iv). Metal alkyls

The addition of a metal alkyl to the Cr/SiO_2 catalyst before it has been exposed to the monomer results in a high initial polymerisation rate (Foilestad *et al.*, 1990). The presence of the metal alkyl results in a higher degree of support fragmentation. The initial blockage of the pores does not take place as is normally the case, and no pressure build-up is needed for fragmentation of the particles (Follestad *et al.*, 1990)

v). Tri-alkyl borane compounds as co-catalysts

The use of tri-alkyl borane compounds with alkyl groups containing 1 to 12 carbon atoms can result in a decrease in the molecular mass of the product (McDaniel & Johnson, 1982) The positive effect caused by tri-ethyl borane (TEB) is the strongest in the case of a $Cr/AlPO_4$ catalyst (McDaniel & Johnson, 1987). The TEB acts as a reducing agent to form new active sites and accelerates the chain transfer reaction by means of an exchange mechanism (McDaniel & Johnson, 1987). If the $Cr/AlPO_4$ has already been reduced by CO, the addition of TEB has no effect on the catalyst activity, but only on the rate of chain transfer (McDaniel & Johnson, 1987). This effect can possibly be caused by an interaction between the alkyls on the boron and the active centre (McDaniel & Johnson, 1987):

$$Cr-R' + BR_3 \rightarrow Cr \cdot R + R_2BR' \tag{2.33}$$

Another possible explanation for the increase in the transfer rate that is observed in the presence of TEB is that the TEB adsorbs on some sites, and changes the termination behaviour of these specific sites (McDaniel & Johnson, 1987) In the case of a Cr/SiO_2 type catalyst the activity is increased slightly in the presence of TEB, but the transfer reaction remains unchanged (McDaniel & Johnson, 1987).

2.3.4.14. Addition of hydrogen to the reactant gas

The addition of hydrogen to the active polymerisation/oligomerisation system results in a decrease in the molecular mass of the product (Hogan & Kitchen, 1965; McDaniel & Johnson, 1982; Krauss & Westphal, 1977; Hogan, 1970). A Cr/AlPO$_4$ type catalyst is especially sensitive to the presence of hydrogen (McDaniel & Johnson, 1987). During the oligomerisation/polymerisation reaction in the presence of hydrogen, consumption of hydrogen takes place, and the process is thus known as termination by hydrogenation. The Cr/SiO$_2$ catalyst only terminates via β-H elimination, and is thus not very sensitive to the presence of hydrogen (McDaniel & Johnson, 1987). However, the presence of hydrogen often results in an increase in the β-hydrogen elimination reaction by means of an unknown mechanism (McDaniel & Johnson, 1987).

2.3.4.15. Oligomerisation/polymerisation pressure

Hogan and Banks (1958) found that the reaction rate increased with an increase in the polymerisation pressure up to a pressure of 31.6 bar At a constant temperature and in the presence of a specific catalyst, an increase in the pressure results in an increase in the mass of the polymer product (Hogan & Banks, 1958; Clark et al, 1956).

2.3.4.16. Nature of the monomer

The polymerisation activity of the catalyst decreases with an increase in the molecular mass of the 1-olefin monomer (Clark et al., 1956). Ethylene gives a 100% conversion while 1-butene gives 77% conversion to polymer and 1-hexene a conversion of 40-56% The olefin reactivity decreases in the order ethylene > propylene > 1-butene > 1-hexene > 1-octene > 1-decene (Skupinska, 1991). The polymer products produced from propylene, 1-butene, 1-pentene, 4-methyl-1-pentene and 1-hexene also have lower molecular weights than the products prepared from ethylene (Clark et al, 1956).

2.4. POISONING OF THE Cr/SiO₂ CATALYST

2.4.1. Carbon monoxide

The addition of CO to the active Cr/SiO₂ catalytic system during ethylene polymerisation results in deactivation of the catalyst (Groeneveld et al., 1983 a). The inhibition is reversible since the presence of ethylene results in the desorption of CO from the active sites which are necessary for polymerisation, and the active catalyst is thus regenerated.

2.4.2. Hydrocarbon monomer

An initial reaction of the hydrocarbon with Cr^{2+} can result in the formation of oxygenated compounds which cause temporary toxification of the catalyst (Hogan, 1970). The initial polymerisation rate may thus be slower before the rate increases with removal of these compounds. Reduction with CO decreases the formation of oxygenated compounds, and results in a faster initiation of the reaction.

2.4.3. Polymer/oligomer product

Vuillaume et al , (1971) and Kazanski and Turkevich (1967) found that the reaction rate for the polymerisation of ethylene over a Cr/SiO₂ catalyst reaches a maximum and then levels off due to blockage of the surface by the polymer. The reaction time before levelling off can vary from minutes to hours.

2.4.4. Oxygen

The quantity of polymer formed during the polymerisation of ethylene decreases linearly with the amount of oxygen added to the system. The active catalyst changes from a blue colour to a black or brown colour when exposed to oxygen (Groeneveld et al.,

1983 a). The poisoning effect of oxygen is explained by Kazanski and Turkevich (1967) in terms of the possibility that the oxygen does not react with the active centre, but with the organic ligand. It is also known that the coordinatively unsaturated Cr^{2+} on SiO_2 is readily oxidized to Cr^{6+} at room temperature with a resultant loss in the activity of the catalyst (Hill & Öhlmann, 1990). (See section 2.3.4.7 for further discussion.)

2.4.5. Water

The absorption of water results in the formation of a distorted chromium octahedral centre similar to those found in aqua complexes of chromium in aqueous solutions (Kazanski & Turkevich, 1967; Przhevalskaya et al., 1975). The presence of moisture in the oxygen/air used during calcination results in destabilisation of the Cr^{6+} at higher temperatures (>400°C). The polymerisation activity was also drastically reduced under these conditions due to hydrolysis of the Si-O-Cr bond (Hogan, 1970; McDaniel, 1982 c). Hogan and Banks (1958) indicated that the presence of 6.5% water vapour in the air used during the calcination step resulted in a 44% decrease in catalyst activity. A catalyst calcined in moist air, turned a bright green colour while a catalyst calcined in dry air turned grey-green (Hogan & Banks, 1958).

2.4.6. Others

Most sulphur-, oxygen-, nitrogen- and halogen compounds are toxic to the Cr/SiO_2 catalytic system (Hogan & Banks, 1958; Havas et al., 1994). Hogan and Banks (1958) found that the concentration of these compound in the feed should not exceed 1000 parts per million and preferably not exceed 100 parts per million, while Havas et al. (1994) found that in the case of compounds such as CO, H_2O, O_2 and NH_3, a mass ratio of the specific substance to the catalyst of 0.001 is sufficient to deactivate the catalyst.

2.5. PROPOSED STUDIES ON THE Cr/SiO₂ CATALYSED OLEFIN OLIGOMERISATION REACTION

The above literature study illustrates that a great deal of research has been done on the polymerisation of α-olefins in the presence of a Cr/SiO₂ catalyst, while the data available on the oligomerisation reaction is limited. Although various patents have appeared on the oligomerisation reaction, the reaction conditions were mostly fixed, and no in-depth study was done on the effect of a variation in the reaction conditions on the oligomerisation reaction and the oligomer products (Wu, 1989 a, 1989 b, 1992; Pelrine & Wu, 1991; Pelrine *et al.*, 1992, 1993; Pelrine, 1991, Wu & Chu, 1994).

The lack of in-depth studies on the Cr/SiO₂ catalysed oligomerisation reaction justifies a more extensive investigation into the Cr/SiO₂ catalysed *oligomerisation* reaction. The assumption made in this thesis is that the polymerisation data also apply for the oligomerisation reaction.

In general the literature data for the polymerisation reaction suggest that the active chromium species is in the Cr³⁺ or Cr²⁺/Cr³⁺ oxidation state and that the reaction mechanism of Arlman and Cossee applies for the polymerisation of 1-alkenes over the Cr/SiO₂ catalyst (Przhevalskaya *et al.*, 1975; Beck & Lunsford, 1981; Rebenstorf & Larsson, 1981, 1983; Ermakov *et al.*, 1971; Groeneveld *et al.*, 1982, 1983 b; Miesserov, 1970; Arlman & Cossee, 1964). Since the determination of the oxidation state of the chromium does not fall within the scope of this thesis these findings will be taken as the basis for interpreting the experimental work produced in this thesis. The Cossee-Arlman mechanism which applies for polymerisation reactions needs to be tested for the oligomerisation reaction. If this mechanism proves not to be valid for the oligomerisation reaction, a more appropriate mechanism will have to be suggested for Cr/SiO₂ catalysed oligomerisation.

It was indicated in the patent literature discussed in the review that the support should be physically strong and have a large pore volume to enable the oligomerisation

reaction to take place (Pelrine & Wu, 1991; Wu & Chu, 1994; Wu, 1989 a, 1989 b, 1991; Hogan & Kitchen, 1965). The effect of the use of different support materials on the oligomerisation reaction was hence not investigated in detail in this thesis. From the polymerisation activity data reported chromium loadings lower than 1.5% were used in the thesis study.

The polymerisation activity of the catalyst was reported to increase with calcination and reduction temperatures (McDaniel, 1982 c; Zecchina et al., 1975; Merryfield et al., 1982). Short reduction times of 2 to 8 minutes were found to produce optimal catalyst activity (Beck & Lunsford, 1981; Groeneveld et al., 1983 a). The effect of the reduction temperature and reduction time on the oligomerisation reaction were hence studied by means of a statistical optimisation program. The effect of the activation temperature on the oligomerisation activity was also studied using "one-variable at a time" experiments. Due to the findings that CO was found to be a better reducing agent than H_2 in the polymerisation studies, CO was also used as the reducing agent in most of the experiments performed in this investigation (Fubini et al., 1980; Groeneveld et al., 1979).

In the limited data available on the oligomerisation reaction, no structural determinations of the various oligomer isomers have been done prior to hydrogenation. It is thus of importance that such an investigation is done. The use of GC-MS and NMR spectroscopy techniques would not only enable such determinations but would also assist in proving the Cossee-Arlman mechanism as being valid or invalid for this specific reaction under investigation.

Although there is literature data available on the effect of the reaction temperature and pressure on the polymerisation reaction, these topics have not been extensively covered in the oligomerisation reaction literature. In addition to a study of the effect of reaction temperature and pressure on the oligomerisation reaction, the need was also identified to establish the effect of a varying LHSV on the reaction. These three

Literature review

variables were hence studied by means of a statistical optimisation program; this has not previously been reported in the literature. To support the statistical optimisation data, several "one-variable-at-a-time" experiments were also performed using these variables.

The 1-hexene feed to be used in this study contained trace amounts of oxygenate compounds. Since the deactivation effect of these compounds was mentioned in the literature, it was identified as an important subject for investigation (Hogan & Banks, 1958; Havas, 1994).

Chapter 3

Molecular sieves and their properties

3.1. INTRODUCTION

Molecular sieves (Y, ZSM-5 and MCM-41) have been shown to have the ability to oligomerise α-olefins to longer-chain products (O'Connor et al., 1991; Garwood & Schoennagel., 1985; Pelrine et al., 1992, 1993; Knifton et al., 1994; Bhatia, 1990). In view of this it seemed appropriate to include a section on the oligomerisation of 1-hexene catalysed by molecular sieves (Chapter 10). A general overview of molecular sieves, their properties and applications, will be given in this chapter. The specific molecular sieves to be studied in this thesis (Y, ZSM-5 and MCM-41) will also be discussed in more detail.

3.2. MOLECULAR SIEVES IN GENERAL

3.2.1. Characteristics

Molecular sieves are porous solids with pores which have molecular dimensions (3 Å - 20 Å in diameter) (Flanigen, 1991). Zeolites are hydrated, crystalline tectoaluminosilicate molecular sieves with a uniform pore size, delineated by their crystal structure (Davis, 1991; Flanigen, 1991). The term zeolite is derived from the Greek words "zeo" and "lithos" which mean boil and stone respectively (Davis, 1991).

Zeolites can be represented by the following empirical formula (Flanigen, 1991; Breck, 1964):

$$M_{2/n}O. Al_2O_3. y\ SiO_2. w\ H_2O \qquad (3.1)$$

where M is a group 1 or 2 element such as sodium, potassium, magnesium or calcium, y ranges between 1 and 10, n is the cation valence and w is the water content of the silica. The exchangeable cations permanently occupy the channels and cavities of the zeolite (Barrer, 1968; Flanigen, 1991).

The three-dimensional zeolite structure consists of a framework of TO_4 tetrahedra (T = tetrahedral atom eg. Si, Al), linked to each other by the sharing of oxygen ions (Flanigen, 1991; Davis, 1991). The framework ratio of O/T is always equal to 2 since there are two oxygen atoms for every tetrahedral atom in the structure (Davis, 1991). These tetrahedral rings form the faces of the polyhedra and also give access to the polyhedral cavities of the zeolite (Barrer, 1968). The cavities usually open into other like or unlike cavities by the sharing of certain faces with these other cavities, which results in the formation of interconnecting channels (Barrer, 1968).

Since each oxygen anion in the zeolite framework bridges two T atoms, and thus shares electron density, the SiO_4 unit in a framework is neutral (Davis, 1991). In the case of an AlO_4^- unit in the framework, the net charge is -1 since aluminum carries a +3 valency (Davis, 1991; Flanigen, 1991). The negative charge created by each Al ion is balanced by a positive ion (M in the above empirical formula) to give electrical neutrality. The channels of the framework structure are occupied by cations and water molecules (Flanigen, 1991).
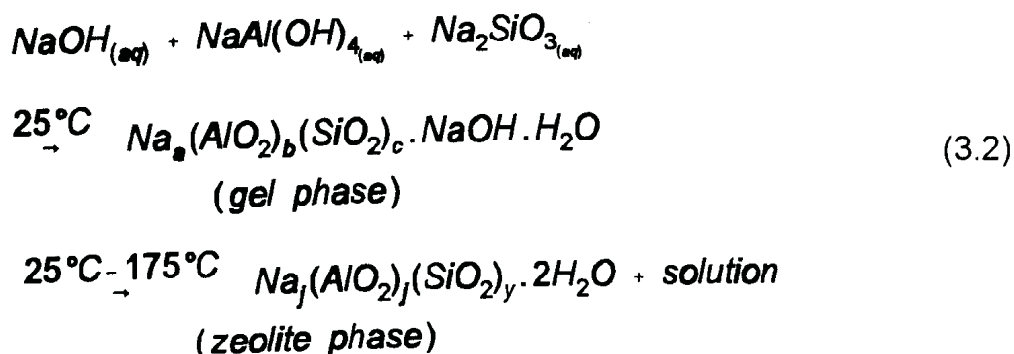
3.2.2. Preparation of molecular sieves

Molecular sieves are mainly prepared by precipitation/crystallisation of an aqueous mixture of reagents at 6 < pH < 14 and temperatures between 100°C - 200°C (Jansen, 1991). The chemical sources required for zeolite synthesis are SiO_2 (primary building units of the

framework), AlO_2 (origin of framework charge), OH^- (mineraliser), an alkali cation (counterion of framework charge) and water (solvent). In some cases use is made of a template molecule. These organic molecules play a central role in nucleating and crystallizing a specific structure (Chatterjee & Vetrivel, 1996).

Crystallization of the hydrous gel with time can be represented by a sigmoidal curve (Breck, 1964). An induction period, which varies from 1 to 4 hours is generally observed and corresponds to the growth of crystal nuclei to a critical size. This is then followed by the rapid growth of the crystallite to the final full-grown zeolite crystals (Breck, 1964). The sequence of reactions that take place during crystallization of the reaction gel are the following (Bhatia, 1990):

$$NaOH_{(aq)} + NaAl(OH)_{4(aq)} + Na_2SiO_{3(aq)}$$

$$\xrightarrow{25^\circ C} Na_a(AlO_2)_b(SiO_2)_c.NaOH.H_2O$$
$$(gel\ phase)$$

(3.2)

$$\xrightarrow{25^\circ C - 175^\circ C} Na_j(AlO_2)_j(SiO_2)_y.2H_2O + solution$$
$$(zeolite\ phase)$$

Isolation of the crystalline material is the final step of the synthesis procedure. In cases where use was made of a template molecule, the prepared zeolite will still contain template molecules after the synthesis reaction. These template molecules are ideally removed by calcination in air in an exothermic reaction (Kouwenhoven & de Kroes, 1991).

3.2.3. Special properties of zeolites

Zeolites are seen as very special when compared to other crystalline inorganic oxide
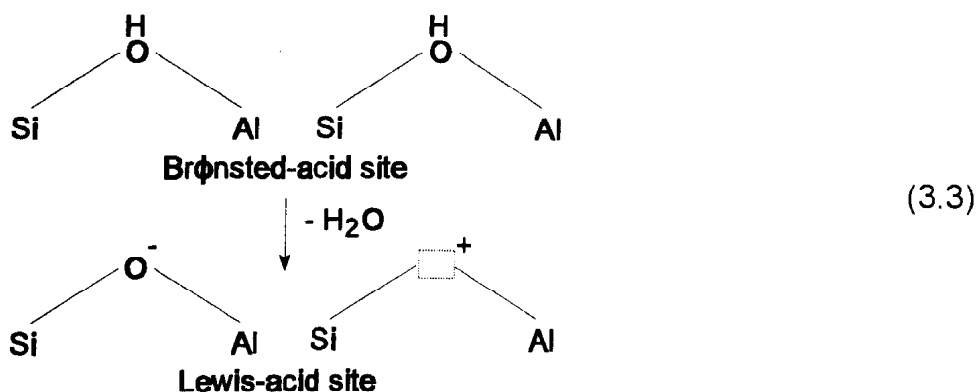
Molecular sieves and their properties

materials due to a combination of special properties (Moscou *et al.*, 1991). Some of these properties are the following (Moscou *et al.*, 1991; Davis, 1991):

i. Microporous character with uniform dimensions. which allows for certain hydrocarbon molecules to enter the crystal pores while others with too large a molecular size are rejected

ii. The pores of zeolites are in the same range as small molecules

iii. The ion-exchange properties

iv. The internal acidity which enables interesting catalytic organic reactions

v. High thermal stability of the zeolites

vi. All metal-oxygen tetrahedra are exposed to the surface while in non-porous inorganic solids only the surface atoms are accessible

vii. Accessibility to modifications such as exchange of charge-compensating cations, replacement of Si and Al in the zeolite framework and introduction of metal particles

viii. Acid site tailoring

The acidity of zeolites is mainly caused by the presence of Brønsted acid sites (van Hooff & Roelofsen, 1991). The Si-O-Al bond angle determines the lability of the proton attached to the Si-O-Al bridge, and thus ultimately determines the acidity of the zeolite (Muscas *et al.*, 1996). The acidic properties of zeolites also depend on variables such as the method of preparation, form of the zeolite, temperature of dehydration and the Si/Al ratio (Bhatia, 1990). After high temperature treatment, Lewis acid sites may also be present.

$$
\begin{array}{cc}
\text{H} & \text{H} \\
\text{O} & \text{O} \\
\diagdown & \diagdown \\
\text{Si}\qquad\text{Al} & \text{Si}\qquad\text{Al}
\end{array}
$$

Brønsted-acid site

$-H_2O \downarrow$

$$
\begin{array}{cc}
\text{O}^- & {}^+ \\
\diagdown & \diagdown \\
\text{Si}\qquad\text{Al} & \text{Si}\qquad\text{Al}
\end{array}
$$

Lewis-acid site

(3.3)

In zeolites where the balancing cation is H^+, the framework is a solid-acid that can reveal shape-selective catalytic properties (Davis, 1991). These properties are the result of confinement of the acidic proton within the zeolite pore structure. Three different types of shape selectivity can be identified with zeolite catalysts (Bhatia, 1990). Reactant selectivity is observed when zeolites only permit certain reactant molecules to pass through the catalyst pores. Product selectivity results when only the product species with the proper dimensions can pass out of the catalyst pores and appear as observed products. In the latter case molecules which are too large to leave the catalyst pores are either converted to less bulky molecules or eventually deactivate the catalyst by blocking the pores. The third type of selectivity is restricted transition-state selectivity, which takes place when certain reactions are prevented by non-formation of a transition-state which would require more space than available in the zeolite cavity (Bhatia, 1990).

3.2.4. Characterisation of zeolites

A wide range of techniques are available for zeolite characterisation. Two common techniques are XRD and IR spectroscopy.

Due to the fact that zeolites are crystalline solids with a regular structure, each one has a characteristic diffraction pattern which can be used to identify the particular zeolite,

Molecular sieves and their properties

determine the degree of crystallinity of the material, and to possibly determine the presence of other crystalline impurities (Bhatia, 1990).

Each specific zeolite also exhibits a typical IR pattern. The IR patterns of zeolites consist of two types of spectra (Breck, 1974):

i.   Those due to internal vibrations of the TO_4 tetrahedra (Internal tetrahedra)

ii.   Vibrations which may be related to the linkages between tetrahedra (External linkages)

The following IR assignments generally apply to the above mentioned two types of vibrations for all zeolites (Breck, 1964):

i. Internal tetrahedra

1250 cm⁻¹ - 950 cm⁻¹: Asymmetric stretch

720 cm⁻¹ - 650 cm⁻¹: Symmetric stretch

500 cm⁻¹ - 420 cm⁻¹: T-O bend

ii. External linkages

650 cm⁻¹ - 500 cm⁻¹: Double ring

420 cm⁻¹ - 300 cm⁻¹: Pore opening

750 cm⁻¹ - 820 cm⁻¹: Symmetric stretch

1150 cm⁻¹ - 1050 cm⁻¹: Asymmetric stretch

3.3. CHARACTERISTICS OF SPECIFIC ZEOLITES USED IN THIS STUDY

3.3.1. Zeolite X and Y (Faujasite)

Faujasite (FAU) is formed by sodalite cages which are connected via double-six rings (Wallau & Schuchardt, 1995). The channel system is thus a three-dimensional circular 12 oxygen atom ring system with spherical 11.8 Å cavities (supercages) which are connected via 7.4 Å windows (Jansen, 1991, Wallau & Schuchardt, 1995). The composition of these zeolites is $Na_{58}[Al_{58}Si_{134}O_{348}].240H_2O$.

The Si/Al ratio in zeolite X is $1 \leq Si/Al \leq 1.5$ and in zeolite Y it is 2.4 ± 0.8 (Jansen, 1991; Davis, 1991). In Figure 3.1 the faujasite structure with its 26-hedral cavities is shown (Barrer, 1968; Wallau & Schuchardt, 1995; Rigutto, 1991).

Figure 3.1: Illustration of the 26-hedral cavities of the faujasite structure (Barrer, 1968; Wallau & Schuchardt, 1995).

Molecular sieves and their properties
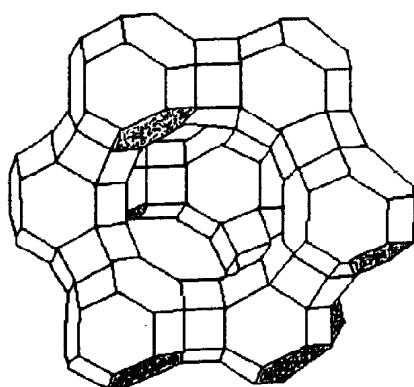
The symmetry of these zeolites is cubic (a=b=c). The unit cell dimensions can thus be characterised by the simple lattice constant a. With increasing Al content the lattice constant will increase due to the fact that Al-O has a longer bond length than Si-O (Blatter & Schumacher, 1990). These zeolites are hydrophylic in character (Jansen, 1991).

The crystallisation phase field diagram for the Na_2O-SiO_2-Al_2O_3-H_2O system is shown in Figure 3.2 (Breck, 1974). From this it can be seen that the gel composition for the formation of zeolite X, Y and A is very similar.

Figure 3.2: Crystallisation field diagram for the Na_2O-SiO_2-Al_2O_3-H_2O system (Breck, 1974):
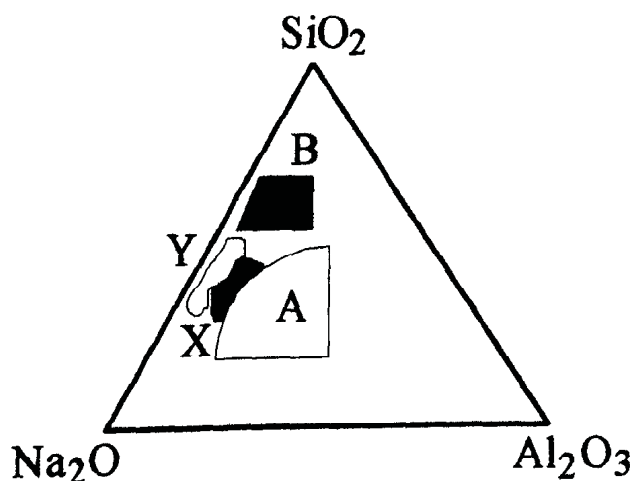
3.3.2. ZSM-5

The composition of zeolite MFI (ZSM-5) is $Na_n[Si_{96-n}Al_nO_{192}].16H_2O$ (n ≤ 8). This zeolite has three dimensional straight 10 oxygen atom rings with 5.2 x 5.7 Å channels which are connected by sinusoidal 5.3 x 5.6 Å channels. The intersection cavities are more or less 9 Å (Rigutto, 1991). A representation of the channel system in these MFI type zeolites can be seen in Figure 3.3.

Figure 3.3:   Schematic representation of the channel system in MFI type zeolites*

(Rigutto, 1991)
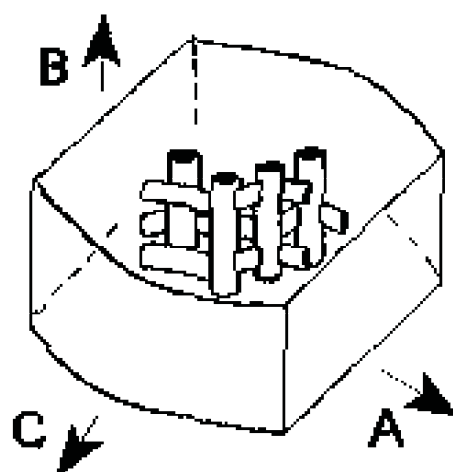
*T-O-T links represented as straight lines

Silcalite-1 *(Si/Al = ∞)*, boralite and TS-1 (Si/Ge-MFI) are some of the important structural isotypes.   Four various single crystal forms of ZSM-5 exist, namely elongated prismatic, cubic-shaped orthorombic, pyramidal and shelf-like (Jansen *et al.*, 1989).

3.3.3. MCM-41

MCM-41 is a mesoporous non-crystalline silicate/aluminosilicate with a hexagonal arrangement of uniformly sized mesopores of 15 - 100 Å (Chen *et al.*, 1993; Kim & Inui, 1996; Beck *et al.*, 1992). *MCM-41 can thus* be classified as a molecular sieve but not as a zeolite. Pure silica MCM-41 prepared from C_{16}TMACl (hexadecyltrimethylammonium-bromide - $C_{19}H_{42}BrN$ as template) has a pore size of 30 Å with a wall thickness of 10 Å. Minimal pore size variations are found in MCM-41 which are normally only found in microporous molecular sieves. In terms of local structure and bonding, MCM-41 resembles *amorphous* silica or aluminosilicates. Aluminosilicate MCM-41 also has an

Molecular sieves and their properties

acidity similar to that of amorphous aluminosilicates (Chen et al., 1993; Zhao et al., 1996). MCM-41 materials (both pure-silica and aluminosilicate) are hydrophobic since the amount of adsorbed organic material greatly exceeds that of adsorbed water (Chen et al., 1993).

Pure-silica MCM-41 can be heated to 850°C in dry air or 800°C in air with 8 Torr water vapour before structural collapse begins (Chen et al., 1993). Both pure-silica and aluminosilica MCM-41 have a high thermal stability, but a low hydrothermal stability (Zhao et al., 1996).

With sodium aluminate as the Al source all the alumina can be converted into tetrahedral aluminium species in the MCM-41, except for very low Si/Al ratios (< 18) where octahedral aluminium species are also present (Janicke et al, 1994). There is thus a limit to the degree of aluminium incorporation into MCM-41. The extent of Al incorporation in the framework is also sensitive to the nature of the aluminium source (Janicke et al., 1994). The presence of aluminium in the framework of the MCM-41 material influences the stability of the structure to calcination (Mokaya et al., 1996; Janicke et al., 1994). The number of acid sites generated (Brønsted & Lewis sites) as well as the activity, increases as the amount of aluminium in the MCM-41 framework increases (Mokaya et al., 1996; Janicke et al., 1994). Due to the fact that the Al in MCM-41 is not bound to oxygen very strongly, the Al-H bond is a strong one, thus making MCM-41 a weak acid (Janicke et al., 1994; Mokaya et al., 1996).

The synthesis mechanism of MCM-41 relates to the formation of randomly ordered rod-like micelles (Chen et al., 1993). These micelles interact with silicate species, and two or three monolayers of silica are encapsulated around the external surfaces of the micelles by condensation (Chen et al., 1993). The hexagonal packing characteristic of MCM-41 is a result of the spontaneous assembly of the composite species (Figure 3.4).

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Figure 3.4: Mechanism proposed for the formation of MCM-41

(Chen *et al.*, 1993; Beck *et al.*, 1992)
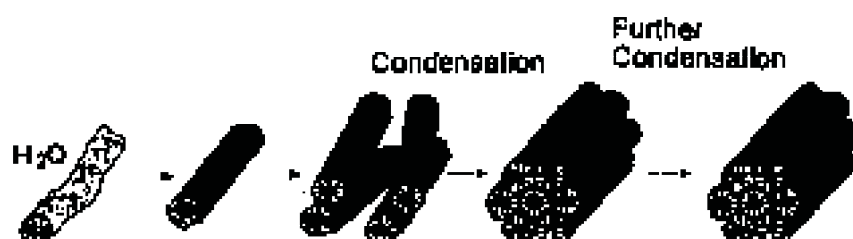
When MCM-41 is further heated, continual condensation of the interstitial spaces in the ordered organic-inorganic composite phase takes place. Since silicon-oxide species are necessary for charge compensation of the occluded alkylammonium ions, complete condensation of the silicate species is not possible (Chen *et al.*, 1993). The XRD pattern of calcined MCM-41 contains d-spacings of 39.8, 22.9, 19.8 and 14.9 Å respectively (Beck *et al.*, 1992).

3.4. APPLICATIONS OF ZEOLITES

3.4.1. General

The four main areas in which zeolites are applied are the following (Moscou et al., 1991; Davis, 1991):

As adsorbants, desiccants and in separation processes. That zeolites are molecular sieves, contain large void fractions (zeolites A and X have almost a 50% void fraction) and are hydrophilic, makes them ideally suitable to be used as adsorbents (Davis, 1991).

As catalysts in petroleum refining, synfuels production, petrochemical production and catalyst supports (Kouwenhoven & de Kroes, 1991). Zeolites can be described as solid acid catalysts which are widely used in hydrocarbon processing such as naphtha cracking, isomerisation, disproportionation and alkylation (Masuda & Hashimoto, 1995). Some of the properties which make zeolites very versatile as a catalyst component, are the variable size and shape of the zeolite crystallites, the high and thermally very stable internal surface area, the well defined pores which are of molecular dimensions,the accessibility of a zeolite structure which may be changed by ion-exchange and post-impregnation with certain salts, the removal of non-lattice ions by ion-exchange, the tetrahedral coordination of the non-oxygen atoms and the chemical composition of the lattice which is dependent on the synthesis conditions (eg Si/Al ratio) (Kouwenhoven & de Kroes, 1991). Weisz and Frilette observed in 1960 that zeolites can be applied as molecular shape-selective catalysts (Wallau & Schuchardt, 1995). Zeolite H-ZSM-5 is specifically used in many catalytic reactions due to the fact that it is a shape-selective catalyst (van Hooff & Roelofsen, 1991). Zeolite Y is specifically used as a cracking catalyst (van

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Hooff & Roelofsen, 1991; Jansen, 1991). MCM-41, with its molecular sieve structure and large pore sizes has great possibilities for use in the catalytic conversion of molecules which are too large to enter conventional zeolite pores (Ryoo et al, 1996)

iii.   As detergent builders (almost exclusively zeolite A) - water softening due to exchange of Ca^{2+} for Na^+

iv.   Miscellaneous applications such as waste water treatment, nuclear effluent treatment, animal feed supplements and soil improvement

## 3.4.2. Oligomerisation in the presence of zeolites

The Brønsted acid sites on zeolites initiate the oligomerisation of olefins. Oligomerisation activity of zeolites is thus determined by the Brønsted acid site density, the Brønsted acidity and the accessibility of these acid sites (Knifton et al., 1994).

According to Knifton et al. (1994), dealuminated Y-zeolites with high silica-to-alumina ratios are effective solid acid catalysts for C_{12} - C_{18} oligomerisation. Knifton et al. (1994) found in their studies on the oligomerisation of 1-tetradecene (C_{14}) in the presence of zeolite Y that an increase in the silica-to-alumina molar ratio resulted in increased conversion and total oligomer formation. Their studies also revealed that the oligomerisation catalysed by Y-zeolites depended mainly upon the acid strength of the zeolitic sites rather than upon the total number of Brønsted sites.

Bhatia (1990) found that rapid isomerisation and oligomerisation reactions are achieved in the presence of medium-pore zeolites such as ZSM-5, ZSM-11 and ZSM-22 at relatively low temperatures. Remarkable selectivity and stability can be achieved which is not found with large pore zeolites (Bhatia, 1990). Garwood (1983) demonstrated shape-selective

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oligomerisation of C_2-C_{10} olefins to higher olefins over ZSM-5. H^+-ZSM-5 zeolites have been proven to be active in the true acid catalysed oligomerisation of C_3-C_4 olefins under mild conditions (Jacobs & Martins, 1991). In the schematic presentation shown below the acid catalysed oligomerisation of C_3 olefins is shown. The carbocationic site is formed at the secondary carbon atom since this would result in a more stable structure (Morrison & Boyd, 1987). The carbocation then reacts with the α carbon atom in another propylene molecule, with the result that brancing occurs and a carbocation is once again formed. The sequence repeats until termination (via hydrogen elimination) steps in (Morrison & Boyd, 1987).

(3.4)
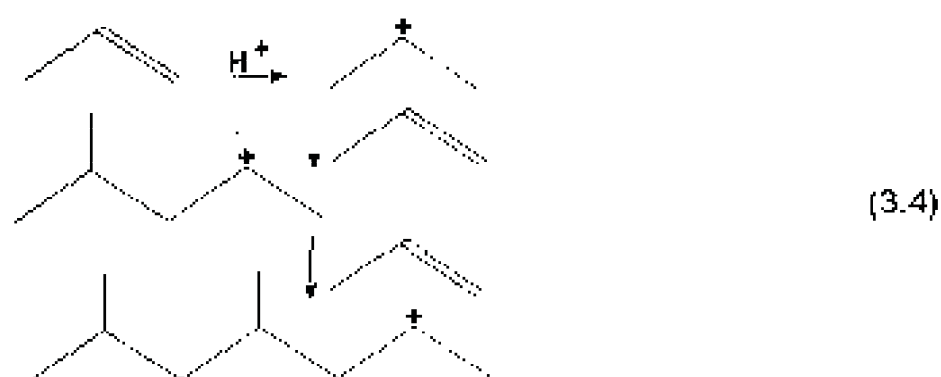
Under more severe reaction conditions, random oligomerisation or olefin interconversion can occur (Jacobs & Martins, 1991):

$$C_3^+ + C_6^+ \rightarrow C_9^+ \rightarrow C_4^- + C_5^+$$ (3.5)

$$C_4^+ + C_4^- \rightarrow C_8^+ \rightarrow C_3^+ + C_5^+$$ (3.6)

Pelrine and Schmitt (1992) and Pelrine et al., (1992,1993) made use of a chromium impregnated MCM-41 catalyst to oligomerise α-olefins to a high viscosity and viscosity index product. A comparison between a Cr/MCM-41 and Cr/SiO$_2$ oligomerisation catalyst indicated that the MCM-41 supported catalyst produced a higher viscosity oligomer than

the silica supported catalyst (Pelrine *et al.*, 1992, 1993). With the use of amorphous supports such as the silica in the Cr/SiO_2 silica catalyst, the product viscosity is largely determined by the reaction temperature (Pelrine *et al.*, 1992, 1993). According to Pelrine *et al.*, (1992, 1993) the use of MCM-41 as support enables the production of a product with a widely differing viscosity without the need to change the reaction temperature. The flexibility of the operation is thus improved and the product characteristics may be modified over a wider range. The large size pores of mesoporous molecular sieves such as MCM-41 makes them potentially useful as heterogeneous catalysts (Mokaya *et al.*, 1996)

Oligomerisation reactions have been performed by various researchers with different zeolite catalysts. The results obtained are summarised in Table 3.1.

Table 3.1: Oligomerisation results obtained over various zeolite catalysts

	Garwood & Schoennagel, 1985	Pelrine et al., 1992, 1993	Knifton et al., 1994	Schwarz et al., 1989; O'Connor et al., 1991*
Catalyst	ZSM-5	2% Cr/MCM-41	Dealuminated zeolite Y	ZSM-5 (Si/Al ≈ 20)
Olefin	1-hexene	1-decene	1-tetradecene (C_{14})	propene
WHSV	$0.5\ h^{-1}$	$1.9\ h^{-1}$ (LHSV)	$0.2\ h^{-1}$	$12\ h^{-1}$
Temperature	230°C	120°C	155°C	300°C
Pressure	102 bar	?	15 bar	50 bar
Conversion	16% (6.4 days)	?	71% (100 hrs) 55% (400 hrs)	95 % (14 hrs)
Viscosity at 40°C	23.6 cSt	2419 cSt	-	-
Viscosity at 100°C	4.6 cSt	238 cSt	4.69 cSt	-
Viscosity index	106	237	125	-

*Although the conditions used in this column are not in the order of the conditions used in the other three columns of this table, the results are nevertheless included for the sake of comparison

From the above table it can be seen that relatively extreme reaction conditions were used for oligomerisation with zeolites ZSM-5 and Y. The conditions used with the Cr/MCM-41 catalyst were *not* as *extreme*, and compare well with the reaction conditions that were

employed for oligomerisation studies done in the presence of Cr/SiO$_2$ (Pelrine *et al*, 1992, 1993).

Chapter 4

Experimental procedure

4.1. INTRODUCTION

This chapter describes the procedures followed in the preparation, testing and characterisation of Cr/SiO_2 and zeolite catalysts as well as the procedures followed in the characterisation of the feed material and the oligomer products.

4.2. PREPARATION AND TESTING OF Cr/SiO_2 AND ZEOLITIC CATALYSTS

The preparation of the active Cr/SiO_2 catalyst involved various steps (support pre-treatment, impregnation of the precursor, drying and calcination of the catalyst and finally reduction to the active state). In the initial experiments used in the preparation and testing of the Cr/SiO_2 catalyst the conditions used in the literature reports of Wu (1989 a, 1991) and Buchanan and Wu (1994) were followed. However, it soon became apparant that the procedures had to be modified to achieve optimum catalytic behaviour in the work described below.

4.2.1. Chemicals and silica supports

The chemicals and silica supports used in the preparation of various catalysts and zeolites as well as in the testing of these compounds are listed below.

Chemicals used in the preparation of the catalysts included*:

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*Supports calcined at 600°C for 15 hours

Aerosil 200 SiO_2: BET surface area: 200 $m^2.g^{-1}$ - Degussa Ltd

Al_2O_3: BET surface area: 190 $cm^{-2}.g^{-1}$ - Südchemie

Chromium(III)nitrate $(Cr(NO_3)_3)$ - Saarchem

Chromium(VI)oxide (CrO_3) - Protea Laboratory Services

Crossfield XP19 SiO_2: BET surface area: 227 $cm^{-2}.g^{-1}$ - Südchemie

Davison 952 SiO_2: BET surface area: 322 $cm^{-2}.g^{-1}$ - Darex Africa

Deionised water (H_2O) - SCI

KA1 92% SiO_2 + 8% Al_2O_3 beads: BET surface area: 108 $cm^{-2}.g^{-1}$ - Südchemie

SiO_2: BET surface area: 230 $cm^{-2}.g^{-1}$ - Chemworld

SiO_2: BET surface area: 135 $cm^{-2}.g^{-1}$ - Aldrich

Sorbead AF25 SiO_2 beads: BET surface area: 423 $cm^{-2}.g^{-1}$ - Südchemie

Supernat 22 SiO_2: BET surface area: 166 $cm^{-2}.g^{-1}$ - Degussa Ltd.

Chemicals used for the zeolite preparation included:

Sodium aluminate $(NaAlO_2)$ - Riedel-de-Haën

Sodium hydroxide $(NaOH)$ - J.T. Baker

Sodium metasilicate $(Na_2SiO_3.5H_2O)$ - BDH Chemicals

Sodium silicate solution (27 wt% SiO_2) - Aldrich

Tetrapropylammonium bromide $(C_{12}H_{28}BrN)$ - Janssen Chimica

Octadecyltrimethylammonium bromide $(CH_3(CH_2)_{17}N(CH_3)Br)$ - Aldrich

Cetyltrimethylammonium bromide $(C_{19}H_{42}BrN)$ - Aldrich

Tetramethylammonium hydroxide $((CH_3)_4NOH)$ (25 wt% in H_2O) - Aldrich

Tetra-ethylammonium hydroxide $((C_2H_5)_4NOH)$ - Aldrich

CAB-O-SIL M5 Fumed silica - BDH Chemicals

Ludox LS 30 coloidal silica - DuPont Chemicals

All the reagents listed above were of the highest purity available from the respective suppliers, and were used without any further purification.

Chemicals used for catalyst and zeolite testing include:

Carborundum (24 grit) - Saarchem

Molecular sieve 3A - Union Carbide

1-hexene (> 98.5 % C_6) - Industrial

C_5/C_6 feed (45% C_6) - Industrial

1-decene (60%) - Industrial

1-hexene (> 96% C_6) - Merck

1-decene (~ 96% C_6) - Merck

1-pentene (> 98.5 % C_5) - Industrial

Zeolite HZSM-5 1/16" extrudates - Südchemie

Zeolite HY 1/16" extrudates - Linde Molecular Sieves (Union Carbide)

CrO_3/SiO_2-Al_2O_3 - *Mallinkrodt Chemicals*

Cr_2O_3/SiO_2 - Mallinkrodt Chemicals

Zirconia based solid acid catalyst - Mallinkrodt Chemicals

4.2.2. Gases

The gases were all supplied by Fedgas Ltd. and were of Ultra High Purity (UHP), accompanied by a certificate of analysis. The following gases were used:

Synthetic Air (21% O_2; 79% N_2; $\le$ 4 vpm H_2O; $\le$ 4 vpm C_nH_m)

Nitrogen 5.0 ($\le$ 2 vpm O_2; $\le$ 2 vpm H_2O; $\le$ 1 vpm CO_2; $\le$ 1 vpm C_nH_m; $\le$ 1 vpm CO)

Hydrogen 5.0 ($\le$ 3 vpm O_2; $\le$ 2 vpm H_2O; $\le$ 0.5 vpm C_nH_m)

Oxygen 5.0

CO 2.0

4.2.3. Preparation methods

4.2.3.1. Catalyst preparation

Procedures have been given in the literature for the preparation of an active CrO_3/SiO_2 oligomerisation catalyst (Wu, 1989 a, 1991, 1992; Buchanan & Wu, 1994; Pelrine & Wu, 1991; Wu & Chu, 1994; Hogan & Kitchen, 1965; Pelrine et al., 1992, 1993; Pelrine, 1991; 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 suggestions made in the literature guided this work. A comparison of the literature data with the procedures followed in this work is given in Table 4.1.

Table 4.1: General procedure and reagents used in the preparation of an active CrO_3/SiO_2 catalyst

	Literature data (Wu, 1989 a, 1991; Buchanan & Wu, 1994)	This work
Support	Silica	Silica or Silica/Alumina
Surface Area $(m^2.g^{-1})$	300	30 - 420
Pore Volume $(cm^3.g^{-1})$	1.0	0.05 - 1.14
Pore Size (Å)	40 - 350	63 - 140
Impregnating Salt	$Cr(CH_3COO)_3$ or $Cr(NO_3)_3$	CrO_3 or $Cr(NO_3)_3$
Liquid Phase	Water/acetone	Water
Drying: 1. Rotavap 2. Oven	1. 80°C + vacuum 2. 250°C- 400°C in N_2 for 2 hours	1. 70°C + vacuum 2. 150°C in N_2 for 2 hours

The incipient wetness procedure was not used in this work, since it was found that an

uneven distribution of chromium was obtained. In the preparation use was thus rather made of an excess quantity of water which was eventually removed on a Büchi Rotavap (Rotary Film Evaporator).

The following representative catalyst preparation method was used:

Silica or silica/alumina (50 g) was soaked for one hour in 200 ml of deïonised water and then the excess water was carefully poured off. Fresh deïonised water was then added again to obtain a total of 100 ml ($\approx$ 100 g) water. The mass of solid CrO_3 needed to obtain a certain mass percentage of chromium on the silica or silica/alumina support was then added to the mixture while stirring. The solution was stirred at room temperature for 1 hour. Thereafter it was connected to a Büchi Rotavap (Rotary Film Evaporator) and completely dried under vacuum at 70°C. If the catalyst was not completely dried on the Rotavap, the chromium was found to migrate on the silica and this gave an uneven distribution on the support. This uneven distribution of the yellow/orange chromium was readily visible by eye.

After drying of the catalyst on the Rotavap, further drying was performed in an oven at 150°C for 2 hours. Atomic absorption spectroscopy was used to determine the chromium content in the sample.

If the silica or alumina support was in the powder form, the catalyst was compressed into the form of pellets after the drying step. The pellets were 2.5 mm in diameter and 1 mm thick. No binder was added to the impregnated catalyst during this pelletising step. If the support used was in the form of pellets or extrudates, the pelletising step was obviously not necessary.

4.2.3.2. Preparation of an extruded silica support

To simplify the above catalyst preparation method an extruded or pelletized support

Experimental procedure

was used. In this work the only silica source that proved to be useful was Davison 952 silica. This support, unlike other supports which were initially studied, could be extruded or pelletized and gave a final product with a high surface area after the calcination step. Initially attempts were made to extrude the support without the use of a binder, but on extrusion all the water added to the silica was forced out of the silica, with the result that the silica could not be extruded. The presence of a binder to minimise this effect was thus essential. Bentonite and norilose (first and second options respectively) were tested as possible binders, using the following method:

1   30% of the binder (by mass) was added to 1 liter of Davison 952 silica.

2   The silica/binder mixture was mixed continiously using a Kenwood mixer whilst 1150 ml of distilled water was added to the mixture.

3.   The mixture was then extruded using a 2 mm nozzle and dried at 120°C for 16 hours.

4.   The extrudates were thereafter calcined at 600°C for 18 hours to remove the binder (except in the case of bentonite which was not removed during the calcination step).

5.   The BET surface area of the extrudates was determined before and after the calcination step (See Table 4.2).

6   As a third option extrudates were prepared using salicylic acid as a binder. The BET surface area of this sample was measured after drying of the extrudates.