Table 4.2: Surface areas of the extruded supports prepared by adding various binders to Davison 952 silica

	Surface Area ($m^2.g^{-1}$)	Pore Volume ($cm^3.g^{-1}$)	Average Pore Diameter[a] (Å)
Davison 952 silica	322	1.135	141
Silica + 30% bentonite before calcination	254	0,806	127
Silica + 30% bentonite after calcination	264	0,903	137
Silica + 30% norilose before calcination	151	0,512	136
Silica + 30% norilose after calcination	32	0,046	63
Salicylic acid before calcination[b]	647	0,339	21

[a]Average pore diameter = 4 x porevolume ($cm^3.g^{-1}$) x 10000 ÷ surface area ($m^2.g^{-1}$) (Hogan & Kitchen, 1965)

[b]No calcination performed due to very low pore diameter

From the data in Table 4.2 it can be seen that the calcined silica + 30% bentonite extrudates would be the most suitable as a support for CrO_3, since the surface analyses data are the closest to that specified in the literature (see Table 4.1). This support was hence used in all the CrO_3/SiO_2 catalysed oligomerisation reactions performed in this investigation unless otherwise specified.

4.2.3.3. Zeolite preparation

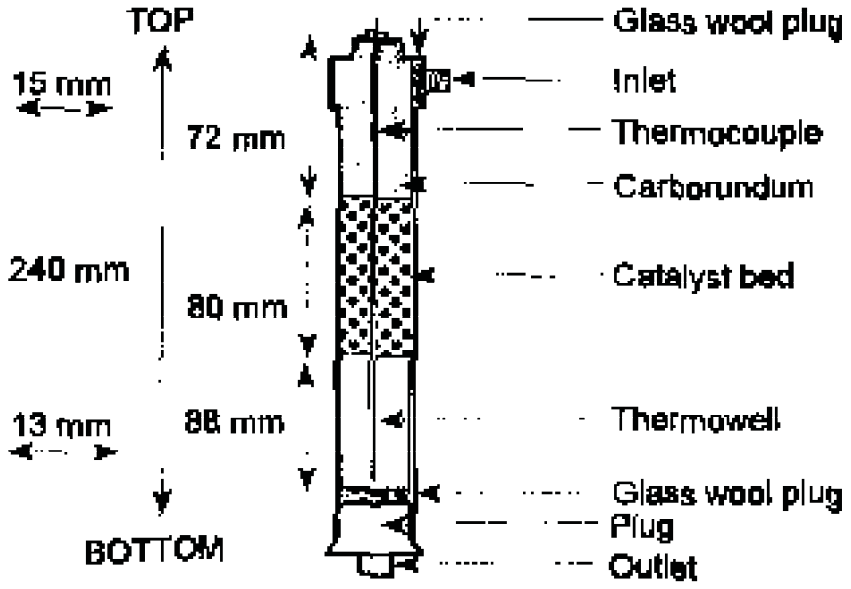
Each zeolite was prepared according to a recipe which produced a certain Si/Al ratio. The purity and crystallinity of each zeolite was verified by XRD analyses

4.2.4 Catalyst activation

Since the catalyst was normally prepared from CrO_3, the chromium was already in the Cr^{6+} state. Calcination was performed to enable a reaction between the chromium and the silica support sites which would result in active catalytic sites after the reduction step had been performed. This was confirmed by comparing the activities of a calcined and uncalcined Cr/SiO_2 catalyst (see Appendix 1). After the reduction step only the catalyst which had been calcined proved to be active.

The catalyst (10 ml) was loaded into a fixed bed stainless steel micro-reactor in which the oligomerisation reactions would be performed. The design of the reactor that was used in the oligomerisation experiments is shown in Figure 4.1.

Figure 4.1: Reactor used for performing the oligomerisation reaction



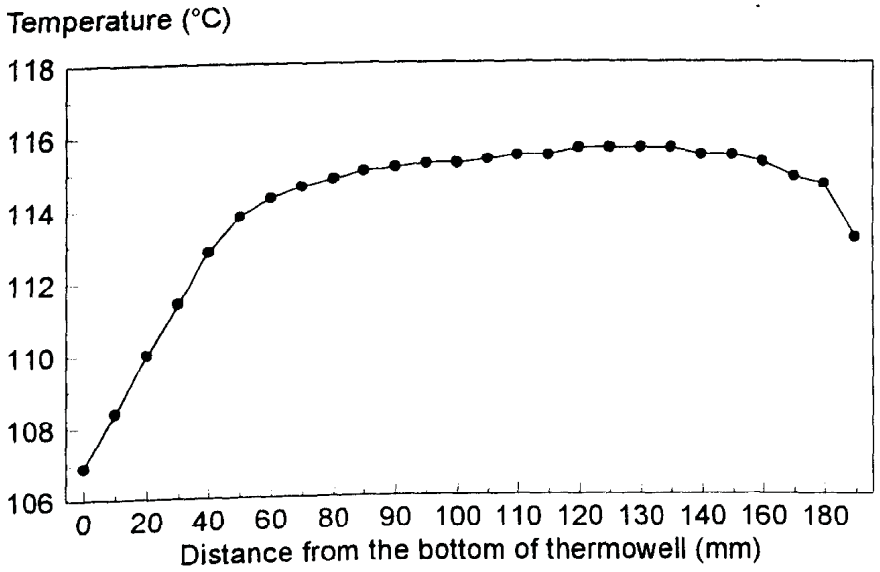
A temperature profile of the reactor was determined while it was loaded with carborundum. The temperature profile can be seen in Figure 4.2. It was found that the optimum temperature zone was between 80 mm and 160 mm from the bottom of the

reactor since very small temperature changes were seen in this zone. Care thus had to be taken to ensure that the catalyst was placed exactly within this zone. The optimum position for the thermocouple then resided in the middle of this optimum zone (and thus the middle of the catalyst bed) which is 120 mm from the bottom of the thermowell, and thus 128 mm from the bottom of the reactor. Since the thermocouple was placed 8 mm from the bottom of the reactor, 88 mm of carborundum had to be loaded into the bottom part of the reactor, followed by 80 mm of catalyst (≈ 10 ml) and 72 mm of carborundum in the top half of the reactor.

A plug of glass wool was inserted at the bottom end of the reactor and at the top end to prevent spilling when loading of the catalyst is performed.

Anti-seize fluid was applied to the stainless steel plug before closing the reactor, to prevent the two stainless steel surfaces from seizing at the high temperatures that were reached during the activation step.

Figure 4.2: Temperature profile over the reactor when loaded with 24 grit carborundum



The procedure used for calcination and reduction suggested in the literature, and the procedures followed in this investigation are compared in Table 4.3 (Wu, 1989 a, 1991; Buchanan & Wu, 1994).

Table 4.3: Procedure followed in the activation of the CrO_3/SiO_2 catalyst

	Literature data (Wu, 1989 a, 1991; Buchanan & Wu, 1994).	This work
Calcination	600°C in air for 12 - 16 hours	470°C - 600°C in air for 15 hours
Reduction	350°C in CO/H_2/metal alkyl containing compounds for 30 - 60 minutes	270°C - 350°C in CO for 4 - 30 minutes

Before calcination, the catalyst was dried in 15 $Nl.h^{-1}$ nitrogen at 120°C for 2 hours. The temperature was then increased to 200°C and 15 $Nl.h^{-1}$ air was introduced into the system. The catalyst was then heated in air to temperatures of between 470°C and 600°C at a rate of 10°C.min^{-1} and kept at the final temperature for 15 hours. After the 15 hours calcination time, 15 $Nl.h^{-1}$ nitrogen was introduced into the system, and the catalyst allowed to cool down to temperatures of between 270°C and 350°C. During this period enough time was allowed for the complete removal of all traces of air. A minimum period of 1 hour was allowed for the complete flushing of the system with nitrogen.

In the Cr^{6+} state the catalyst is hydrophilic and turned brown when it has absorbed water from the atmosphere. Upon calcination in air at elevated temperatures the colour returned to orange and the chromium thus returned to the Cr^{6+} state.

15 $Nl.h^{-1}$ CO was introduced into the system at the desired reduction temperature and

reduction was performed for a period of time varying between 4 minutes and 30 minutes. The reduction reaction was exothermic since temperature increases of between 1°C and 11°C were seen upon initial introduction of CO. This temperature rise depended on the concentration of chromium in the catalyst and the initial reduction temperature. During the reduction step the colour of the catalyst changed from the orange Cr^{6+} state to the blue/green active $Cr^{2+/3+}$ state.

After the reduction step care had to be taken to avoid contamination of the catalyst with air or water since this would result in deactivation of the catalyst. Hence, 15 Nl.h^{-1} nitrogen was once again introduced into the system. The reactor was allowed to cool to the desired reaction temperature while all traces of CO were removed by flushing with nitrogen.

4.2.5. Catalyst testing

The oligomerisation reaction was performed under the following reaction conditions:

Temperature:	76°C - 136°C
Pressure:	1.0 bar - 9.0 bar
Gas:	N_2
Gas flow rate:	0.15 Nl.h^{-1}
LHSV of feed:	0.6 h^{-1} - 20 h^{-1}
Feed:	1-pentene, 1-hexene, 1-decene, 1-hexene/1-pentene

The reactor (Figure 4.1) was placed in a copper block around which the oven was fastened. SC1 temperature controllers (*manufactured in house*) were used in combination with K-type thermocouples which were inserted between the oven and the copper isolation block. Fluke 51 K/J handheld thermometers connected to K-type thermocouples which were inserted into the thermowell of the reactor were used for temperature readout. The thermocouples were placed exactly in the middle of the catalyst bed. A cross-*sectional view of* the reactor, isolation block, oven and position

of the thermocouples, seen from above, is shown in Figure 4.3.

Figure 4.3: Cross-sectional view of the reactor system as seen from above

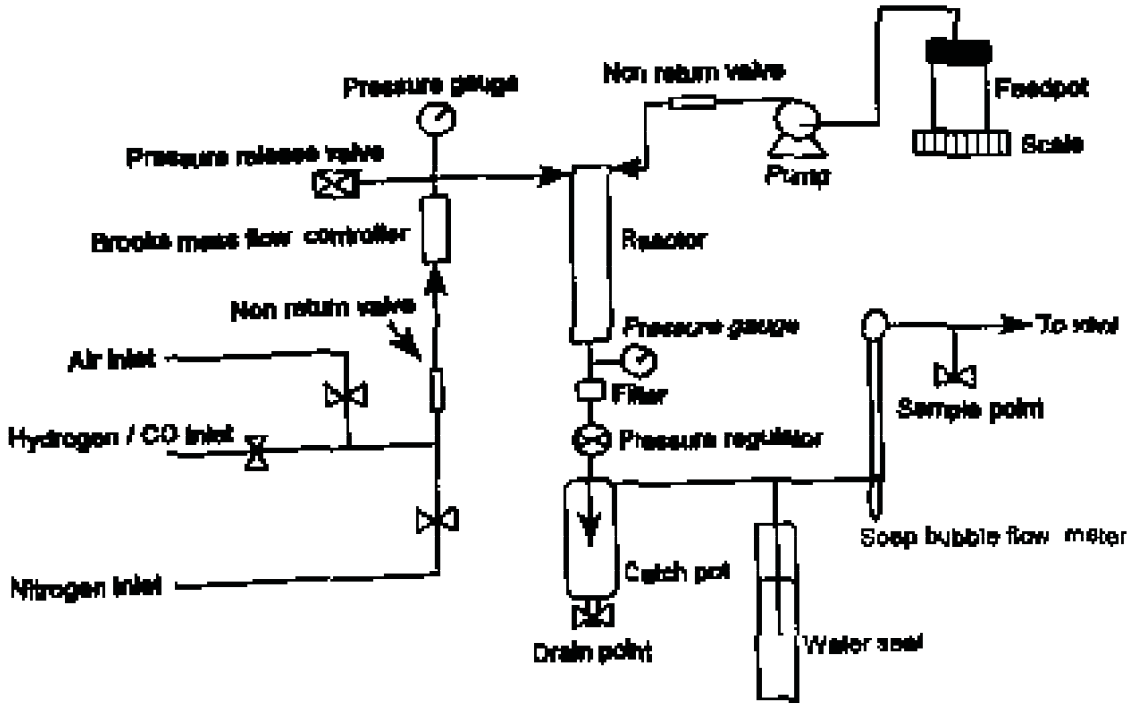
Since calcination temperatures as high as 600°C were required, it was important to make use of a Cu heat transfer block instead of a stainless steel block. The reactor, Cu block and oven were designed for a snug fit, since open spaces between the reactor and the block, or the oven and the block, could cause losses in temperature transfer as well as deformation of the heat transfer block.

During the calcination step an isolation blanket was wrapped around the whole reactor system shown in Figure 4.3. The function of this isolation blanket was to minimise heat losses during the calcination step and to minimise the chances of an injury caused by the hot outer surface of the oven.

The reaction system used for testing of the various catalysts can be seen in Figure 4.4. The pressure regulators used on the reactor system were GO regulators while Dräger Tescom pressure regulators were used on the high pressure gas cylinders. Swagelok pressure gauges were used. A Spectrachrom P100 isocratic pump was used for feeding the 1-alkenes into the reactor. All the tubing indicated on the left hand side of

the reactor in Figure 4.4 was 1/4 inch stainless steel. To minimise void spaces, the tubing shown on the right hand side of the reactor was 3/8 inch stainless steel. The on/off valves, the sample point valves (except the drain point valve) as well as the pressure release valves were from Hoke. The non-return valves were from Swagelok. A Nupro 7 micron filter was used to remove any large particles before the product was fed through the regulator. The gas flow was regulated by a Brose 5878 Mass Flow Controller unit in combination with Brooks 5850 TP Mass Flow Controllers (0 - 30 $Nl.h^{-1}$) through which the gas was fed. The drain point valve was a glass stopcock typically used in vacuum distillation experiments. Dow Corning vacuum grease was used to keep this stopcock lubricated.

Figure 4.4: Reaction setup used for testing the oligomerisation reaction



To eliminate the possibility of water poisoning the catalyst, pre-dried (at 200°C for 18 hours) molecular sieve (3Å) was used to absorb any water present in the feed, before

it was fed into the reactor.

4.2.6. Regeneration of the catalyst

After deactivation of the catalyst to conversions below 1%, the catalyst was dried under 15 Nl.h^{-1} N_2 for 1 hour at the reaction temperature. The temperature was then increased to 320°C and the reactor kept at this temperature for two hours. The system was allowed to cool down to a temperature of 200°C, whereafter 15 Nl.h^{-1} air was introduced into the system and the normal calcination and reduction procedures were followed (See Table 4.3). The effect of an increasing number of regenerations on the maximum conversion of 1-hexene to oligomer product is described in Chapter 6.

4.3. Characterisation of the oligomerisation catalysts and zeolites

The techniques and equipment that were used for the characterisation of the Phillips type oligomerisation catalysts and the zeolites prepared in this study are shown in Table 4.4.

Table 4.4: Characterisation techniques and equipment used

Characterisation technique	Instrument
Thermogravimetric analysis (TGA)	Perkin-Elmer TGA 7 Thermogravimetric Analyzer
Differential thermogravimetric analysis (DTG)	Setaram TG-DTA 92 apparatus
BET surface area	Gemini 2360 V 3.03[a]
Chemisorption	Micromeritics ASAP 2000
Pulse Chemisorption	Micromeritics Pulse Chemisorb 2700
Temperature Programmed Reduction	Micromeritics TPD/TPR 2900[b]
Temperature Programmed Desorption	Micromeritics TPD/TPR 2900
Atomic Absorption	Perkin-Elmer 1100 flame AAS[c]
CH and N micro analysis	Carlo Erba 1106 elemental analyzer
X-ray photoelectron spectroscopy (XPS)	VG ESCALAB MK 11 XPS apparatus (CSIR)[d]
X-ray diffraction (XRD)	Philips PW 1830/1840 X-ray Diffraction apparatus[e]
Infrared determinations (IR)	Bruker IFS Infrared apparatus and Nicolet 20 SXB FTIR Spectrometer[f]
Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)	Bruker IFS 85 FTIR with a Harrick DRIFTS cell which can be heated to 500°C[g]
Scanning electron microscope (SEM)	Jeol JSM-35 Scanning Electron Microscope[h]
Gold sputtering of SEM samples	Edwards S150B sputter coater

[a]Saturation pressure: 657.61 mmHg; Evacuation time: 1.0 minute
[b]Attenuation: 10 mV; Chart speed: 10 cm.h^{-1}; Bridge current: 100 mA; Gas flow: 40 ml.min^{-1}; Heating rate: 10°C.min^{-1}. During reduction of the catalyst with H_2, H_2O is formed. Since the conductivity of H_2 and H_2O are quite different, a change is seen by the TCD detector which registers a reduction peak at that specific temperature. Since the reduction of CO results in the formation of CO_2 which has a conductivity similar to that of CO, no peaks can be detected if CO is used as the reducing agent. No attempt was made to develop a method which would allow for the TPR determination with CO as the reducing agent.
[c]The samples were digested in a mixture of HNO_3/HCl/HF. A microwave sample preparation system (controlled by pressure) with Teflon (PFA) vessels was used for the digestion. The samples were thereafter analysed by flame-AAS
[d]Magnesium anode
[e]Copper or K_1K_2 radiation tube
[f]Samples were recorded as KBr pellets
[g]ZnS windows were used in the cell. The apparatus was connected to a gas manifold for the purpose of passing gas over the sample
[h]SEI: 5; Gun Bias: 5; Acceleration voltage: 20 kV; Load current: 70 µA; Maximum voltage: 30 kV

Gravimetric determination of the silica content in samples

The sample (1 g) was dissolved in HCl and then dried in a sandbath to allow for precipitation of the silica. HCl was added once again to the sample, which was then filtered through a 42 Whatman Filter. The silica was washed with boiling 5% HCl. The filter paper was incinerated in a platinum dish at 500°C for 30 minutes and at 900°C for 45 minutes. The dish containing the silica was weighed and then treated with a solution of 2 drops H_2SO_4 in 10 ml HF. The silica was allowed to evaporate at 500°C for 30 minutes and at 900°C for 45 minutes. The weight difference after this treatment gives the weight of silica present in the sample.

4.4. Characterisation of the Feed

Since industrial 1-hexene was used as feed for the work described in most of the chapters in this study (except Chapter 9), only the 1-hexene characterisation data are included in this section. The characterisation data of other feeds are included in Chapter 9.

4.4.1. Determination of oxygenates in the feed

a). *Total oxygenates:* A HP 5890 Series II GC-AED (Atomic Emission Detector) with a 25 meter DB-Wax column was used. The 1-Hexene sample (2 ml) was passed through a silica column to concentrate the oxygenates. Hexane (4 ml) was then passed through the column to remove impurities. Finally the column was rinsed with 4 ml methanol. This solution was analysed under GC conditions to obtain the concentration of oxygenates in the sample. See Table 4.5 for results.

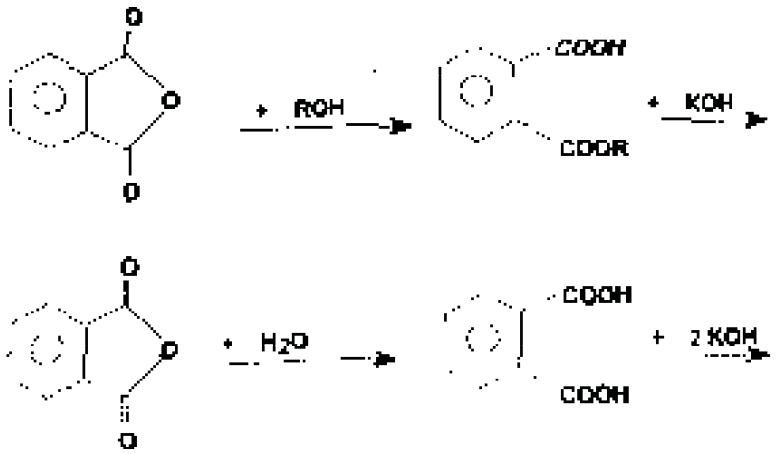
b). Carbonyl analysis: The DNPH spectrophotometric procedure was used. The carbonyls in the sample were reacted with 2,4-diphenyl hydrazine in acid media, followed by an alkalising step to form the corresponding hydrazone. The hydrazone

formed has a wine red colour and can be measured spectrophotometrically at 515 nm. See Table 4.5 for results.

c). *Acid number:* This was determined by an acid-base titration in a non-aqueous matrix by means of an indicator titration. See Table 4.5 for results.

d). *Alcohol analysis:* An excess of phthalic anhydride, in a pyridine matrix, was added to the sample. Under reflux the alcohol reacts with anhydride to form a disubstituted benzene ring which has an acid and an ester group attached to it. The unreacted phthalic anhydride is then hydrolysed and a benzene ring with two acid groups is formed. The acid groups are then titrated with standardised KOH and from the difference the alcohol content can be calculated. See Table 4.5 for results. The reactions involved in the analysis are summarised in Figure 4.5.

Figure 4.5: Reactions involved in the determination of alcohols in the feed



From the results in Table 4.5 it can be seen that there are limited quantities of oxygenates in the 1-hexene feed.

Table 4.5: Results of the determination of oxygenates in the 1-hexene feed

Analysis	Units	Value	SASOL Method
a) Total oxygenates	mass %	< 0.2	-
b) Carbonyls as CO	$mg.kg^{-1}$	12	D 150
c) Alcohols as ethanol	% m/m	< 0.2	2.61 R1
d) Acid number	mg $KOH.g^{-1}$	0.002	B 102

4.4.2. Specification analysis

A specification analysis on the 1-hexene feed used in this study was performed by SASOL Synthetic Fuels. In Table 4.6 the results can be seen as well as the SASOL method that was used for each analysis.

Table 4.6: Specification analyses on 1-hexene

Analysis	Units	Limits	Method
Density @ 20°C	$g.cm^{-1}$	0.670 - 0.680	A.231 (SASOL)
Peroxides	$mg.kg^{-1}$	1.0 maximum	D.152 (SASOL)
Carbonyls	$mg.kg^{-1}$ as CO	2.0 maximum	D.150 (SASOL)
Sulphur	$mg.kg^{-1}$	1.0 maximum	A.239 (SASOL)
Water	$mg.kg^{-1}$	10 maximum	B 182 (SASOL)
Chlorides	$mg.kg^{-1}$	1.0 maximum	D.153 (SASOL)
Hexene-1	% m/m	98.50 minimum	H.190 (SASOL)
Carbons < C_6	% m/m	0.25 maximum	H.190 (SASOL)
Carbons > C_6	% m/m	0.25 maximum	H.190 (SASOL)
Other C_6	% m/m	2.00 maximum	H.190 (SASOL)
Internal olefins, branched olefins & paraffins	% m/m	2.00 maximum	H 190 (SASOL)
Methanol	$mg.kg^{-1}$	1.0 maximum	H.183 (SASOL)

The actual CO concentration that was obtained in Table 4.5 is much higher than that specified in the specification analyses (Table 4.6).

4.4.3. Hydrocarbon distribution

A GC analysis was done on the *1-hexene to determine the hydrocarbon* distribution in the feed. The results can be seen in Table 4.7.

The equipment used for the determination was a Hewlett Packard HP 5890 Gas Chromatograph fitted with a Hewlett Packard PONA column. The column dimensions were *50* m x *0.2* mm and *a 0.5 µm* film thickness. The column was protected against

air with an installed OXY-TRAP. A Hewlett Packard HP 7673 auto-sampler and Hewlett Packard HP 7673 controller were also connected to the system. Due to the overlap of the 3-methyl-cyclopentene peak with certain other peaks in the oven programs that were used, two different oven programs were run in order to determine the mass % of 3-methyl-cyclopentene in the feed. In the first oven program, 3-methyl-cyclopentene and 3-methyl-pentene-2 overlapped while in the second oven program, 3-methyl-cyclopentene and 2-methyl-pentene-2 overlapped. The mass % of 3-methyl-cyclopentene in each of the overlapping peaks could thus be determined by subtraction of the known concentration of the other compound.

The sample was injected neat into the GC (0.2 μl), and the mass percentage (i.e. area percentage) was used for quantification.

Table 4.7: GC analysis of the 1-hexene feed[a]

Compound	(mass %)
3-Methyl-pentane	0.18
1-Hexene	98.47
Unknown	0.01
Hexane	0.02
3-Hexene (c + t)	0.02
2-Hexene (t)	0.01
2-Methyl-pentene-1	0.11
2-Methyl-pentene-2	0.63
3-Methyl-pentene-2 (c)	0.14
3-Methyl-pentene-2 (t)	0.01
C_6H_{10}(3-Methyl-cyclopentene)	0.40

[a]Injector temperature: 280°C; FID detector temperature: 350°C; Split: 1:100; Purge vent: 1 ml.min^{-1}; Carrier gas: Helium (1 ml.min^{-1}); Make-up gas: Helium (32 ml.min^{-1}); First oven program: 50°C (10 min) up to 250°C (2 min) at a rate of 15°C.min^{-1}. Second oven program : 0°C up to 250°C at a rate of 4°C.min^{-1}

4.4.4. Solubility of water in 1-hexene

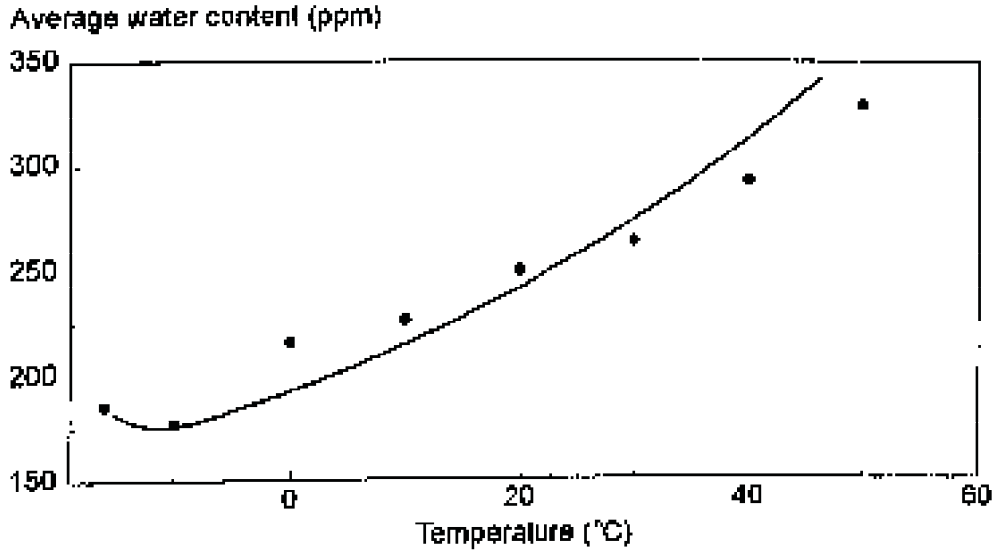
Tests done on the solubility of water in 1-hexene at various temperatures showed that water is highly soluble in the alpha olefin feed. The experiments were performed by saturating 1-hexene with water and taking samples at various temperatures. The water content of the 1-hexene at the various temperatures was determined with the use of a Kyoto KF moisture titrator. The results observed are shown in Table 4.8 and Figure 4.6

Table 4.8: Solubility of water in 1-hexene at various temperatures

Temperature (°C)	Average H_2O content (ppm)	Standard deviation
-16	186	28.3
-10	177	20.3
0	216	13.1
10	226	6.5
20	250	5.1
30	264	5.9
40	293	14.4
50	329	21.5

From the results in the above table it can be seen that at room temperature (± 20°C) an average of ± 250 ppm water is soluble in 1-hexene.

Figure 4.6: Solubility of water in 1-hexene at various temperatures



Since water is soluble in 1-hexene, contact of the feed with a moist atmosphere could have an effect on the oligomerisation reaction.

4.5. Oligomer Characterisation

The oligomeric product was separated from unreacted 1-hexene by distillation at the boiling point (63°C) and atmospheric pressure (Lide & Frederikse, 1994). Thereafter characterisation of the oligomer product using the equipment and techniques shown in Table 4.9 was performed.

Table 4.9: Equipment and techniques used for characterisation of the oligomer product

Technique	Instrument
High Temperature GC	Varian 5890A High Temperature GC[a]
Viscosity and viscosity index determination (See Appendix 2)	Haake Rotovisco RV Rotational 2.3.16 viscometer in combination with a RC 20 Rheocontroller[b]
Nuclear Magnetic Resonance (NMR) determination	Varian 400 MHz Unity Inova Nuclear Magnetic Resonance spectrometer[c]
Gas Chromatography - Mass Spectrometric (GC-MS) determination	Hewlett Packard 5890 Series II GC in combination with a Hewlett Packard 5972 MS Detector.
Bromine number determination	Kaufmann SASOL Analytical Method 2.75/95[d]
Infra-red determination	Nicolet 20 SXB FTIR
High Pressure Liquid Chromatography (HPLC)	Hewlett Packard 1090 HPLC and Hewlett Packard 1047A Refractive index detector[e]
Shortpath distillation	Janke & Kunkel RW 20 DZM shortpath distillation equipment
UV/Visible Spectrophotometric determination	Varian Cary 1 UV/Visible Spectrophotometer

[a] Column: Aluminium clad; Solvent: 1-hexene; Initial Column temp: 60°C; Hold Time: 5 minutes; Column Ramp Rate: 10°C/minute; Final Temperature: 440°C; Initial Injector Temp: 40°C; Hold Time: 0 minutes; Injector Ramp Rate: 70°C/minute; Final Injector Temp: 420°C; Hold Time: 48 minutes; Carrier Gas: H_2; Detector Temp: 450°C

[b] PK, (1°), PK, (1") and PK, (1') spindles

[c] Probe: 5 mm; 4 nucleus switchable

[d] The sample, dissolved in carbon tetrachloride, was treated at room temperature with an excess of a 0.1 M bromine solution. The excess bromine was reduced with potassium iodide and the liberated iodine determined by titration with a sodium thiosulphate solution. The bromine number is given by the grams of bromine that will react with 100 g of the sample under the conditions of the test

[e] Columns: 2 x Lichrosorb Si 60, 250 x 4.6 mm, 5 µm; Mobile phase: n-hexane; Flow rate: 1.2 ml.min^{-1}; Oven temperature: 40°C; Injection volume: 50 µl; Analyses stop time: 35 minutes; Detector range: 2 x 10^{-4} RIU/F.S; Detector temperature: 40°C. The standards used were dissolved in cyclohexane and contained the following: Monocyclic aromatic: o-xylene, 1.0% (m/m), Bicyclic aromatic: 2,3-dimethyl naphtalene: 1.0% (m/m), Polycyclic aromatic: phenanthrene: 1.0% (m/m). The samples were diluted 1:1 in cyclohexane to enable the determination.

4.6. CALCULATIONS AND MASS BALANCES OF HYDROCARBON MATERIAL

The mass of hydrocarbon material was calculated as follows:

In: a) Mass of feed pumped per hour (obtained by weighing the feed pot) - mass of C_6 lost by evaporation

Out: a) Mass of total product (oligomer + unreacted 1-hexene) formed per hour

b) Mass of 1-hexene in the outlet gas (obtained by GC analyses of the outlet flow, measured with a soap bubble meter)

Samples of the outlet gas (20 in total) were taken at various stages of an oligomerisation run, and with various nitrogen flow rates varying from 0.15 $Nl.h^{-1}$ to 1.0 $Nl.h^{-1}$. The GC analyses of all the samples indicated no presence of any C_6 or other hydrocarbons in the gas. Since the flow rates under which the samples were taken were representative of the nitrogen gas flow rate (0.15 $Nl.h^{-1}$) that was used in the oligomerisation experiments, it was assumed that the amount of C_6 that is lost by gas transfer can be ignored for all practical purposes.

The mass balances were generally 100 ± 5%.

Chapter 5

Preliminary studies on the CrO_3/SiO_2 catalyst

5.1. Introduction

Various studies have been reported on the optimisation of the Cr/SiO_2 catalyst for polymerisation (of mainly ethene) and the possible reactions that take place on a catalyst surface (Hogan & Kitchen, 1965; Witt, 1974; Whiteley *et al.*, 1992; Pasquon & Giannini, 1984; Kosirov *et al.*, 1976; Pelrine *et al.*, 1993; Fouad *et al.*, 1994; Buchanan & Wu, 1992; Fubini *et al.*, 1980; Hogan 1970; McDaniel, 1985; Groeneveld *et al.*, 1979; Hill *et al.*, 1980; McDaniel, 1981, 1982 a, 1982 b; Rebenstorf & Larsson, 1981; Richter & Ohlmann, 1988; Ellison *et al.*, 1985; Ermakov *et al.*, 1971; Beck & Lunsford, 1981; Beattie & Haighl, 1972; Ghiotti *et al.*, 1983; Hogan & Banks, 1958; McDaniel & Johnson, 1987; Ermakov *et al.*, 1971; Tait, 1989; Groeneveld *et al.*, 1983 b; Witt, 1974; Hogan, 1970; Arlman & Cossee, 1964; Ghiotti *et al.*, 1988; Henrici-Olivé & Olivé, 1977; Van Reijen & Cossee, 1966; Pasquon *et al.*, 1989; Gavens *et al.*, 1982; Cossee, 1964; Young & Lovell, 1991; Porri & Giarrusso, 1989). The same cannot be said for the use of Cr/SiO_2 catalysts for olefin oligomerisation reactions; only a limited number of references, mainly in the patent literature, have appeared (Pelrine & Wu, 1991; Wu & Chu, 1994; Wu, 1989 a, 1989 b, 1991; Buchanan & Wu, 1994; Pelrine *et al.*, 1992, 1993; Pelrine, 1992; Scarano *et al.*, 1994; Zecchina *et al.*, 1994; Hogan, 1970; Tait, 1989, Witt, 1974; Whiteley *et al.*, 1992; Hogan & Kitchen, 1965; Krauss & Westphal, 1977).

In initial experiments, attempts were made to reproduce the literature reaction conditions used to oligomerise olefins. The olefin used in this study was 1-hexene. Surprisingly, difficulty was experienced in producing any oligomerisation products under the referenced conditions and this meant a re-consideration of the initial catalyst choice

A range of CrO_3/SiO_2 catalysts were thus synthesized with different morphological characteristics. Since initial tests with various CrO_3/SiO_2 catalysts gave no oligomerisation activity, development had to be done to obtain a catalyst which would be active after the initial activation steps and one that could be regenerated. Most important was the requirement that the catalyst be in particle form (eg. pellets, beads, extrudates etc.), since use was made of a fixed bed reactor. Initially, the catalysts were prepared in the powder form (eg. on a silica gel support) and then pelletised by hand. As the catalyst development proceeded, an extruded support was made from Davison 952 silica which had been mixed with 30% bentonite. This CrO_3/SiO_2 + 30% bentonite catalyst was then used for most of the further experimentation in this investigation.

5.2. EXPERIMENTAL

The oligomerisation of olefins can in principle be performed with any alkene. Since industrially pure 1-hexene (98.5%) is available in huge volumes, this alkene was chosen for the initial studies.

The various CrO_3/SiO_2 oligomerisation catalysts prepared for this study are summarised in Table 5.1. The catalysts were prepared as described in paragraph 4.2.3.1 of Chapter 4.

Table 5.1: Catalysts prepared from various silica sources

Cat No.	Composition	% Cr	BET surface area ($cm^2.g^{-1}$)	Pore volume ($cm^3.g^{-1}$)	Pore diameter (Å)	Conversion (> 1%)
1	$Cr(NO_3)_3/SiO_2$	1.0 ± 0.07	132	0.53	161	No
2	CrO_3/Crossfield XP19 SiO_2	0.6 ± 0.04	212	0 71	134	No
3	CrO_3/Al_2O_3	0.6 ± 0.04	176	0.63	143	No
4	CrO_3/Chemworld SiO_2	2.4 ± 0.17	191	0.23	48	No
5	CrO_3/Chemworld SiO_2	0 9 ± 0.06	203	0 26	51	No
6	CrO_3/Südchemie KA1 SiO_2 beads	0.9 ± 0.06	108	0.45	170	No
7	CrO_3/Degussa Supernat 22 SiO_2	0.9 ± 0.06	153	0.53	138	No
8	CrO_3/Davison 952 SiO_2	1.1 ± 0.08	217	0.87	160	Yes
9	CrO_3/SiO_2-Al_2O_3 (Mallinkrodt catalysl)	60.0 ± 4.2	18	0.03	67	No
10	Cr_2O_3/SiO_2 (Mallinkrodt catalyst)	1.3 ± 0.09	14	0.02	57	No
11	CrO_3/Sorbead AF25 commercial SiO_2 beads	1.0 ± 0.07	Fresh: 423 Spent: 224	Fresh: 1.03 Spent: 0.85	Fresh: 97 Spent: 153	No
12	CrO_3/(Davison 952 + 30% bentonite) extrudates	1.1 ± 0.08	Fresh: 218 Spent: 220	Fresh: 0.79 Spent: 0.80	Fresh: 144 Spent: 145	Yes

The characteristics of the Davison 952 silica and Davison 952 silica + 30% bentonite extrudates which were the only supports to give oligomerisation results are given below.

i). Surface area and pore volume determinations

The BET surface area and pore volume results obtained on the Davison 952 silica and the silica + 30% bentonite extrudates are given in Table 4.2 of Chapter 4.

ii). Other characteristics

The characteristics of the Davison 952 silica as obtained from the support data sheet are listed in Table 5.2 (W.R. Grace Africa (Pty.) Ltd.).

Table 5.2: Characteristics of Davison 952 silica used for the preparation of the two active catalysts (W.R. Grace Africa (Pty.) Ltd.: Grace Davison 952 data sheet)

	Davison 952 support
Pore Volume (H_2O) ($cm^3.g^{-1}$)	1.55 - 1.90 (GRACE Q 53 method)
Surface Area (BET) ($m^2.g^{-1}$)	280 - 355 (GRACE Q 58 method)
Total Volatiles (%)	10.0 maximum (GRACE Q 57 method)
SiO_2 (dry basis) (%)	99.3 minimum (DIN 55921 method)
Na_2O (dry basis) (%)	0.12 maximum (GRACE Q 91 method)
Al_2O_3 (dry basis)(%)	0.20 maximum (GRACE Q 91 method)
Particle Size:	
< 45 µm (%)	30.0 maximum
> 150 µm (%)	17.0 maximum
> 250 µm (%)	0.05 maximum (GRACE Q 51 method)

iii). XRD

The X-ray diffraction pattern of the silica + 30% bentonite extrudates after calcination at 600°C for 18 hours indicates the presence of amorphous silica and the absence of any crystallinity. The amorphous band is broader in the case of uncalcined Davison 952 silica. The calcination thus causes some limited degree of order in the silica structure. The loss of adsorbed water might be responsible for the changes that were observed after calcination of the support.

iv). DSC and DTG analyses

The DSC and DTG results of the Davison 952 silica as well as the silica + 30 % bentonite extrudates are shown below (Table 5.3). The changes observed probably relate to the loss of adsorbed water from the support material.

Table 5.3: DSC and DTG results of the support*

	DSC (Differential Scanning Calorimetry)		DTG (Differential Thermogravimetric analysis)	
Sample	**Temperature (°C)**	**Heat Flow (μV)**	**Temperature (°C)**	**% Mass change**
Silica + 30% bentonite extrudates	160 270	-6.25 (endo) -2.80 (endo)	100-200	-1.5
Davison 952 silica uncalcined	-	-	50-150	-5.5

*Determinations were done with 19 mg samples in air at a heating rate of 20°C.min^{-1}.

After preparation of the catalysts, they were activated and tested as mentioned in paragraphs 4.2.4 - 4.2.6 of Chapter 4. The specific activation and testing conditions

used are given below:

Activation

Conditions used were:
Drying: 120°C for 4 hours in 15 Nl.h^{-1} N_2
Calcination: 600°C for 16 hours in 15 Nl.h^{-1} Air
Reduction: 350°C for 4 minutes in 15 Nl.h^{-1} CO

Oligomerisation

Conditions used were:
Temperature: 120°C
Pressure: 10 bar
N_2-flow: 0.15 Nl.h^{-1} N_2
1-hexene LHSV: 0.6 h^{-1}

Regeneration

Conditions used were:
Drying: 120°C for 1 hour in 15 Nl.h^{-1} N_2; 320°C for 3 hours in 15 Nl.h^{-1} N_2
Oxidation: 600°C for 16 hours in 15 Nl.h^{-1} Air
Reduction: 350°C for 4 minutes in 15 Nl.h^{-1} CO

5.3. Results and discussion

5.3.1. Testing of the catalysts

Catalysts 1 - 7 and 9 - 11 proved to be totally inactive or showed very little activity (maximum 1% conversion) towards the oligomerisation of 1-hexene. For most of these

catalysts the average pore volume was much lower than the 1 $cm^3.g^{-1}$ specified in the literature and this property could possibly account for the catalyst inactivity (Wu, 1989 a + 1991; Buchanan & Wu, 1994). An exception was catalyst 11. A large decrease in the BET surface area and an increase in the pore diameter was observed after testing of the catalyst activity. These changes in the catalyst structure could explain the catalyst inactivity towards oligomerisation. As the preliminary data showed that catalysts 8 and 12 were active, they were studied in more detail in the oligomerisation reaction. Activity data obtained for these two active catalysts are tabulated in Table 5.4.

The first step in generating the active catalyst entailed reducing the chromium to its active $Cr^{2+/3+}$ oxidation state. The reduction step for the two active catalysts (8 and 12) was found to be exothermic. This is indicated by a temperature increase from 350°C to 355°C and 270°C to 276°C for catalyst 8 and 12 respectively when CO is introduced into the system. The oligomerisation reaction is also highly exothermic, and introduction of 1-hexene into the system gave a temperature increase as high as 70°C. The temperature normally dropped to the initial reaction temperature as soon as the system had stabilised.

Table 5.4: Oligomerisation results obtained with catalysts 8 and 12

	Catalyst 8[a] 1.1% Cr on Davison 952 silica		Catalyst 12[b] 1.1% Cr on Davison 952 silica + 30% bentonite extrudates	
	High Conversion[d]	**Low Conversion[e]**	**High Conversion**	**Low Conversion**
Cycle 1[c]	0.5% after 17.5 hours	< 0.5% after 43 hours	1.3% after 5 hours	< 0.5% after 40 hours
Cycle 2	32% after 45 hours	< 0.5% after 166 hours	64% after 17 hours	< 0.5% after 49 hours
Cycle 3	37% after 46 hours	*< 0.5% after 186* hours	76.3% after 20 hours	< 0.5% after 65 hours
Cycle 4	0.5% after 18 hours	< 0.5% after 23 hours	40% after 4 hours	< 0.5% after *24 hours*
Cycle 5	0.4% after 4 hours	< 0.4% after 6 hours	0.3% after 2 hours	< 0.3% after 3 hours

[a]For activation and oligomerisation conditions see section 5.2

[b]Catalyst 12 ; *Activation:* Drying: 120°C for 4 hours in 15 Nl.h^{-1} N_2; Calcination: 470°C for 16 hours in 15 Nl.h^{-1} Air; Reduction: 270°C for 8 minutes in 15 Nl.h^{-1} CO. *Oligomerisation*: Temp. 99°C; Pressure: 8 bar; N_2-flow. 0,15 Nl.h^{-1}; 1-hexene LHSV: 1,12 h^{-1}. *Regeneration*: Drying: 120°C for 1 hour in 15 Nl.h^{-1} N_2; 320°C for 3 hours in *15 Nl.h^{-1}* N_2; *Oxidation*: 470°C for 16 hours in 15 Nl.h^{-1} Air; Reduction: 270°C for 8 minutes in 15 Nl.h^{-1} CO

[c]Oligomerisation cycle: Cycle 1 follows directly after activation, cycle 2 after the first regeneration, cycle 3 after the second regeneration, cycle 4 after the third regeneration and cycle 5 after the fourth regeneration

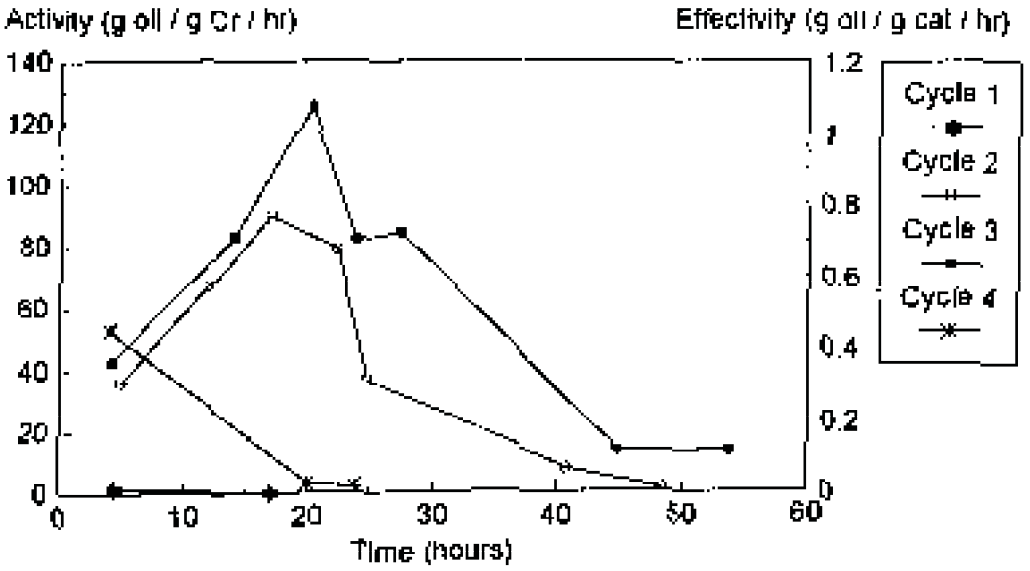
[d]Maximum conversion measured in an *oligomerisation cycle*

[e]Lowest conversion measured in an oligomerisation cycle. Normally followed by termination of the reaction

Five reaction cycles were performed, with each oligomerisation run performed under a given set of reaction conditions. After deactivation of the catalyst in the first cycle, regeneration was performed, and the second cycle followed. The third, fourth and fifth cycles were performed after the *second, third and fourth* regenerations respectively. Due to the very low conversions in the fifth cycle, the data from this cycle are not included in further discussions.

The activity and effectivity of catalyst 12, as a function of time for cycles 1 to 4 (Table 5.4), are shown (Figure 5.1). These responses follow more or less the same trend as the conversion data.

Figure 5.1: Activity and effectivity of catalyst 12 for each of the 4 cycles listed in Table 5.4.

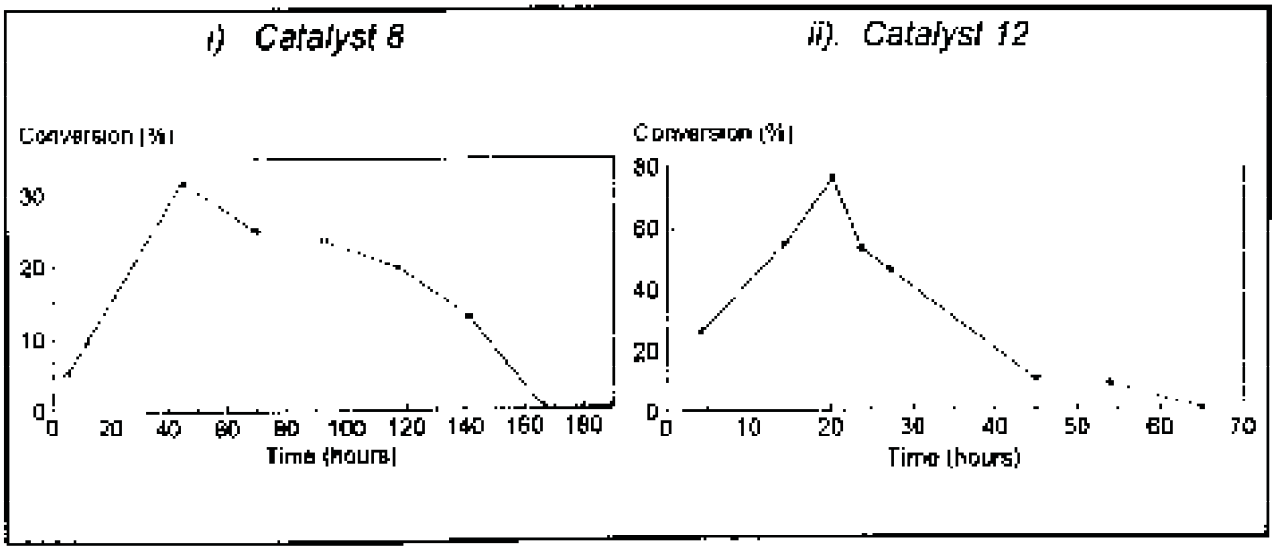


The highest activities and effectivities were obtained in cycle 3, while the lowest values were obtained in cycles 1 and 4. It was decided to use the results from cycle 3 for the evaluation of the experimental data in future runs in this investigation.

The same trends were observed with catalyst 8. Again, cycle 3 produced the maximum activity (26.8 g oil. g^{-1} Cr h^{-1}) and effectivity (0.32 g oil. g^{-1} catalyst. h^{-1}).

The conversion of 1-hexene to oligomer product is plotted as a function of reaction time for the results in cycle 3 (see Table 5.4) in Figure 5.2.

Figure 5.2: Conversion as a function of time for the results obtained in cycle 3 (Table 5.4).



In the above graph it can be seen that the initial conversions are low for both catalysts. Thereafter they increase to a maximum. The initial low conversions can be attributed to the initiation step which must take place before an active oligomerisation catalyst is obtained (Groeneveld *et al.*, 1983 a, 1983 b). During the initiation reaction it has been proposed that monomers are adsorbed onto the coordinated unsaturated chromium ions to form alkyl groups. Once formed, these active species are responsible for the high conversion rates observed (Groeneveld *et al.*, 1983 b; Witt, 1974).

5.3.2. Characterisation of the active oligomerisation catalysts: Catalysts 8 and 12

Due to limited quantities of the two active catalysts, the characterisation techniques were in some cases only performed on one of the two catalysts.

i). XPS Analysis of catalyst 8

No chromium ($2p_{3/2}$ line: 573 to 581 eV) was detected on the catalyst surface (Figure 5.3 and Table 5.5). Sputtering of the samples with Ar^+ for 5 seconds to remove the first few surface layers of the sample also did not allow for the detection of chromium by XPS. This would suggest that either the impregnated chromium had penetrated deep into the silica support or that the detection limit is lower than the chromium content in the sample. The latter seems unlikely since the detection level of XPS is ~ 1 mass % and the total chromium concentration is 1.1 mass %.

Figure 5.3: XPS spectrum of fresh catalyst 8

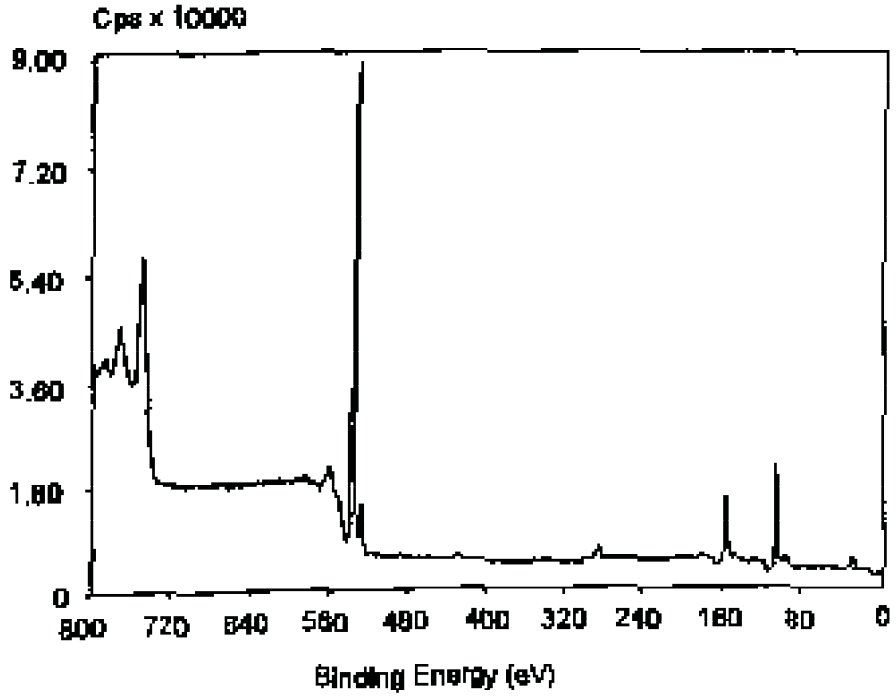


Table 5.5: Major signals in the widescan XPS spectrum (recorded at 0 - 800 eV)

Peak (eV)	Height (cts/s)	Area (eV/ms)	Assignment
25.5	2165	9.1	O
63.5	670	1.5	Na
103.5	16845	47.4	Si
154.5	10370	36.6	Si
282.0	1925	7.0	C
533.0	79765	236.4	O

ii). XRD and SEM measurements of unreacted catalysts 8 and 12

Both the XRD and SEM determinations of the two catalysts did not reveal the presence of chromium on the catalysts. However, the colour of the catalysts after impregnation of the chromium onto the support indicated the definite presence of chromium. A possible explanation for the results that were obtained could be that the chromium concentration in the samples was below the detection limit used in the two methods. Chromium contents as high as 10 wt % are often needed to permit detection of crystalline phases (Richter *et al.*, 1988). This possibility is supported by the fact that Best *et al.* (1977) found that silica supported chromium catalysts which had been subjected to temperatures below 400°C contain only amorphous chromium.

iii). TPR profile of unreacted catalysts 8 and 12

The catalysts (30-60 mg) were calcined for a period of 15.5 hours at 600°C. A 5% H_2/Ar mixture was passed over the samples in the TPR apparatus while the temperature was raised at a rate of 5°C.min^{-1} . The TPR spectrum of catalyst 8 had two peak maxima (337°C and 434°C - Figure 5.4) while the spectrum of catalyst 12 had only one reduction peak (414°C - Figure 5.5).