) was also tested in the presence of CrO_3/SiO_2 (Chapter 9). Other α-olefins were found to also oligomerise in the presence of the CrO_3/SiO_2 catalyst. Sensitivity of the catalyst towards oxygenates was however indicated.

Chapter 10 concerns testing of the oligomerisation of 1-hexene in the presence of other catalysts. The catalysts employed were zeolite Y, ZSM-5 and MCM-41, with and without the impregnation of metal ions (mostly chromium). In view of the fact that these catalysts can be classified as solid acid catalysts, a commercially available solid acid catalyst (Mallinkrodt Chemicals) was included in this investigation for the sake of comparison. An in-depth characterisation study was also performed on these catalysts. 1-Hexene was used as feed material, using standard reaction conditions. The oligomerisation activities obtained using the different catalysts were interpreted in terms of the catalyst characterisation data. The effect of the number of acid sites and the strength of these sites was also taken into consideration when comparing their oligomerisation activity.

Additional information which was not included in the various chapters is contained in the Appendix.

Chapter 2

Literature review on oligomerisation and polymerisation reactions in the presence of CrO_3/SiO_2

2.1. INTRODUCTION

The greek words "polys" which means many and "meros" which means unit, form the basis of the word polymerisation (Billmeyer, 1982). Thus polymerisation is defined as a process in which macromolecules are formed by a chemical reaction between 5 or more identical/similar units called monomers (Lewis, 1993; Young & Lovell, 1991; Billingham & Ledwith, 1974). The Greek meaning of "oligo" is a little or very few. Oligomerisation is thus a polymerisation process where only a few (2 to 4) monomer units are coupled to form a dimer, trimer or tetramer (Lewis, 1993). By contrast, according to Skupinska (1991) oligomerisation can be defined as a chain formation reaction which involves between 2 and 100 monomers, while polymerisation involves more than 100 monomers. Since the definition of the word oligomerisation is only relative, and various definitions exist for the length of an oligomer chain, it will be accepted for the purpose of this study that an oligomer is a macromolecule formed by the coupling of up to 30 monomer units.

A wide range of conditions, including catalytic conditions, have been used in the polymerisation/oligomerisation of olefins. Since the products are valuable, much time and work has been spent in both industrial and academic laboratories exploring issues (activity, selectivity, mechanistics etc.) relating to the above problem. This thesis entails an investigation of one aspect of the above: the study of a Cr/SiO_2 catalyst and its use in the oligomerisation of liquid 1-alkenes. To place the work in perspective, a review of some important concepts relating to this study as well as a review of literature

important to the thesis work has been done. This is given below.

2.2. GENERAL

2.2.1. Polymerisation and Oligomerisation in general

The reversible propagation reaction for a general polymerisation/oligomerisation reaction can be represented by the following equation (Groeneveld *et al.*, 1983 a; Cowie, 1989):

$$M_n + M \underset{k_{-p}}{\overset{k_p}{\rightleftharpoons}} M_{n+1} \qquad (2.1)$$

where M_n is the growing polymer chain; M is the monomer molecule and k_p and k_{-p} are the reaction constants for the propagation reaction and the reverse reaction respectively. The rate constants for the above equation are given by:

$$k_p = k_p^0 . e^{\left(\frac{E_p}{RT}\right)} \qquad (2.2)$$

$$k_{-p} = k_{-p}^0 . e^{\left(-\frac{E_{-p}}{RT}\right)} \qquad (2.3)$$

$$\frac{k_p}{k_{-p}} = K_{pol} = e^{\frac{\left(-\Delta H_{pol}^0 + T\Delta S_{pol}^0\right)}{RT}} \qquad (2.4)$$

where E_p and E_{-p} are the activation energies for the propagation reaction and the reverse reaction respectively; K_{pol} is the polymerisation equilibrium constant and $_\Delta H^0_{pol}$ and $_\Delta S^0_{pol}$ are the molar polymerisation enthalpy and entropy respectively

At low temperatures the reverse reaction is relatively slow since E_p (= $_\Delta H^0_{pol}$) is ca.107 kJ.mol^{-1} smaller than E_{-p} (Groeneveld *et al.*, 1983 a). The propagation reaction thus predominates. Since the rate of the propagation reaction increases with an increase in temperature, an increase in the total activity will occur. Due to the fact that E_p is

negative for many polymerisation systems, it is however often observed that the polymerisation rate and chain length increase with a decrease in the reaction temperature (Hamielec & Tobita, 1992). Above a certain temperature the rate of the reverse reaction becomes greater than the propagation rate, and no polymer will thus be formed (Groeneveld *et al.*, 1983 a; Cowie, 1989; Hamielec & Tobita, 1992). This temperature, T_c, is called the platform temperature and can be calculated from the following formula:

$$T_c = \frac{\Delta H^0_{pol}}{(\Delta S_{pol} + R\ln[M])} \qquad (2.5)$$

The platform temperature is thus a function of the free monomer concentration, [M]. For a given concentration of monomer there will be a specific T_c-value where the monomer is in equilibrium with the polymer chains (Cowie, 1989). The value of T_c is a function of the pressure of the system. The Clapeyron-Clausius equation,

$$\frac{dT_c}{dP} = \frac{T_c \Delta V}{\Delta H} \qquad (2.6)$$

is applicable, with a linear relation between log T_c and the pressure (Cowie, 1989).

The polymerisation and oligomerisation of a large variety of unsaturated hydrocarbons is promoted by supported chromium oxide catalysts (Clark *et al.*, 1956; Wu & Chu, 1994; Wu, 1989 a, 1989 b, 1991, 1993; Pelrine, 1992; Pelrine & Wu, 1991; Weiss & Krauss, 1984; Hogan & Banks, 1958; Groeneveld *et al.*, 1983 a & b; Kazanskii & Turkevich, 1967; McDaniel, 1981, 1982 c, 1985; Zecchina *et al.*, 1975 a; Ellison *et al.*, 1985; Charcosset *et al.*, 1967; McDaniel & Johnson, 1982, 1986, 1987; Krauss & Westphal, 1977; Merryfield *et al.*, 1982; Witt, 1974; McDaniel *et al.*, 1983; Welch & McDaniel, 1983; Groeneveld *et al.*, 1979; Fubini *et al.*, 1980; Ellison & Overton, 1994; Follestad *et al.*, 1990; Hogan & Kitchen, 1965; Vuillaume *et al.*, 1971; Havas *et al.*, 1994; McDaniel & Welch, 1983; Hogan, 1970; Hogan & Witt, 1971; Weckhuysen *et al.*, 1996). Branching of the starting material influences the composition of the final product. Thus, only for 1-olefins with branching further than the 4-position relative to

the double bond will polymerisation occur (Clark *et al.*, 1956). When the branching occurs closer than the 4-position, a small quantity of liquid dimers and trimers is produced, but no polymers (Clark *et al.*, 1956).

2.2.2. Types of polymerisation reactions

Polymerisation reactions can be classified into chain growth or step growth reactions (Hamielec & Tobita, 1992). The difference between these two reactions relates to the speed of the reaction; step growth polymerisation reactions are much slower than chain growth reactions (Hamielec & Tobita, 1992). In step growth polymerisation monomers, oligomers or polymers are involved in the coupling reaction. Growth of the polymer chains takes place from both end points, and the reaction can take hours to reach completion. Chain growth polymerisation concerns the presence of an active centre which can be a free radical, cation or anion, and the reaction can reach completion within seconds (Hamielec & Tobita, 1992). Chain growth polymerisation is initiated by a reactive species which is obtained from an initiator or catalyst (Hamielec & Tobita, 1992). This type of polymerisation can be divided into metal catalysed, free radical, anionic or cationic polymerisation.

2.3. METAL CATALYSED OLIGOMERISATION/POLYMERISATION

2.3.1. General

During a heterogeneously catalysed reaction, molecules are adsorbed onto the catalyst surface where they undergo a chemical reaction to form adsorbed products which eventually desorb (Kapteijn *et al.*, 1993). The composition and structure of the catalyst surface determines the overall catalytic activity and this activity can be modified by promotors. The use of promotors or catalyst modifiers results in the formation of specific surface sites which increase the selectivity by decreasing undesired reaction paths or enhancing required pathways (Kapteijn *et al.*, 1993).

In the case of a homogeneous catalytic system, the reaction rate depends on the rate of complex formation between the species and the catalyst. The total number of active sites remains constant in both homogeneous and heterogeneous catalytic reactions, hence the rate equations for homogeneous and heterogeneous catalysts are similar (Kapteijn *et al.*, 1993). The two main principles that should be taken into account with homogeneous/heterogeneous catalytic systems are (Kapteijn *et al.*, 1993):

a. The reaction equilibrium is not affected by a catalyst, but only by the reaction rate of the reacting molecules

b. The total number of catalytic active sites remains constant. The number of active sites for a heterogeneous system is expressed as the number of sites per kg or per surface area of the catalyst.

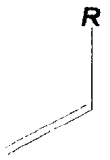
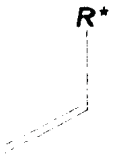
2.3.2. Heterogeneous 1-alkene oligomerisation catalysed by a CrO_3/SiO_2 catalyst

In 1950 Hogan and Banks at Phillips tested a chromium salt in a homogeneous reaction as a promotor for ethylene polymerisation and found that a white substance, namely poly-ethylene was formed. From this observation the Phillips catalyst was developed. This catalyst is currently used in many commercial plants for poly-ethylene synthesis (Moulijn *et al.*, 1993).

The use of the Phillips catalyst for the *oligomerisation* of α-olefins is a more recent development. Various patents and publications have appeared from 1988 on the preparation of a synthetic lubricant with a low branching ratio, high viscosity index and low pour point by oligomerisation of 1-alkenes in the presence of a reduced Cr catalyst (Wu, 1989 a, 1989 b; 1992; Pelrine & Wu, 1991; Pelrine *et al.*, 1992, 1993; Pelrine, 1991, Wu & Chu, 1994). The reaction conditions involved pressures from 0.1 atmospheres to 340 atmospheres, contact times from 1 second to 24 hours and reaction temperatures of between 90°C and 250°C (Pelrine & Wu, 1991; Pelrine *et al.*, 1992, 1993; Wu, 1992). The product mixture contained material with C_{30} to C_{1300} hydrocarbons, number average molecular masses of between 300 and 18000 and

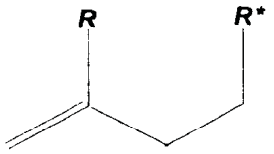
branching ratios[a] of less than 0.19 (Pelrine & Wu, 1991). The molecular mass distribution[b] of these oligomers was found to be between 1 and 5, and the pour point of the liquid lubricants lower than -15°C (Pelrine *et al.*, 1992, 1993; Pelrine & Wu, 1991; Wu, 1989 a & b). The viscosities varied from 3 cSt to 5000 cSt with viscosity indexes (VI) of 200 and higher (Pelrine *et al.*, 1992, 1993; Pelrine & Wu, 1991).

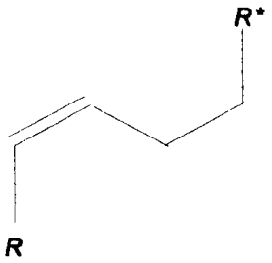
The similarities and differences between oligomerisation and polymerisation results obtained by different researchers under varying reaction conditions are summarised in Tables 2.1 and 2.2 respectively.

The alpha-olefin double bonds are not isomerised during the oligomerisation reaction and the product oligomers are atactic with predominantly head-to-tail connections and head-to-head connections within the molecule itself (Buchanan & Wu, 1994; Pelrine *et al.*, 1993). The oligomer normally has a high degree of linearity (Pelrine *et al.*, 1992, 1993; Wu, 1989 a). For two olefinic molecules, represented by  and  C^1H_2=CH-R and C^2H_2=CH-R respectively, the head-to-tail and head-to-head connections are shown below:

[a]Ratio of CH_3 groups to CH_2 groups (Wu, 1989 a & b; Wu, 1992)

[b]Ratio of mass average molecular mass to number average molecular mass

head-to-tail: 

; head-to-head: 

An induction period is often observed in the CrO_3/SiO_2 catalysed oligomerisation (and polymerisation) reactions (Krauss *et al.*, 1993; Pelrine *et al.*, 1992, 1993). An explanation for this effect in the olefin polymerisation reaction has been proposed, and presumably holds for the oligomerisation reaction as well. According to Krauss *et al.*, (1993) the more active catalytic sites formed during the reduction with CO, tend to retain the reducing agent. On addition of olefin, an oxygen containing organometallic surface species is then formed which is inactive towards polymerisation. The induction period seen in many CrO_3/SiO_2 catalysed polymerisation, and presumably oligomerisation, reactions is thus caused by the slow replacement of these species by an oxygen free organometallic surface compound which is active in the polymerisation/oligomerisation reaction (Krauss *et al.*, 1993).

After the oligomerisation reaction, the lighter components in the product can be distilled off (Buchanan & Wu, 1994; Pelrine & Wu, 1991). Hydrogenation of the remaining olefinic product can be performed at an elevated temperature and pressure with Ni, Pd or Pt on carbon, silica, alumina etc. (Buchanan & Wu, 1994; Pelrine & Wu, 1991; Van Zon *et al.*, 1994). The higher molecular mass unsaturated HVI-PAO (High viscosity index poly-alpha olefin) oligomers are sufficiently stable even prior to hydrogenation (Pelrine & Wu, 1991; Pelrine *et al.*, 1992, 1993; Wu, 1989 a, 1989 b). The HVI-PAO product contains mainly mixtures of di-alkyl vinylidenic and 1,2 di-alkyl or tri-alkyl mono-olefins.

Table 2.1: Oligomerisation results obtained by various researchers[a]

Source	Wu & Chu, 1994; Wu, 1991; Pelrine, 1992	Wu, 1993; Pelrine & Wu, 1991; Wu, 1989 a & b	Wu, 1989 a; Wu, 1993	Wu, 1993; Wu, 1989 a & b	Wu, 1989 a; Wu, 1993; Pelrine & Wu, 1991
Reduction	CO; 300°C (1 hour)	CO; 300°C (1 hour)	CO; 300°C (1 hour)	CO; 300°C (1.5 hrs)	CO; 300°C (1 hour)
Feed	a) C_3H_6 b) C_3H_6 c) C_3H_6/C_2H_4 = 3	1-Hexene	a) 1-Decene b) 1-Hexene c) 1-Hexene	1-Hexene	1-Hexene
Space Velocity (g feed.g^{-1} cat.h^{-1})	a) & b) 1.67 c) 2.04	4.275	a), b) & c) 5.5	5.472	2.1375
Total pressure (bar)	a) 15 b) 20-27 c) 14-20	10.5	a) 17-22 b) 1.0 c) 1.0	1.0	1.0
Temp (°C)	a) 180-190 b) 170 c) 190	150	a) 100 b) 110 c) 200	100	a) 100 b) 50
% conversion	a) 69% (16 hrs) b) 72% (14 hrs) c) 75% (15 hrs)	a) 10% (2 hrs) b) 41% (3.5 hrs) c) 74% (5.5 hrs) d) 31% (21.5 hrs)	a) ? b) 46% c) 3%	a) 73% (3.5 hrs) b) 64% (4.5 hrs) c) 59% (6.5 hrs) d) 21% (22.5 hrs)	a) 8.2% (20 hrs) b) 8.0% (44 hrs)
Viscosity at 100°C (cSt)	a) 28.55 b) 39.85 c) 46.03	a) 26.1 b) 17.1 c) 14.5 d) 20.4	b) 206 c) 47	a) 102 b) 151 c) 197 d) 437	a) 620 b) 1048
Viscosity index (VI)	a) 78 b) 81 c) 112	a) 159 b) 151 c) 142 d) 143	b) 174 c) 185	a) 108 b) 164 c) 174 d) 199	a) 217 b) 263
Remarks	More specific for C_9-formation	0.58% Cr/SiO_2	0.58% Cr/SiO_2	Commercial 1% Cr/SiO_2	0.58% Cr/SiO_2

[a] CrO_x/SiO_2 catalysts calcined at 600°C in air for 16 hours

Table 2.2: Polymerisation results obtained by various researchers

Source	Clark *et al.*, 1956	Weiss & Krauss, 1984	Hogan & Banks, 1958	Pelrine & Wu, 1991	Hogan & Banks, 1958
Oxidation	510°C	800°C	500°C (16 hrs)	600°C (16 hrs)	500°C
Reduction	In situ	350°C	In situ	0.5 hours; 350°C a) CO (1st cycle) b) CO (2 nd cycle) c) CO d) H_2	In situ
Feed	a) Ethylene b) Propylene c) 1-Butene d) 1-Hexene e) 1-Pentene f) 4-Methyl-1-pentene	a) Propylene b) 1-Butene c) 1-Pentene d) 1-Hexene e) 1-Heptene f) 1-Octene	Propylene (25% propylene, 75% propane)	a) 1-Decene b) 1-Decene c) 1-Hexene d) 1-Hexene	93 mass % propylene, 97 mass % iso-octane
Space Velocity (g feed .g^{-1} cat .h^{-1})	2.0 (LHSV)	batch: 3.7g and 6.6g catalyst quantities	2.0 (LHSV)	2.2	4.6-5.2 (LHSV)
Total pressure (bar)	35.0	?	42.0	?	28.0
Temp	88°C	a) + b) -60°C to -20°C c) - f) 20°C	71°C	a) & b) 125°C c) & d) 60°C	154°C
% conversion	After 6 hrs: a) 100% b) 91% c) 77% d) 40 - 56% e) 82% f) 80%	After 20 hrs: a) 37% b) 69% c) 99% d) 2% e) 70% f) 99%	After 5 hrs: a) Cr_2O_3-CrO_3: 86% b) NiO & ThO_2: 79% c) Fe_2O_3: 60% d) MnO_2: 32% e) MoO_2: 44% f) No metal: 33%	a) 54% b) 80% c) 84% d) 12.5%	After 5 hours a) 83% b) 95% c) 100% d) 93%
Remarks	* Slurry-bed reactor *3% Cr on SiO_2-Al_2O_3	1% Cr on SiO_2	Support = 90% silica + 10% alumina co-presipitated and treated with steam	*0.58% C/SiO_2 *Oligomeri-sation reaction	a) 0.17% Cr b) 0.66% Cr c) 2.25% Cr d) 7.66% Cr

2.3.3. Oligomerisation and polymerisation in the presence of CrO_3/SiO_2

Since there is very little literature data available on the oligomerisation reaction, the results obtained from polymerisation studies will be included in this section.

The polymerisation or oligomerisation reaction on the Phillips catalyst involves chain transfer, termination of a growing chain and the initiation of a successor on the same active site (McDaniel & Johnson, 1987). The polymerisation mechanism generally accepted for the CrO_3/SiO_2 catalyst is that proposed by Cossee for the Ziegler-Natta catalyst. The process of chain termination is however still not understood in detail (Zecchina *et al.*, 1975 a). Some of the various mechanisms that have been suggested for the Cr/SiO_2 catalysed oligomerisation reaction are discussed below.

2.3.3.1. Oxidation state of Cr in the Cr/SiO_2 catalyst

In spite of all the research that has been done on the chromium on silica catalyst, researchers have still not reached an agreement concerning the characterisation of the chromium species and the active sites of the catalytic system. The uncertainty concerning the nature of the active chromium species is a result of the fact that there are chromium ions of all valence states in the catalysts prepared from a Cr^{6+} salt (Przhevalskaya *et al.*, 1975). Over time every valence from Cr^{2+} to Cr^{6+} has been proposed as the active site, either alone or in combination with a species of another valence. Some of the view points that have arisen concerning the active chromium species are the following:

- After reduction of the Cr^{6+}/SiO_2 catalyst in CO or H_2, isolated coordinatively unsaturated Cr^{2+} species are responsible for catalyst activity (Krauss *et al.*, 1975, 1987; Pelrine & Wu, 1991; Krauss & Stach, 1968; Welch & McDaniel, 1983; Merryfield *et al.*, 1982; Best *et al.*, 1977; Ruddick & Badyal, 1997). The polymerisation rate increases linearly with an increase in the Cr^{2+} content which

indicates that Cr^{2+} is the active centre (Krauss & Stach, 1968). The activity of the Cr^{2+} active centre is inversely proportional to the hydroxyl population of the support (Welch & McDaniel, 1983).

- Mononuclear Cr^{3+} ions in a low coordination state with at least two available coordination sites are responsible for catalyst activity (Przhevalskaya *et al.*, 1975; Beck & Lunsford, 1981). It was found that catalysts prepared from trivalent chromium had a high activity while catalysts prepared from divalent chromium had no activity, and that reduction of the trivalent chromium into the divalent state sharply decreased the activity (Przhevalskaya *et al.*, 1975). The initial activity for ethylene polymerisation was also found to correlate with the concentration of isolated Cr^{3+} ions (Beck & Lunsford, 1981).

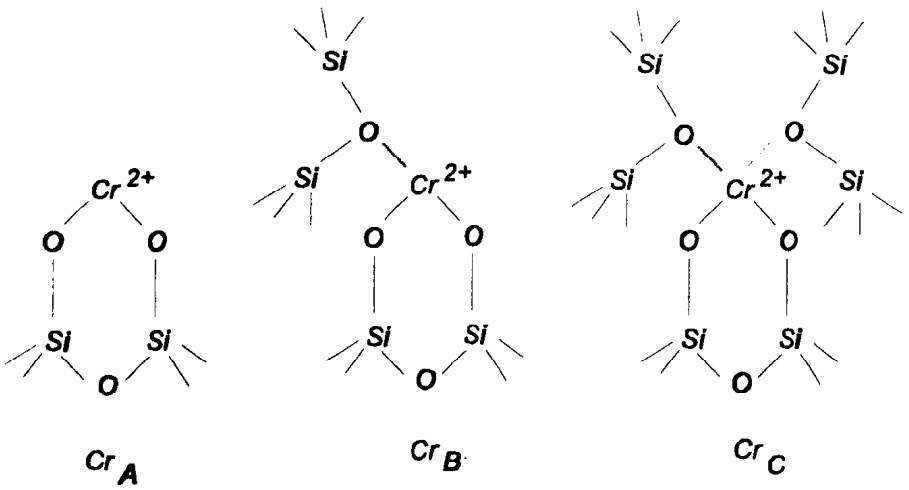
- Coordinatively unsaturated dinuclear Cr^{2+} and/or Cr^{3+} species are active towards polymerisation (Rebenstorf & Larsson, 1981, 1983; Ermakov *et al.*, 1970, 1971). A similar mechanism is applicable to both catalytic centres. The main difference between coordinatively unsaturated Cr^{2+} and Cr^{3+} ions is the ability to bring into effect chain propagation. In the case of Cr^{3+} sites the chains formed are shorter, while Cr^{2+} sites are more involved in the formation of longer chains (Scarano *et al.*, 1994).

- Cr^{5+} is the active polymerisation centre during the polymerisation of ethylene (Kazanskii & Turkevich, 1967; Kazanskii & Pecherskaya, 1968; Van Reijen & Cossee, 1966). A definite relation between the number of Cr^{5+} ions and the total activity of the catalyst has been indicated (Kazanskii & Pecherskaya, 1968).

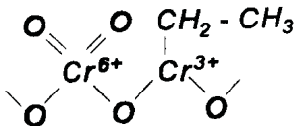
- The active site for the polymerisation reaction is a Cr^{2+} cation which is situated next to a silanol group. The silanol group plays an important role in the determination of the catalyst activity by encouraging the reoxidation of Cr^{2+} to Cr^{3+}. The activity of the Cr on silica catalyst is determined by the Cr^{2+}/Cr^{3+} ratio.

The active site thus involves a combination of Cr^{2+} + Cr^{3+} or Cr^{2+} + H^{+} sites (Groeneveld *et al.*, 1983 a, 1983 b).

- Reduction with CO at 350°C produces an active catalyst which contains 98% Cr^{2+}. The other 2% is in the inactive Cr^{3+} form (Fubini *et al.*, 1980; Ghiotti *et al.*, 1983; Zecchina *et al.*, 1975a, 1975 b, 1975 c; Krauss *et al.*, 1987). Four different divalent species can be distinguished: Two reactive species namely Cr_A and Cr_B, and two less reactive species, Cr_{C1} and Cr_{C2}. High temperature heating of the catalyst in vacuum results in thermal deactivation, with Cr_A changing to Cr_C, while Cr_B is not affected. Even in the most active Cr/silica catalyst approximately 30% of the inactive Cr is present, while 45% and 25% is in the Cr_A and Cr_B forms respectively (Fubini *et al.*, 1980; Ghiotti *et al.*, 1983; Zecchina *et al.*, 1975 a, 1975 b, 1975 c, 1994; Krauss *et al.*, 1987). The reoxidation of Cr_A and Cr_B takes place with reaction heats of 480 and 425 $kJ.mol^{-1}$ respectively *via* an unactivated process. The oxidation of Cr_C only takes place by activation under O_2 pressure. The Cr_A type ions are unstable towards thermal treatment probably as a result of binding to only two oxygen surface atoms, while the Cr_B type ions are coupled to three surface oxygen atoms (Ghiotti *et al.*, 1983). The Cr_{C1} type ions are not very active, and are generally present on deactivated samples. The Cr_{C2} type ions are almost totally inactive, and are bonded to the surface by means of 4 oxygen atoms (Ghiotti *et al.*, 1983). The three types of Cr^{2+} complexes, namely Cr_A, Cr_B and Cr_C are shown schematically below (Zecchina *et al.*, 1994; Ghiotti *et al.*, 1983; Fubini *et al.*, 1980).



- The active site on the chromium oxide polymerisation catalyst is formed by an interaction of the catalyst surface with the monomer, and can be represented as follows:



A fraction of the Cr^{6+} atoms are reduced to the trivalent state and alkylated. The active centres thus involve alkylated trivalent chromium atoms in combination with a Lewis acid (Miesserov, 1970). The strenghtened Lewis acid properties of the CrO_3 causes redistribution of electron density in the complex, and transfer thereof to the hexavalent chromium ions (Miesserov, 1970). A decrease in the positive charge of the hexavalent chromium atoms explains the appearance of Cr^{5+} atoms on the surface. The Lewis acid decreases the electron density on the Cr^{3+} atom, and thus increases the ability of the Cr^{3+} atoms to coordinate with monomer molecules (Miesserov, 1970). The Cr^{3+}-C bond is weakened by