Synthesis and Characterisation of Porous Polymers

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University of St Andrews

Thesis for PhD Degree

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Declaration

i. I, Christopher James Love, hereby certify that this thesis, which is approximately 30,000 words in length, has been written by me, that it is the record of work carried out by me and that it has not been submitted in any previous application for a higher degree.

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Abbreviations And Definitions

δ	Chemical shift
BET	Brunauer Emmett Teller
BJH	Barrett Joyner Halenda
EXAFS	Extended x-ray absorption fine structure
IR	Infrared
Karstedt's Catalyst	Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, solution in xylene
MAS	Magic angle spinning
MIBK	Methyl isobutyl ketone
m/z	Mass/charge ratio
NMR	Nuclear magnetic resonance
POSS	Polyoligomeric silsesquioxane
RT	Room temperature
Schwartz's Reagent	Bis(cyclopentadienyl)zirconium chloride hydride
TBHP	*t*-Butyl hydroperoxide
TGA	Thermal gravimetric analysis
THF	Tetrahydrofuran
XANES	X-ray adsorption near edge structure
XRF	X-ray fluorescence

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Contents

1 Abstract

Highly porous silsesquioxane based copolymers, deriving from vinyl and hydridosilsesquioxane monomers, have been synthesised. These materials have been characterised in order to determine their chemical structure, with particular emphasis upon the surface area and porosity. A number of slight variations to the composition has also been considered, showing similar physical properties to those prepared earlier. In most cases the materials produced are observed to be highly porous, with surface areas typically around $500m^2/g$. Additionally the thermal behaviour was investigated, with the copolymers seen to start breaking down at temperatures over 150°C.

Subsequently these silsesquioxane copolymers have been used as supports for a number of different transition metal species. This was achieved by means of opening the silsesquioxane ring structure in the presence of a base, before insertion of chlorine containing complexes of titanium, zirconium, molybdenum or cobalt. The porosity of these was comparable to results prior to the insertion, with only a slight reduction in surface area.

The preparation of copolymers containing zirconium and cobalt species was also attempted by preparing monomeric silsesquioxanes possessing these metals, and then conducting the polymerisation. From this a zirconium containing porous polymer was successfully prepared.

Extended x-ray absorption fine structure (EXAFS) was used to determine the structure of the metal containing species, and results compared with samples with the metal species having been inserted in monomeric species. From this data a number of likely structures for these materials was proposed.

2 Introduction

2.1 Definitions

2.1.1 Siloxanes

Siloxanes are a group of organic-inorganic hybrid materials formed using four different building blocks[1]. The simplest of these is the silicate $SiO_{4/2}$ group, and following on from this up to three of the oxygen links can be substituted for an organic group, R. This results in $RSiO_{3/2}$, $R_2SiO_{2/2}$ and $R_3SiO_{1/2}$ as the other possibilities. These four individual units can potentially combine to give a large number of different products.

To illustrate this the $R_2SiO_{2/2}$ unit will lend itself to forming chains, whereas if the $RSiO_{3/2}$ unit was inserted into such a chain, it will lead the formation of three dimensional structures[2]. $R_3SiO_{1/2}$ groups are useful because they can act as terminal groups. All such materials deriving from these building blocks can be referred to as siloxanes[1], and may contain any number of different units, resulting in a series of silicon-oxygen-silicon bonds.

2.1.2 Silsesquioxanes

One specific class of siloxanes are known as silsesquioxanes, these are compounds which can be constructed from the $RSiO_{3/2}$ siloxane unit alone[3,4].

Forming three siloxane linkages, it enables a variety of three dimensional structures to be obtained, either in discrete units or as polymeric compounds. Possibly the most notable of the former is the (approximately) cubic species $(RSiO_{3/2})_8$ ***(figure 2.1)***[5,6]. The structure of which can be viewed as a double-four ring, similar to units found within zeolites. Other structures formed from six or ten silsesquioxane groups are structured along similar lines[5,7], consisting of a double-three and double-five rings respectively, although neither of these units occur in zeolites.

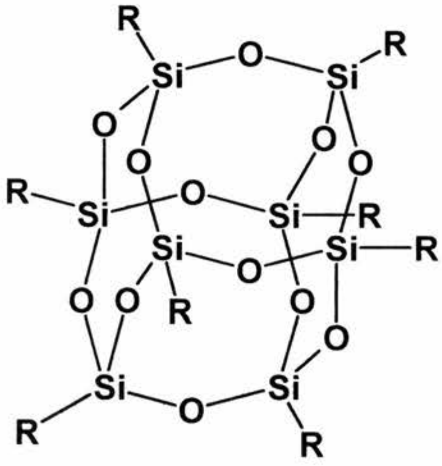

Figure 2.1: Cubic silsesquioxane $(RSiO_{3/2})_8$

These compounds are organic-inorganic hybrids, which can be perceived as a central inorganic cage surrounded by organic groups, which define the functionality of the molecule.

2.2 Siloxanes And Silsesquioxanes

2.2.1 Early Discoveries

Compounds containing the siloxane linkage, Si–O–Si, have been known for a long time. Friedel and Crafts provide an early example[8] with reports of the formation of various silicates from the condensation reactions of compounds such as silicon chloride in the mid 19th century. Ladenburg was investigating similar materials[9], but results from these experiments were seen to be somewhat uncertain, although all appeared to only show one siloxane linkage.

Subsequently, in the early 20th century Khotinsky and Seregenkoff successfully prepared a number of different substances deriving from the condensation reactions of silicon ethoxides[10]. They managed to prepare compounds consisting of a central silicon atom which was bonded to three others by way of a siloxane linkage (***figure 2.2***). One molecule of the initial reactant ethoxide provides the central unit of the products, with another three used in the formation of the branches.

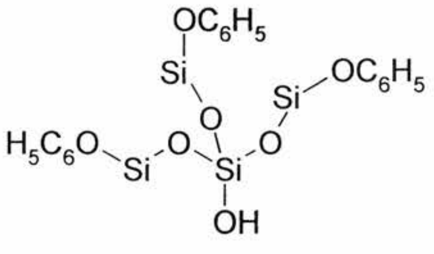

Figure 2.2: An example of the compounds prepared by Khotinsky and Seregenkoff

Also around this time, Kipping[11-14], together with several co-workers, were conducting a long term investigation into the organic derivatives of silicon. Whilst many of the compounds they prepared are not siloxanes, they managed to show the formation of a number of such species.

Starting from materials such as diols and trichlorides they were able to synthesise materials such as acids and anhydrides together with siloxanes in ring and chain (***figure 2.3***) formations. The latter structures in particular deriving from using the diols as the starting point for their experiments. It can be observed in the procedures they used, that an acid or alkali was employed to help promote the condensation reactions, a feature also seen for some more recent preparations of similar compounds.

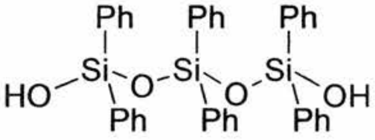

Figure 2.3: Chain phenyl siloxane

2.2.2 Siloxane Rings

In these early years of the 20th century Dilthey showed a three membered siloxane ring with organic alkane groups present (***figure 2.4***)[15]. The structure of this is not dissimilar to some of the monomeric silsesquioxane compounds prepared more recently, which can be viewed as consisting of interlinked siloxane rings.

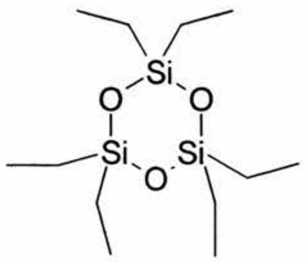

Figure 2.4: 2,2,4,4,6,6-Hexaethyl-[1,3,5,2,4,6]trioxatrisilinane

In a similar vein to Dilthey, Melzer was also preparing cyclic compounds[16], in his case the formation of acids. The preparation he uses, which is a condensation reaction of silicon chlorides, is particularly interesting.

2.2.3 Polymeric Siloxanes

The work of Rochow and Gilliam reports the preparation of a silsesquioxane unit as part of a polymeric species (***figure 2.5***)[17]. Deriving from the reactions of either a Grignard mechanism or through the condensation of the recently prepared methyl trichlorosilane[18] and the dimethyl equivalent, the product is observed as containing both $RSiO_{3/2}$ and $R_2SiO_{2/2}$ units.

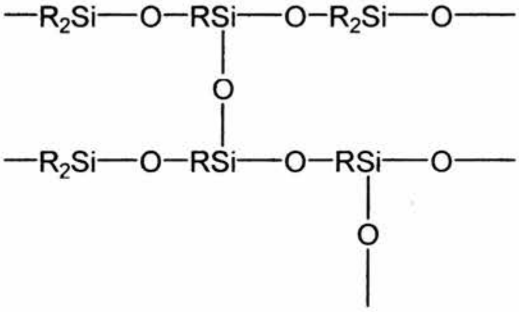

Figure 2.5: Siloxane cross-linked polymer

Whilst both of these methods were observed to give almost identical products, the condensation of the silanes appears as though it has greater control over the products of the reaction. As it was carried out almost instantaneously, however, this tends towards the formation of polymeric species, despite largely being the same procedure with respect to the methyl trichlorosilane used to prepare cubic silsesquioxanes.

Hyde and DeLong synthesised polymeric species from the hydrolysis of organo-silane diols[19]. Their procedure although still producing a polymeric species, differs from earlier attempts in that the addition of the silane to water is conducted over a longer period of time. However, this shows an increasing similarity towards the conditions needed to form monomeric species, although the addition is to pure water, not a mixture with another solvent.

Another chemist involved with research into the hydrolysis reactions of silanes was Scott[20]. Investigating the thermal rearrangement of methylpolysiloxanes, was able to propose several ring species containing some $RSiO_{3/2}$ units (***figure 2.6***).

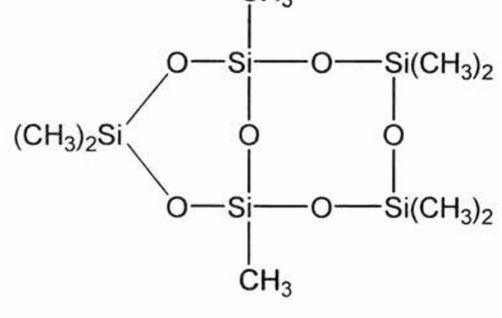

Figure 2.6: Example of siloxane prepared by Scott, showing two of the units found in silsesquioxanes

Patnode and Wilcock exploited the preparation of silanes by Rochow to look at siloxane polymers[21], although not those using units found in silsesquioxanes, was able to prepare cyclic systems, including a ring containing four silicon atoms, similar to half a cubic silsesquioxane (***figure 2.7***).

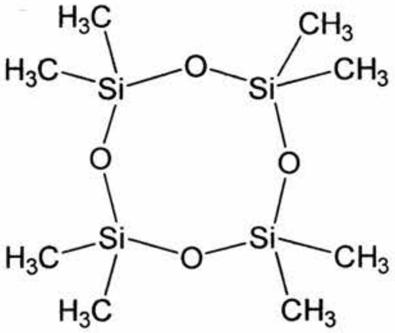

Figure 2.7: Cyclic siloxane

2.2.4 Monomeric Silsesquioxanes

The first instances of cubic silsesquioxanes were reported in 1955, by Sprung and Guenther[22], soon followed by Barry and co-workers[5]. The structure derived by the former was hypothesised to explain the product formed from the slow hydrolysis of ethyltriethoxysilane in small quantities of water suspended in ethanol. Their proposal was the formation of cubic (***figure 2.8***) and triangular prism shaped (***figure 2.9***) species.

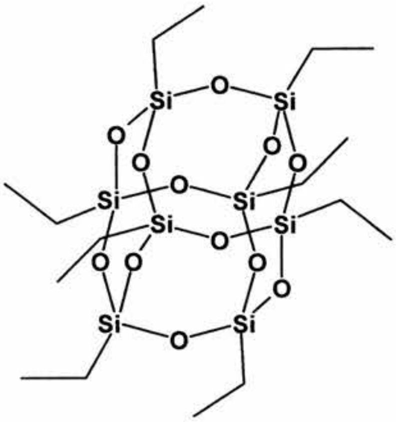

Figure 2.8: Octaethylsilsesquioxane structure proposed by Sprung and Guenther

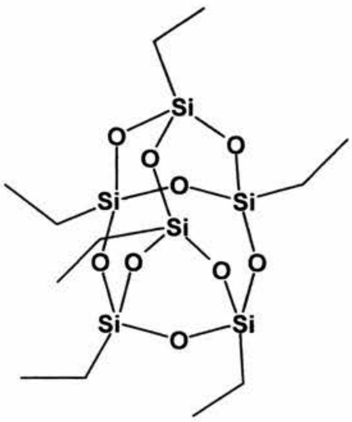

Figure 2.9: Proposed hexaethylsilsesquioxane structure

Both of these structures can be viewed as two linked ring structures. The former of two four membered rings with respect to silicon, the latter having only three. Using various simple organic groups on triethoxysilanes, Barry and co-workers were able to synthesise a number of similar compounds. They proposed that these discrete silsesquioxanes, when formed, would need to consist of an even number of $RSiO_{3/2}$ groups, citing the cubic and hexagonal prismatic structures as being the more likely.

These first discrete-unit silsesquioxanes were prepared with small alkyl groups only, however since then a number of different functional groups have been used in the preparation.

Vogt and Brown were two further researchers into the field of these early silsesquioxane materials[23], specifically looking at the skeletal arrangements of methyl silsesquioxanes, which revealed the twin ring structures seen above for the smaller species, although leaving some uncertainty over the structure of $(CH_3SiO_{3/2})_{12}$. Also observed was a ladder structure (***figure 2.10***) which was seen in linear polyphenylsilsesquioxanes.

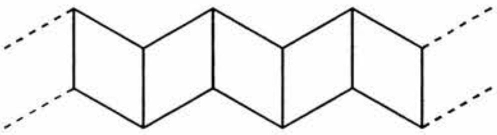

Figure 2.10: Linear structure of polyphenylsilsesquioxanes

One of the first discrete monomeric cubic silsesquioxanes was octahydridosilsesquioxane, which was first obtained accidentally by Müller in 1959[24], albeit in a very small yield (approx. 0.2%), whilst attempting the synthesis of a straight chain siloxane polymer from the hydrolysis of trichlorosilane, with the structure later being confirmed by Larsson[25]. The preparation used for this material has been refined initially by Frye and Collins, who employed 'scarce water' conditions[26], acting as a control for the rate of synthesis. Addition of trichlorosilane directly reacts quickly, which favours the formation of a uncontrolled polymeric product, but adding the water slowly favours the cubic octahydridosilsesquioxane. Their method was more recently improved upon by

Agaskar[7,27], who used a similar method, where the reaction is conducted in a biphasic system. The silane and silsesquioxane product are suspended within the organic layer, allowing for the reaction to occur slowly at the interface. His method enables the possible synthesis of several different hydridosilsesquioxanes. The cubic form is the favoured form, and therefore easier to isolate, but in particular he was able to produce decahydridosilsesquioxane in significant quantities.

Since these earlier preparations, a large number of different silsesquioxane structures have been formed. From the condensation reactions of both chlorosilanes and ethoxysilanes, a variety of synthetic conditions have been used, varying with the reactivity of the silanes in the presence of water.

One such material is octavinylsilsesquioxane developed by Voronkov and co-workers[28,6], similar to the work of Andrianov and co-workers[29]. The reaction differs noticeably from the corresponding reaction for the octahydridosilsesquioxane. Vinyltrichlorosilane is significantly less prone to polymerisation than trichlorosilane, therefore a larger quantity of water can be used, yet still to produce a useable yield requires the reaction to be left for a significantly longer period of time, although unlike the former reaction has a large tendency to only give the one product.

However, in contrast to this preparation of octavinylsilsesquioxane, the allyl equivalent (***figure 2.11***) has been shown not to be synthesised as readily[30,31], proving difficult to isolate from the solvents used in the reaction.

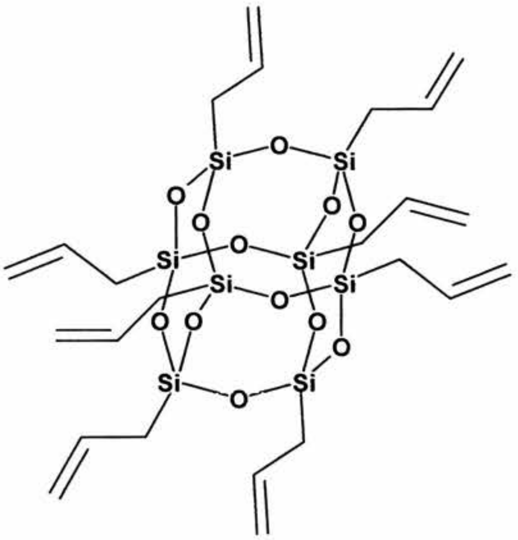

Figure 2.11: Structure of octaallylsilsesquioxane

Other silsesquioxanes[32] synthesised include slightly larger alkyl groups than those used for the early syntheses; *i*-propyl[33,34], *i*-butyl[34,35], *n*-hexyl[36-38] and cyclohexyl[5,39]. These didn't necessarily result in formation of the cubic product, although in all cases as would be expected they contain an even number of $RSiO_{3/2}$ groups. Non-alkyl groups for which silsesquioxanes have been prepared include benzyl, chlorobenzyl, 2-C_4H_3S[40], $ON(CH_3)_4$[41] and $OSi(CH_3)_3$[41]. Also the formation of silsesquioxane anions has been reported[42,43].

2.3 Silsesquioxane Variants

2.3.1 Derivations Of Silsesquioxanes

As silsesquioxanes can be prepared using a large number of different functional groups, opening up the potential for a large number of functionalised silsesquioxanes.

2.3.2 Dendrimers And Substitutions

The cubic silsesquioxanes possess eight functional groups around the edge of the molecule. These cubes can then be used as the central point upon which the organic groups can be extended and branched (***figure 2.12***)[44], eventually resulting in a large, approximately spherical molecule, such as those prepared by Jaffrès and Morris (***figure 2.13***)[45].

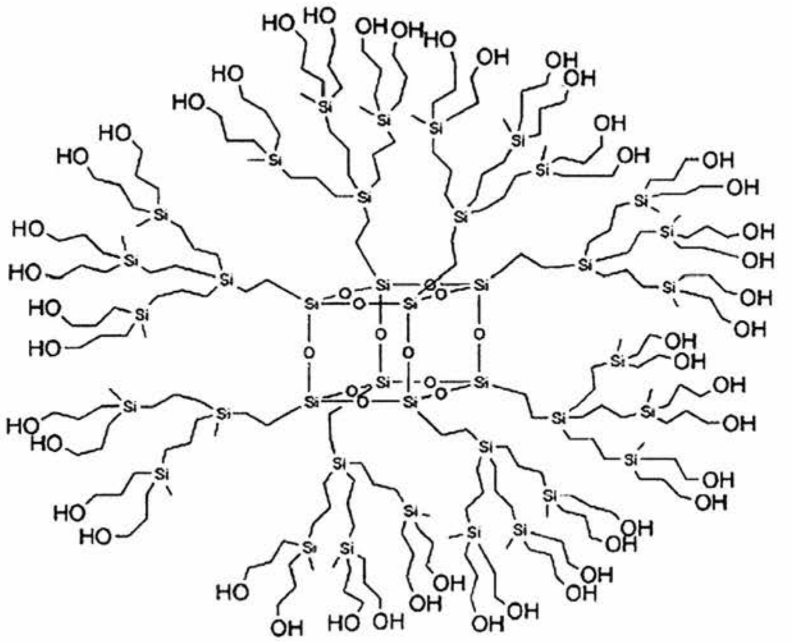

Figure 2.12: Silsesquioxane with dendrimers, resulting in an approximately spherical molecule

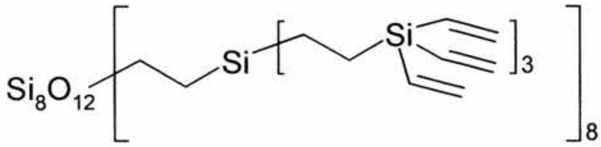

Figure 2.13: Simplified view of a larger system of dendrimers surrounding a cubic silsesquioxane core

Methods for building these chains can involve either entirely constructing the chain prior to attaching it to the core, or by using a series of reactions upon which the groups are added to in generations[44,46].

Whilst these can be prepared to several generations, the single step reaction can also be useful to apply additional functionality via means of a known reaction to the organic groups present. One example of such a reaction is the hydrosilation reaction[47,48] which vinyl group undergo with a silane such as chlorodimethylsilane (***figure 2.14***), an example of this addition occurs in the work of Tarrant and co-workers[49].

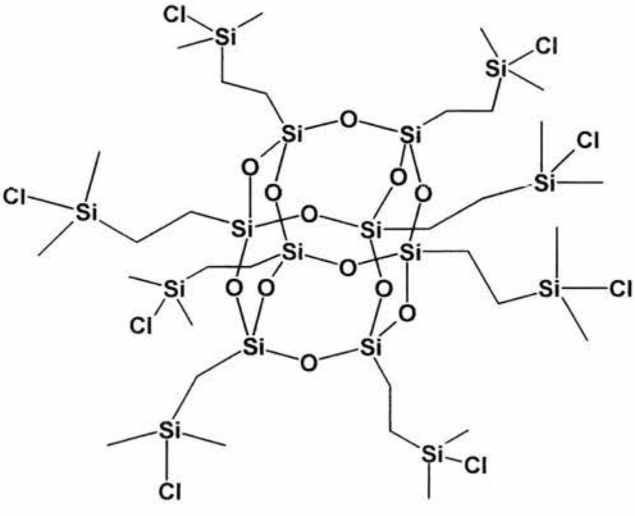

Figure 2.14: Octa-2-(chlorodimethylsilyl)ethylsilsesquioxane

Adding to an existing organic group to form dendritic compounds is one way in which the functionality of a group can be altered. A different variation is illustrated by Calzaferri and co-workers[50], with the addition of cobalt to a cubic silsesquioxane by means of a substitution reaction with octahydridosilsesquioxane. The product (***figure 2.15***) is found to lose all hydrogen atoms if sufficient quantities of cobalt are used.

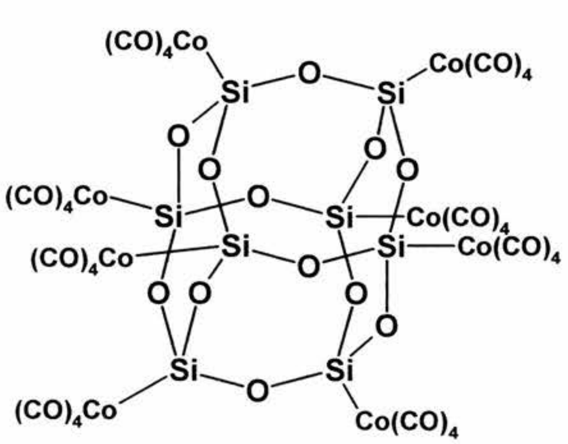

Figure 2.15: Octakis(tetracarbonylcobalto)octasilsesquioxane

2.3.3 Incompletely Condensed Silsesquioxanes

When preparing discrete unit silsesquioxanes, the final product results from a number of condensation reactions, until it is no longer possible for further such processes to occur. However, it has been shown by Brown[51] and subsequently by Feher and co-workers[52] that it is possible to prepare similar materials which are incompletely condensed (***figure 2.16***).

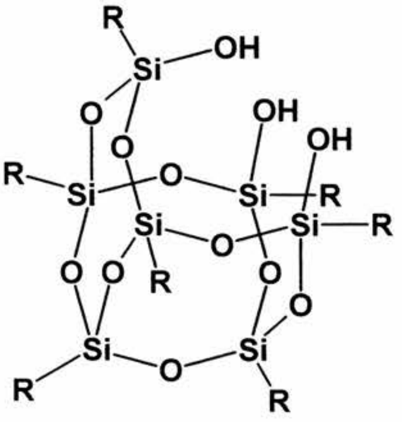

Figure 2.16: Example of an incompletely condensed silsesquioxane structure

These compounds contain a number of silanol groups, the above example (***figure 2.16***) shows three silanol groups present, all surrounding the same missing silicon atom removed from the structure, although it is possible for other splitting to occur, an example of which would be for one edge of the cube to be opened, leaving two silanol groups, but with no loss of silicon (***figure 2.17***).

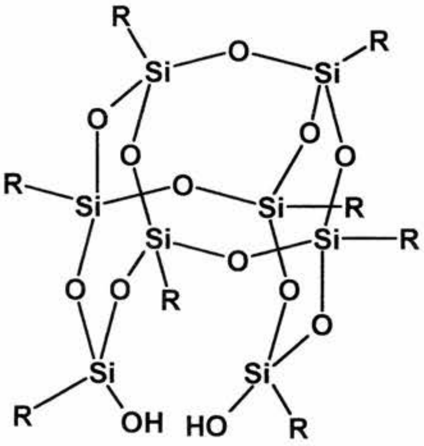

Figure 2.17: Incompletely condensed silsesquioxane disilanol species

Two general methods have been shown for the preparation of such materials. One method is to directly synthesise such compounds from the silanes, using similar methods to the preparation of completely condensed silsesquioxanes[53,54]. Such syntheses are observed to result in a variety of products, although all contain the silanol groups remaining where complete condensation has not occurred.

An alternative synthesis of such compounds is from the hydrolytic cleavage of a completely condensed silsesquioxane[55,56]. This is achieved in the presence of either a strong acid (***figure 2.18***) or base, and could potentially enable the formation of materials that would not be possible with the direct synthetic method.

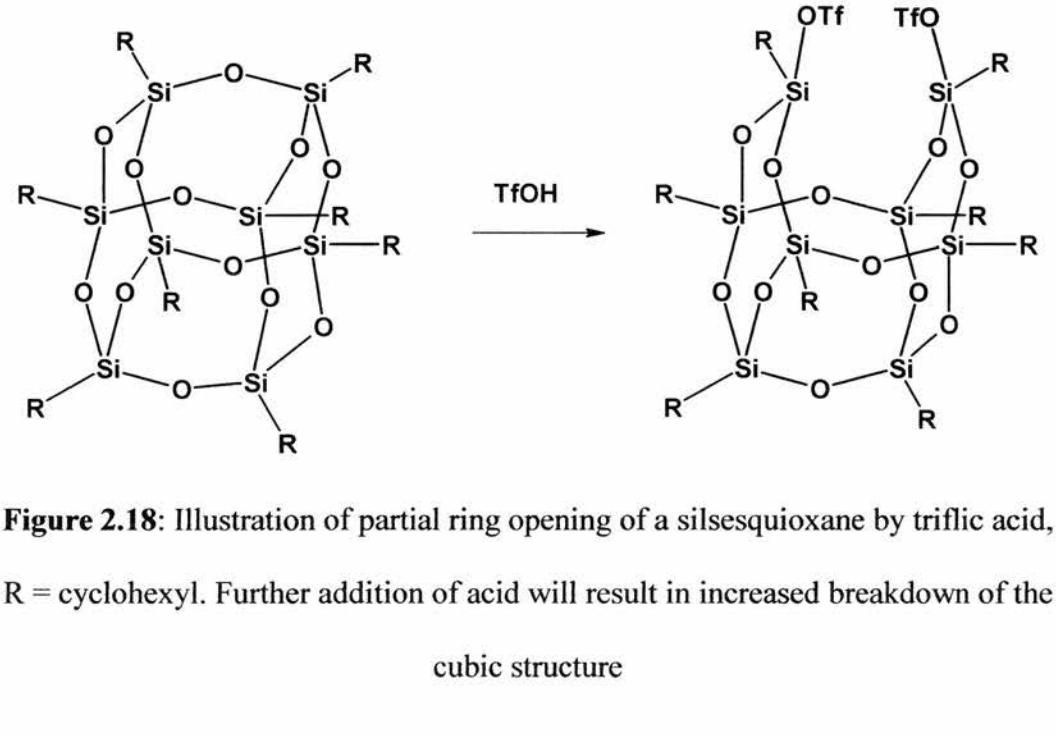

Figure 2.18: Illustration of partial ring opening of a silsesquioxane by triflic acid, R = cyclohexyl. Further addition of acid will result in increased breakdown of the cubic structure

Currently incompletely condensed silsesquioxanes have only been prepared for a small number of groups, of which the organics present on such molecules have been simple alkyl[51] or cycloalkyl[53,54] groups, which do not offer much potential for further modifications.

2.3.4 Metal Containing Silsesquioxanes

Incompletely condensed silsesquioxanes can in turn be used to form the basis for the insertion of metals within the general structure of the inorganic cages of these materials. A number of groups have successfully identified compounds containing a wide variety of different metals.

Crocker and co-workers are one group to have investigated the insertion of titanium[57,58] within these incompletely condensed materials resulting in a number of different conformations of products. They were able to insert the metal into both disilanol and trisilanol groups on such silsesquioxanes, together with forming dimers of two units with the titanium acting as the bridge between them (***figure 2.19***).

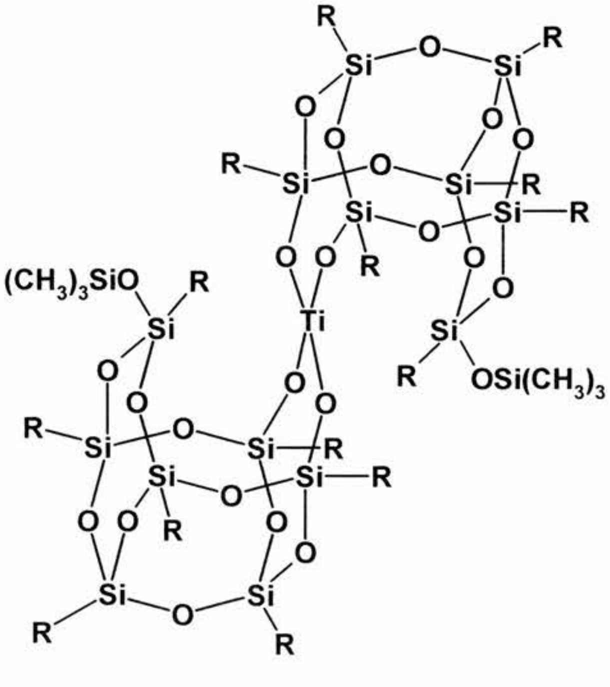

Figure 2.19: Titanium as a bridge between two incompletely condensed silsesquioxanes

Abbenhuis and co-workers observed that the silanol groups within incompletely condensed silsesquioxanes reacted readily with tetrabenzyltitanium[59]. They found that approximately 80% of the possible insertions had occurred based on the number of silanol groups measured using solid state silicon NMR.

Similar insertions of tungsten have been studied by Verdonck and co-workers[60]. The most notable difference in comparison with titanium[61-63] is the formation of six co-ordinate metal atoms within the silsesquioxane structure. When monomeric species are formed this results in a corner of an incompletely condensed silsesquioxane trisilanol effectively being capped (***figure 2.20***).

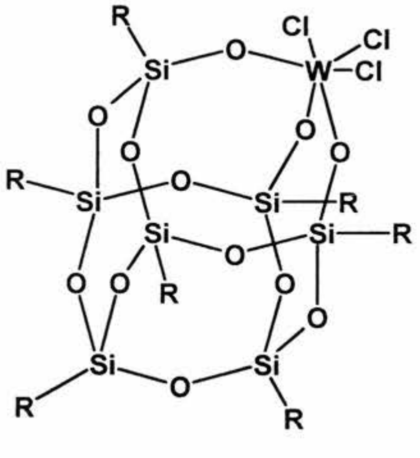

Figure 2.20: Incompletely condensed silsesquioxane capped using tungsten chloride

Likewise, the equivalent dimeric species (***figure 2.21***) sees the tungsten bonded to three oxygen atoms on each individual silsesquioxane, not leaving any groups free other than the organic groups deriving from the original silsesquioxane.

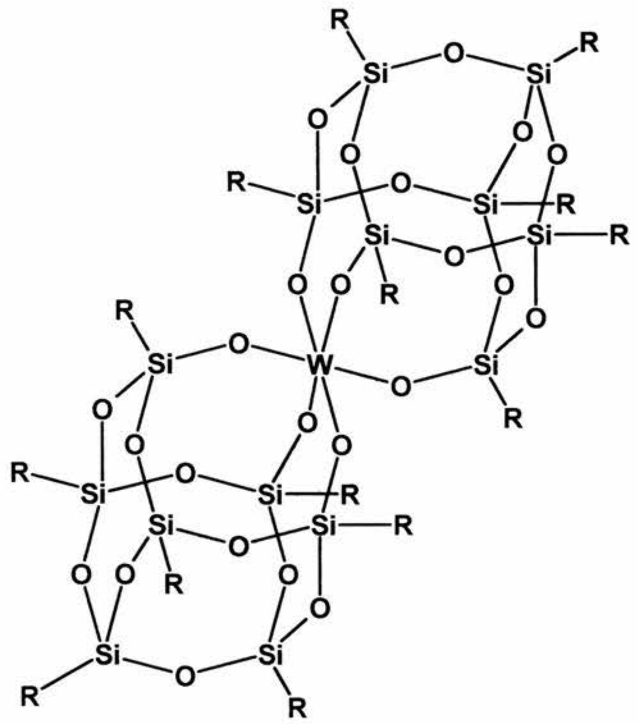

Figure 2.21: Tungsten bridged silsesquioxane dimer

In the instances of titanium and tungsten, both these insertions have been conducted using a trisilanol incompletely condensed silsesquioxane. An example of this type of synthesis being used starting from a disilanol containing silsesquioxane is the insertion of cerium reported by Gun'ko and co-workers[64]. This also formed a dimeric species (***figure 2.22***), with co-ordinated pyridine from the solvent attached to the bridging metal.

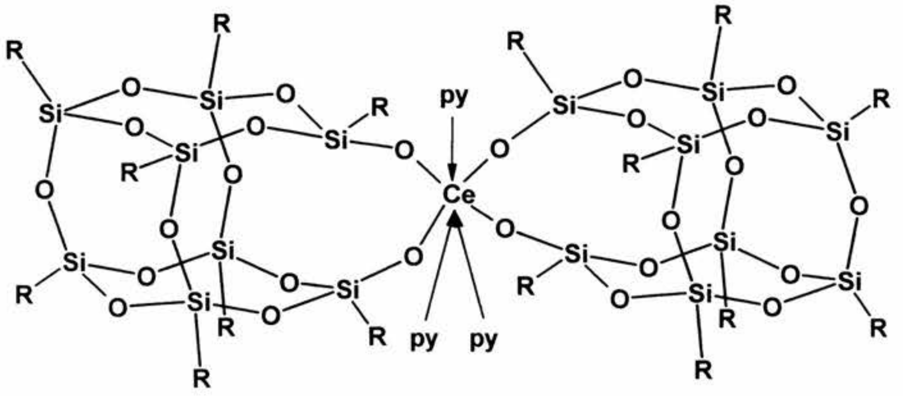

Figure 2.22: Cerium bridging two incompletely condensed silsesquioxanes, with co-ordinated pyridine (py)

Another type of bridging metal found in the formation of silsesquioxane dimers was observed by Aspinall and co-workers[65] to occur with a number of M^{3+} metal ions such as chromium, gallium and vanadium. The previous structures shown have always had only a solitary metal atom within the bridge, but in cases such as these two metal atoms are seen (***figure 2.23***).

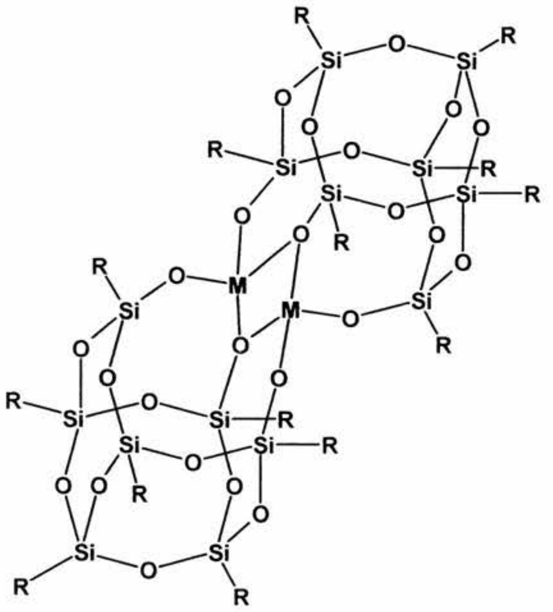

Figure 2.23: Dimeric structure of two incompletely condensed silsesquioxanes with M^{3+} bridge

For these dimers, they also found it to be possible to split them to give monomeric species akin to the earlier tungsten compound. However, due to the limited co-ordination possibility of these metals, only one ligand is attached to the metal other than the oxygen from the silsesquioxane (***figure 2.24***).

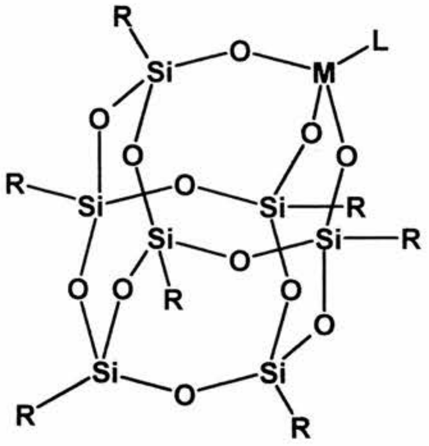

Figure 2.24: Four co-ordinate M^{3+} silsesquioxane monomer

These structures represent only some of the metals for which it has been observed that insertion within the structure of an incompletely condensed silsesquioxane occurs. Similar effects are reported in the literature for a diverse range of elements, including molybdenum[66], gallium[67], zirconium[68], hafnium[68], chromium[69], magnesium[70], tantalum[71] and platinum[72].

2.3.5 Polymers

There are two conceivable methods by which silsesquioxanes could be incorporated into a polymeric structure, allowed by the possible functionality of the organic groups present around the inorganic core.

One method is to attach the silsesquioxane onto an organic chain polymer. This type of compound is seen in the works of Coughlin and co-workers[73], Yuchs and Carrado[74] together with those of Hybrid Plastics Inc[75]. The former used a cubic silsesquioxane with seven unreactive cyclopentyl groups and one featuring a norbornylene group (***figure 2.25***). The double bond on the latter could then undergo copolymerisation with either ethene or propene to form a polymer with a number of silsesquioxane units attached.

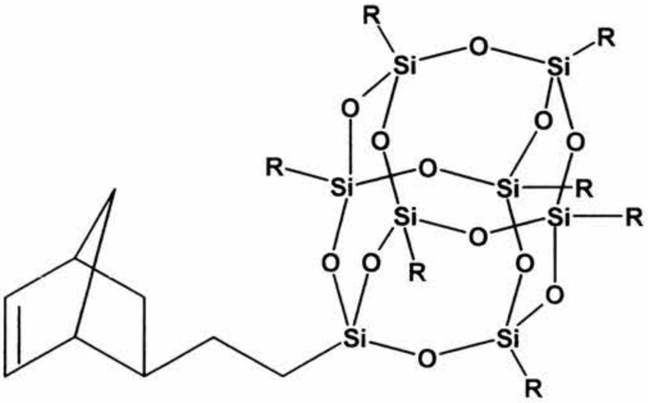

Figure 2.25: Silsesquioxane species used in formation of polymers, R = cyclopentyl

A second method of forming polymers exploits the number of possible groups available on a silsesquioxane to form three dimensional structures, with the inorganic cores linked by a series of organic bridging groups (***figure 2.26***). Based on this idea a small number of different polymers have been prepared, examples noted by Harrison and Kannengiesser[76] and Laine and co-workers[77] show links formed by hydrosilation reactions of vinyl and hydrido groups on the silsesquioxanes, or by using a longer chain diamino compound to tether cubes together[78].

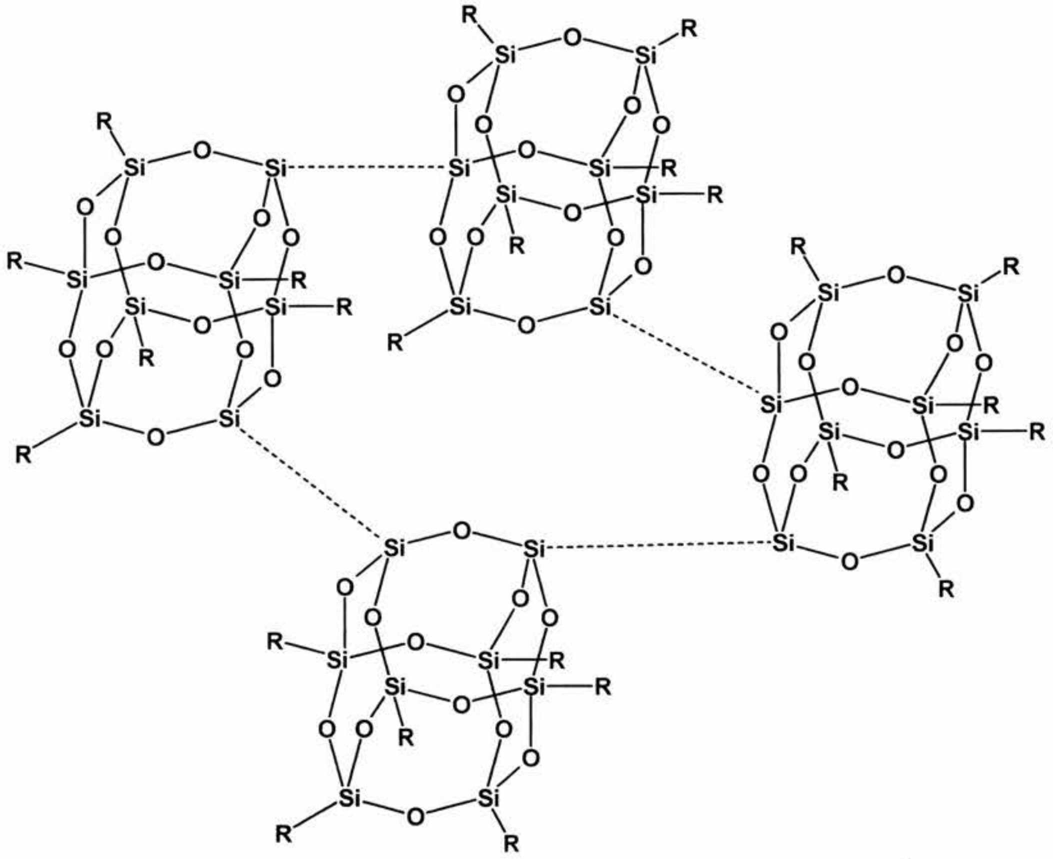

Figure 2.26: Example of a possible structure of a silsesquioxane based polymer, dashed lines represent organic bridging groups and R is an organic group which has the possibility of extending the structure, or remaining unreacted

The exact structure of such a species is not fixed, and despite the potential for a cubic silsesquioxane to form links to eight other similar species, steric and kinetic factors in the reaction system make this often an impossibility.

After synthesising a number of such materials, Laine and co-workers characterised and compared the differences between the various groups which acted as the bridges linking the silsesquioxane cages. Whilst longer organic groups resulted in more rapid polymerisation, they sacrificed a significant degree of porosity in the process.

2.3.6 Silsesquioxane Films

Whilst the definition of a silsesquioxane does not imply that the structure has to be a small discrete unit, it is also possible to form thin films possessing the same chemical formula. Yang and Chen[79] provide an example of this type of compound with their investigations into the structure of the properties of hydrogen silsesquioxanes. Both structures have the formula $(RSiO_{3/2})_x$, but whereas the discrete units have a small value of x, for the films it is much greater, and forming an insoluble product.

2.4 Modelling

2.4.1 Overview

When preparing silsesquioxanes and their derivatives to enable structures to be determined, common spectroscopic techniques are useful to help determine this. However, theoretical studies can also be of use to understand the physical properties of these compounds.

2.4.2 Theoretical Models Of Simple Silsesquioxanes

Pandey and co-workers[80], Calzaferri and co-workers[81], and Earley[82,83] have conducted theoretical investigations into the properties of simple cubic silsesquioxanes. The work of the former was primarily concerned with using the silsesquioxanes as a simplified model for zeolite A, but does give a good idea about the infra-red behaviour[84] of these compounds. Coupled with earlier work upon the IR of deuterated octahydridosilsesquioxane[85] and NMR investigations[86], this enables the assignment of peaks in these spectra to the symmetry of the compounds involved.

The work of Earley, is of an entirely theoretical outlook and is concerned with quantum mechanical and electronic structural calculations of silsesquioxanes. They show the structure to be as expected, in that they are not entirely cubic, with a Si–O–Si bond angle of being approximately 150°, and also notes a correlation between the decreasing bond angle in the siloxane linkages and the increase in the Si–O bond length, which implies a slightly larger bond distance for discrete silsesquioxanes with a smaller number of $RSiO_{3/2}$ groups present.

2.4.3 Computer Modelling Of Dendrimers

Another theoretical technique that has been used to investigate the behaviour of silsesquioxane derived species is the use of computer modelling to predict the structures of dendrimer containing species[87]. This shows such materials to have some element of disorder within the structure, and can be used in comparison with data collected for less complex materials to relate some of the properties of the free dendrimer to these when it is used as a ligand in a catalytic process.

2.5 Applications

2.5.1 Overview

Although it has only been within the past two decades that silsesquioxanes and derivations thereof have been increasingly extensively studied, a number of potential applications have been identified, and the feasibility of these is currently being determined.

2.5.2 Catalysis

Silsesquioxane based materials offer the opportunity for a number of different derived catalytic materials[88,89]. Dendrimer containing compounds have been shown to be useful as ligands for known catalysts. One example of this is the hydroformylation of oct-1-ene by a rhodium catalyst demonstrated by Cole-Hamilton and co-workers[44], whereas Harrison and Hall have reported rhodium attached directly to the silsesquioxane core[90].

The silsesquioxane compound is used in this instance by building up a system of phosphorus containing dendrimers to which the rhodium complex can co-ordinate. Whilst any ligand can affect the course of the catalysis, such as its efficiency and the products obtained, the significant advantage of this compound is its size, which enables recovery of the expensive rhodium by ultra-filtration.

Another potential catalytic use has been observed by Thomas and co-workers[91] by considering the insertion of titanium within an incompletely condensed silsesquioxane. Preparing compounds (***figure 2.27***) containing titanium with an –OXPh3 group (X = Si, Ge or Sn) these were tested using epoxidation reactions, proving highly selective in the conversion of TBHP.

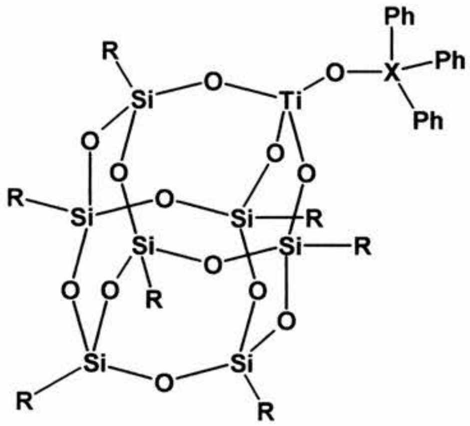

Figure 2.27: Titanium containing epoxidation catalyst, X = Si, Ge or Sn

2.5.3 Models Of Silica Surfaces

The work of Feher and co-workers[52] into the properties of incompletely condensed silsesquioxanes has been considering these molecules to be models for the silica surfaces of larger compounds[92], by insertion of another species into these the bonding around this should be the same as on silica surfaces.

Potentially such a model offers the chance to study such compounds with techniques that would not be possible with the material that information would be desired from. Techniques used in analysis cannot be applied to all compounds, so this enables the study of such materials as would not have been previously possible.

2.5.4 Additives And Incorporation Into Polymer Systems

Silsesquioxanes have been seen to have beneficial effects when incorporated into organic polymers as pendant groups attached to the chain. These can be used to alter the physical properties of the material to which they are added, through the specific type used, and the relative quantities present, thereby allowing for the properties of the substance concerned to be changed on demand[75,93]. An example of the effects of the addition of silsesquioxane units to a polymer could have is the ability to alter the viscosity of a coating or resin by introducing relatively bulky units into the material.

Another possibility opened up by such an addition are to increase the glass transition temperature of a material. Coupled with a tendency to increase the heat required for combustion of a material to occur, leads to the potential for using existing compounds at higher temperatures, making them suitable in fire retardant materials.

2.5.5 Silica Substitute

Another potential advantage of these materials is to be used as a replacement for silica within products as a filler compound[75]. Whilst the chemical nature of the two is similar, and silsesquioxanes can be disposed of as easily, the fixed structure provided by the inorganic cage possesses a lower density. Therefore this can enable increasingly lightweight commercial materials.

2.5.6 Zeolite Type Chemistry

Silsesquioxanes bear a strong resemblance to the basic building blocks found within zeolites (***figure 2.28***)[94], in terms of both structure and chemical composition. It is therefore one possibility that polymers prepared from silsesquioxanes could potentially find similar applications.

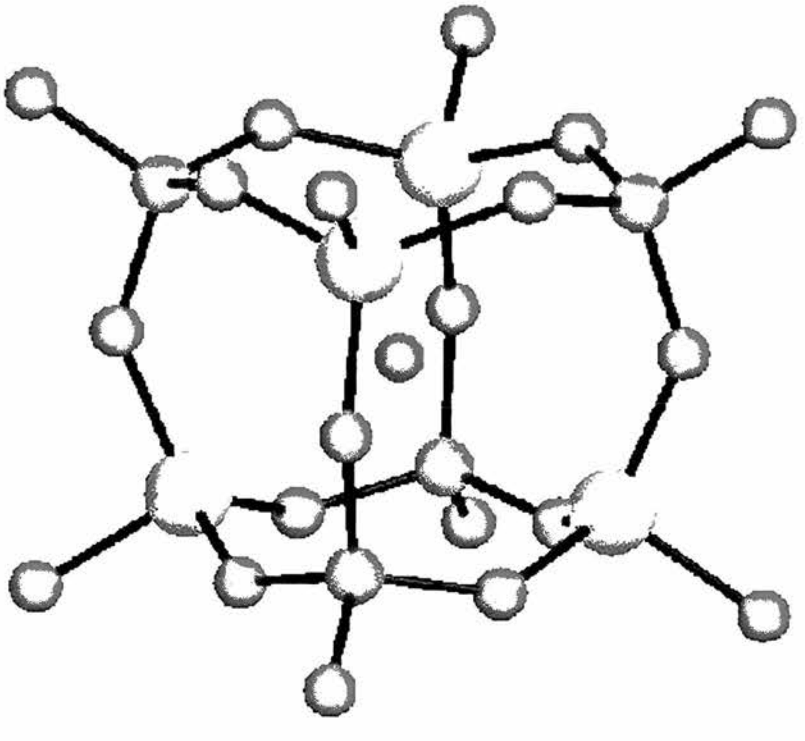

Figure 2.28: Close-up of a double-four ring structure found in a zeolite, to which silsesquioxanes bear a strong resemblance. Al grey, P purple, O red, F green

One notable difference between the two is, however, the need for a counterbalancing cation in zeolites to offset the negative charge on the aluminosilicate framework. This tends to lead to zeolites being solid state acids[95]. While this can be advantageous to many catalytic processes, there are others where such conditions might not be suitable. Therefore the use of a neutrally charged silsesquioxane based copolymer could prove useful for such reactions.

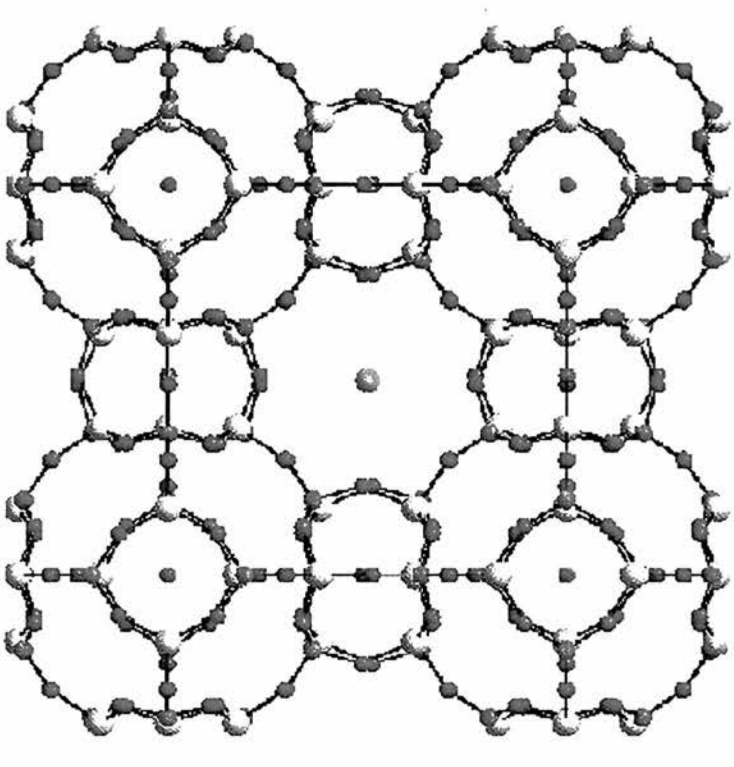

Figure 2.29: Well defined structure of a zeolite structure, in this case a Linde Type A structure[96] of an aluminium phosphate, showing Cu^{2+} (blue, surrounded by cyclam) and F^- ions (green) within the pores[97]. Al grey, P purple, O red.

Another potential disadvantage of some zeolites is their preparation. The time required for the reaction needed to create them may be long and also require the presence of conditions which may be relatively difficult to achieve in order to prepare the intended structure[94]. Potentially silsesquioxanes could offer more simplicity, although they also sacrifice the well defined structures possessed by zeolites (***figure 2.29***). Whilst it is conceivable that not all reactions would be prevented without a well defined structure, it is a possibility that selectivity might be reduced.

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3 Experimental Techniques

3.1 Introduction

Within this work, a number of techniques have been used to analyse the materials prepared. Three particularly important methods used are described in more detail here. The adsorption of gases onto surfaces, solid state MAS NMR and EXAFS.

3.2 Gas Adsorption

3.2.1 Overview

The adsorption and desorption of gases onto the surface of a solid can be used to determine a number of properties regarding the surface of a material, both by calculation and observation. When investigating porous polymers, it is useful to know both the surface area of the materials, as well as a pore size distribution, which acts as a useful comparison between similar materials.

A gas is adsorped by exposing it to the solid, previously degassed under vacuum, in set pressure increments, recording the weight gain of the sample. Similarly the desorption works by recording weight loss as incremental steps are created when reducing the gas pressure.

The shape of these isotherms obtained can be used to calculate the properties of the material concerned. The surface area is calculated using the equations of Brunauer, Emmett and Teller[1], with the pore size distribution modelled using the methods of de Boer[2,3], based upon the earlier work of Barrett, Joyner and Halenda[4].

3.2.2 Theory

The BET equation[1] used for calculating the surface area (***equation 3.1***) allows for the directed calculation of a monolayer of the gas concerned. Only from knowing the physical properties of the gas concerned can a surface area be determined from the data.

$$\frac{z}{(1-z)V} = \frac{1}{cV_m} + \frac{(c-1)z}{cV_m} \qquad z = \frac{p}{p^*}$$

Equation 3.1: The BET equation for calculating the volume of a monolayer of adsorped gas on a porous solid, V_m. V is the total volume of gas adsorped, p is the initial pressure and p^* after exposure to the sample

This equation is a modification of the earlier work of Langmuir[5] to include the effects of subsequent layers of adsorption following the initial monolayer. The volume of the monolayer can easily be determined from a plot of z against (1-z)/V[6], the intercept and gradient of a line of best fit through the data can be used to calculate both c and more importantly V_m. As a result of knowing the size of a single molecule of the adsorbed gas, the surface area of a monolayer can then be calculated from this figure.

In addition to calculations being possible as to the surface area of the solid, the work of de Boer and co-workers[2,3] has provided a method for the calculation of the pore size. Using nitrogen as the absorbent gas, they calculated a simple equation (***equation 3.2***) to determine the thickness of the adsorped layer, t. Essentially this is similar to the work of Barrett, Joyner and Halenda[4], but with the addition of a small corrective factor.

$$t = 3.54\left(\frac{V_a}{V_m}\right)\mathring{A}$$

Equation 3.2: Calculation to adsorped nitrogen by de Boer, t = thickness, V_a = volume of nitrogen adsorped, V_m = volume of monolayer

Derived from this is a second equation representing the diameter of the pores (***equation 3.3***) and by plotting the cumulative surface areas of pores with a diameter larger than a specified value enables a pore size distribution curve to be plotted.

$$d = 3.7 + 2t$$

Equation 3.3: Diameter of pore sizes derived by de Boer

This technique only is used to calculate pore size distributions from partial gas pressures of 0.08 upwards. Which corresponds to a diameter of approximately 10Å.

3.2.3 Isotherm Shapes

The shape of the isotherms can indicate properties regarding the materials without using any analysis. These can be categorised into a number of different groups (***figure 3.1***)[7] which can act as an indicator of type of structure present within the material being studied.

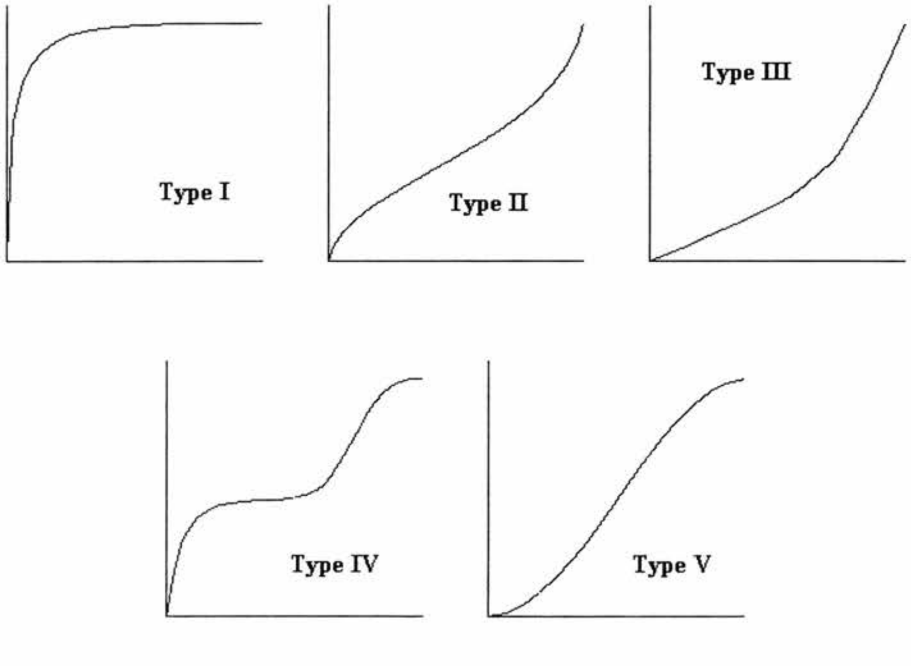

Figure 3.1: Adsorption isotherms of types I to V

Type I is the Langmuir isotherm which corresponds to the formation of a single monolayer being deposited upon the surface, if additional layers of the adsorbate gas were to form, an isotherm of type II would result. These are the two most common variants seen, with type III being dependant upon the heat of adsorption in relation to that of liquidation. The final two more complex isotherms both derive from capillary effects within the material.

In addition to the adsorption isotherms, the behaviour upon desorption can also assist a determination of the structures involved. Whilst it is possible for this to take the same pathway as adsorption, it is possible the two curves do not overlay each other, this is referred to as hysteresis, of which there are two basic types (***figure 3.2***)[8].

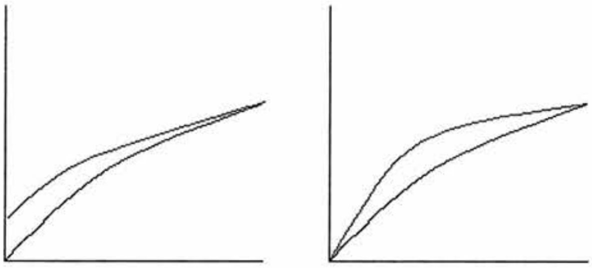

Figure 3.2: Hysteresis observed upon desorption (blue) after adsorption (black)

The former type does not see the full volume of adsorbed gas removed from the surface of the material, which is indicative of a change in nature of the surface after the adsorption. In contrast the closed hysteresis is a sign of an ink-bottle effect, with large with only a small opening, or neck, for the gas to be removed.

3.2.4 Experimental

Adsorption of gases was conducted on a modified Hiden Analytical IGA -002, with additional results recorded using a Micromeritics Gemini 2360 instrument, and prior to analysis the samples were degassed in high vacuum to ensure no adsorbates remained upon the sample, allowing the absorbent gas to attach to the surface. Measurements were recorded at various partial pressures allowing suitable time for the sample to equilibrate, and when a constant weight was achieved this result was recorded. From the weight gained, the volume of the gas adsorbed could therefore be calculated.

During the adsorption of nitrogen all samples were cooled to -196°C with liquid nitrogen, whereas cyclopentane adsorption was recorded at 5°C using water as a coolant.

3.3 Solid State MAS NMR

3.3.1 Overview

In solution NMR is seen to be a very useful technique used to determine the structure of a wide variety of compounds. When applied to solids NMR spectra are affected by interactions within the material, resulting in poorly resolved data possessing very broad peaks, obscuring any potential detail. When studying species such as network polymers, it is not possible for these to be prepared in solution.

Solid state magic angle spinning (MAS) NMR has been developed in order to obtain an increased resolution from such materials. It can be viewed as spinning the sample at high speeds, whilst at an angle to the magnetic field.

3.3.2 Theory

The magic angle from which this technique derives its name is calculated from the equations to determine the peak separation to the dipolar interactions within the sample being studied (***equation 3.4***)[9].

$$\text{a) } \Delta V = \frac{3}{2}\frac{\gamma_I^2 \hbar^2}{r^3}(1-3\cos^2\theta) \quad \text{b) } \Delta V = \frac{\gamma_I \gamma_S \hbar^2}{r^3}(1-3\cos^2\theta)$$

Equation 3.4: Peak separations for a) like spins, b) unlike spins, θ = angle to magnetic field

It can be seen from both these equations that regardless of the other parameters, setting $1\text{-}3\cos^2\theta$ to equal zero will remove the whole term. This angle, θ, known as the magic angle, is 54°44'. By spinning at high frequencies at this angle (***figure 3.3***) the isotropic chemical shift is what determines the NMR spectra seen, which is what is observed in solution.

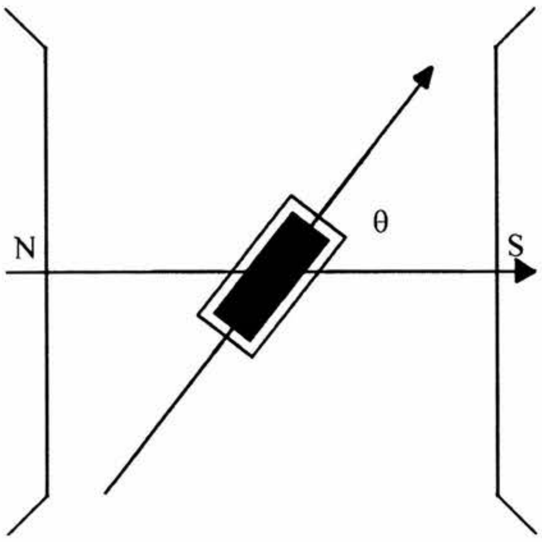

Figure 3.3: Sample spinning at the magic angle, θ = 54°44'

The actual spin rate is determined by the anisotropy of the sample being studied, the range over which this occurs is the frequency of the spin used. Spinning the sample at lower speeds will result in the presence of side bands in the spectra, with the spinning frequency equal to that of the gap between the peaks.

Data for ^{13}C spectra was collected on a Varian Unity+ 300, this was also used for recording ^{29}Si spectra in addition to a Varian Infinity 500 MHz solid state NMR spectrometer.

3.3.3 Experimental

The collection of spectra from solid samples additionally depends upon the actual element for which data is collected. Carbon and silicon spectra have been obtained but the low abundance of titanium proved too low to enable the collection of information regarding such samples.

3.4 EXAFS

3.4.1 Overview

Extended x-ray absorption fine structure (EXAFS)[10-15] is a form of x-ray spectroscopy which is used as an aid to determine the environment around a specified element. The most direct implication of this would be the bond distances to neighbouring atoms, however it is also possible to determine distances to other non-bonded atoms at further distances from the central atom. Additionally both the co-ordination number around the element concerned, together with a measure of the disorder of the surrounding atoms.

At its simplest the process can be viewed as the absorption of an x-ray, which results in the loss of a photoelectron. As these are released they interact with the neighbouring atoms, and are in turn scattered away from these. This backscattering results in interference (***figure 3.4***) of the backscattered wave with the outgoing wave, to create peaks and troughs. The neighbouring atoms are responsible for the amplitude and phase of the backscattered wave.

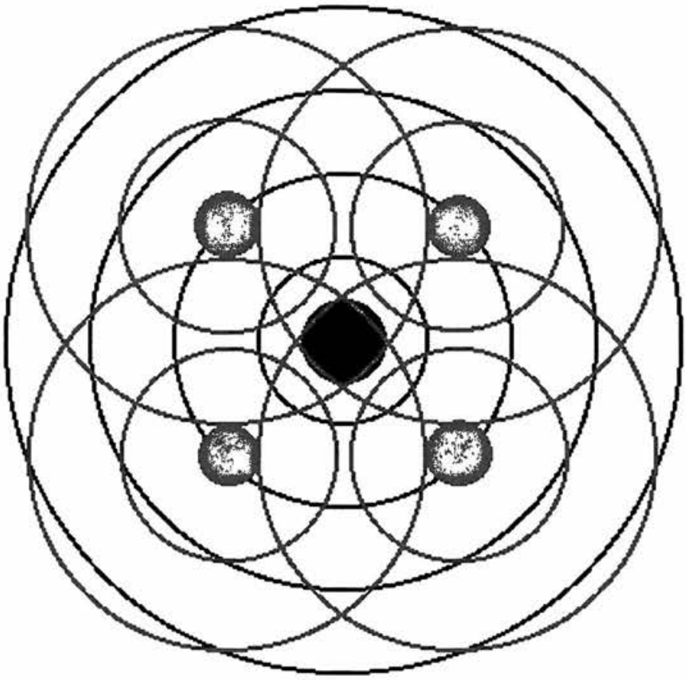

Figure 3.4: Interaction of outgoing wave of photoelectrons with backscattering

The effects of the interference can be collected through either fluorescence or transmission detectors, and the sample is analysed through means of comparison of experimental data with a theoretical model.

3.4.2 Theory

The measurement of EXAFS data involves the comparison of theoretical and experimental results. The former is calculated from a number of factors (***equation 3.5***)[16] which are used to model the oscillation of the wave.

$$\chi(k)=\left(\frac{1}{k}\sum_{i}\frac{f_i(k)}{r_i^2}e^{-\sigma_i^2k^2}e^{-2\mu r_i}\sin[2kr_i]n_i\right)AFAC$$

Equation 3.5: EXAFS oscillations

This equation is made up of a number of individual components, all of which have an effect upon the EXAFS, χ, which is seen to be a function of k. This variable represents the ejected photoelectron and is defined in terms of the charge, mass and energy (***equation 3.6***).

$$k = \frac{\sqrt{2m(E - E_0)}}{\hbar}$$

Equation 3.6: Definition of χ, $\hbar$ = Planck's constant

The other terms seen are $f_i(\chi)$ which is an amplitude term relating to the size of the central atom ejecting the photoelectron and μ is the adsorption coefficient of this. σ_i^2 represents the uncertainty about the location of an atom, giving rise to the Debye-Waller factor. r_i is simply the distance between the central and backscattering atoms.

This relatively basic equation for the EXAFS data assumes only single scattering between atoms, although Lee and Pendry[10] have calculated the effects of scattering by multiple atoms on the EXAFS.

3.4.3 Experimental

The EXAFS data collection was conducted using a double crystal monochromator to control the energies of the x-rays used, enabling a scan to be conducted over a range. Harmonic rejection is used at 50% to remove the vast majority of the high order energy levels. Either transmission or fluorescence emissions from the sample are then taken, the latter is more likely to result in extra noise present, so the former is preferred although it may not be able to detect some of the samples in a lower concentration.

The collected data (***figure 3.5***) is observed to have a sudden increase in the detected signal at the edge position, which corresponds to the point at which the excitement of the electrons occurs for a particular element occurs. In this specific case of titanium shown, this appears at 4964.72eV.

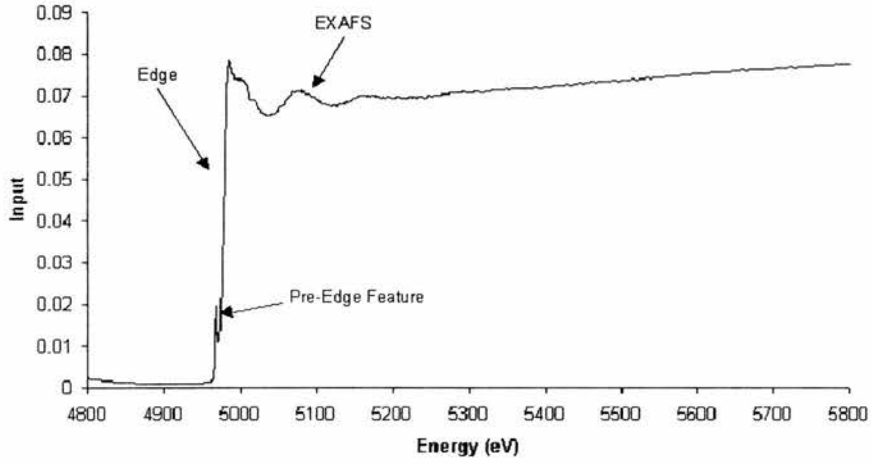

Figure 3.5: Collected EXAFS data, this particular example is from a sample containing titanium

Also seen in the diagram is the pre-edge feature, which is useful in another technique, x-ray adsorption near edge structure (XANES), which helps with determination of the co-ordination and oxidation of the central atom, together with the EXAFS themselves which are seen as oscillations after the edge.

In order to study the data this provides, individual experiments have to firstly be calibrated and combined to form an average of several results, before then removing the background, to just leave the EXAFS themselves.

The first part of this was conducted using the program EXCALIB. This enables several spectra to be added together, and in the case of fluorescence EXAFS monitor the individual detectors, and for those that gave poor quality data to be removed from consideration.

Background removal was carried out using one of either EXBACK, EXBROOK or EXSPLINE. Although each of these operates using different routines they all serve the same purpose. The most useful of these was EXSPLINE[17], which enables the subtraction to be conducted using a graphical interface. In all cases the pre-edge was extended and this subtracted from the data. Following on from this step a curve was defined fitting through the middle of the EXAFS oscillations. For EXSPLINE this is determined by a series of splines through several points of the curve.

The final step it compare this data to a theoretical model using the EXCURV98[18] program. The quality of the EXAFS collected varies, and this needs to be truncated and the data with a high noise level removed, as it is impossible to fit theoretical data to this.

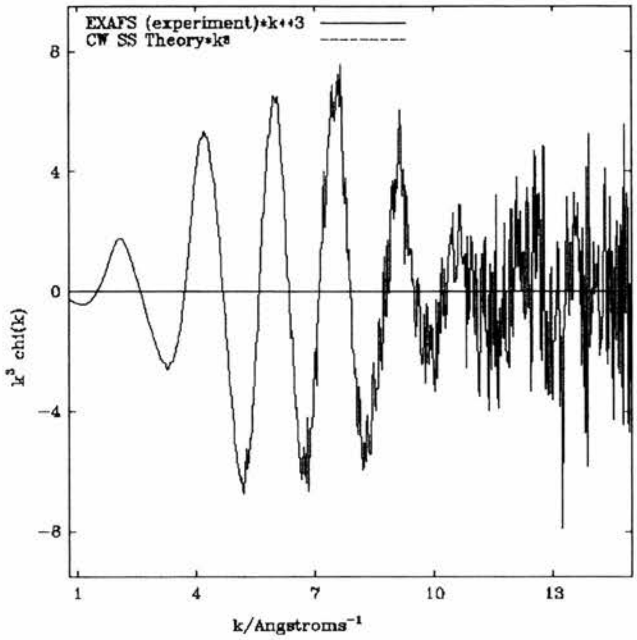

Figure 3.6: EXAFS of molybdenum containing species

To illustrate this is the EXAFS data obtained for a sample of a molybdenum containing compound (***figure 3.6***). This is a good example as it shows the data having no noise initially, yet throughout the level of this noise noticeably increases to the point whereby it is impossible to identify even the general trend of where the curve should appear. As this point approaches the data has to be truncated, which would occur with k around 10 in the above example.

There are many parameters that can be refined, or set to a specified fixed value, of which a limited number have been used. The total number of such refined parameters (not variables which are defined and fixed as constants) for which the results are valid depends upon the range fitted in k-space and real space (***equation 3.7***)[19].

$$Np = \left[\frac{(2\Delta k \Delta R)}{\pi} \right] + 1$$

Equation 3.7: Number of independent points (Np) that can be fitted to the EXAFS data. Δk is the range in k-space which the attempted fit is made and ΔR is the corresponding figure in real space

For the molybdenum species shown above (***figure 3.6***), the range in k-space used would be from the intersection where the curve crosses the *x*-axis near 3Å^{-1}, up to the intersect around 10.5Å^{-1}.

Whilst it is the EXAFS themselves which the refinements are based, it is easier to view the data in real space, via a Fourier transform (***figure 3.7***). In the case of this molybdenum containing species, a large peak appears slightly above 2Å, which as one of the reactants contains two cyclopentadienyl groups complexed to the transition metal, would suggest trying to fit these as ten identical carbon atoms would be a reasonable starting point for a first shell.

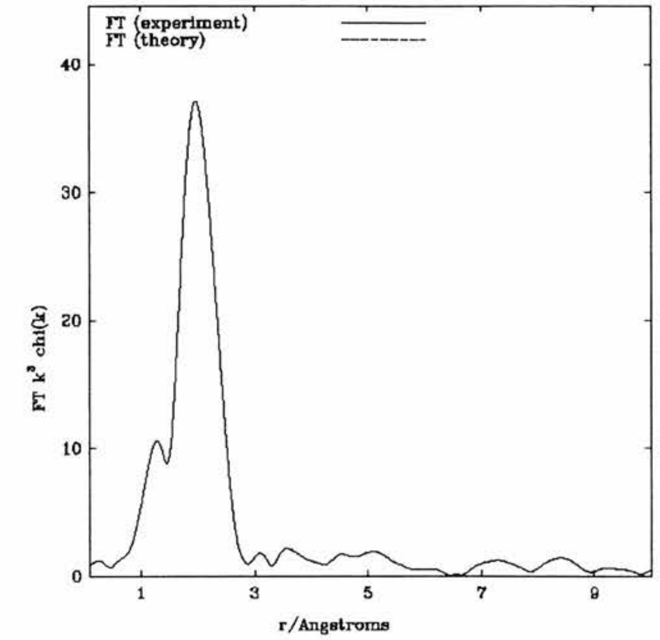

Figure 3.7: Associated Fourier transform of molybdenum containing species

Refinement has been concentrated on three variables. Firstly the bond distance, r_x, which is important for all atom shells, giving the distance from the central atom. This does not actually require a direct bond between the two, it is simply the distance in space. A second parameter is refined for each atoms individually. This is the Debye-Waller factor, σ^2_x, which is a measure of disorder. A smaller value for this represents an increased certainty for the location of the particular atoms, a higher number implies its location is less certain.

In addition to these two parameters for each shell of atoms the fermi energy, E_f, is refined, this defines the edge position, effectively a factor to adjust the whole data slightly as a correction.

Several other variables can be considered, the most important of these is the shell occupancy, n_x. This former defines the number of atoms present within that shell, and is more convenient to keep fixed. If the refinement of data using this value is poor then other values of n can be considered to see if an improvement is obtained.

A final factor left constant is the AFAC parameter which is the average proportion of excitations contributing to the EXAFS. By setting this figure to a lower value it will reduce the amplitude to the EXAFS.

The process of refining the data involves selecting either one, or a combination of the parameters defined, starting with only one shell of atoms, and allowing for these to be changed using a least squares refinement until the closest match is obtained. After repeating with other parameters for the first shell, resulting in as accurate a fit as possible, in turn other shells of atoms were introduced and similarly refined.

After refinement the quality of the fit concerned is obtained by a fit factor, R. Expressed as a percentage, the lower the value is the closer the match between the theoretical and experimental data. Ideally this would be below 20%, but the higher figures obtained here still give a reasonable indication as to the structure of the materials examined.

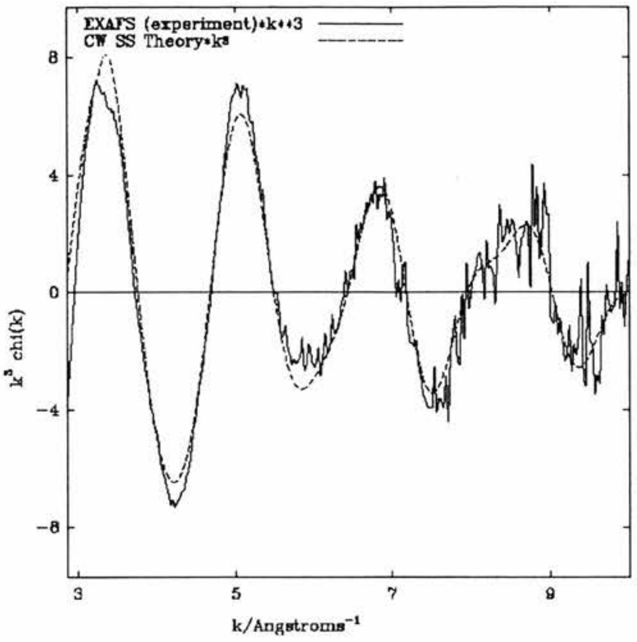

Figure 3.8: Fitted EXAFS of a zirconium containing species

Using EXAFS collected from a zirconium containing sample (***figure 3.8***), the theoretical data (shown as a dashed line), closely follows that of the experimental (solid line), although particularly noticeable with the increased noise to the right of the data, the calculated theoretical curve is only an average with the noise observed. This particular refinement resulted in a R value of slightly under 25%.

The results obtained from EXAFS data such as this can indicate a strong correlation with other techniques used for obtaining the structure of a particular material. However, it does only consider the structure relative to the specified atom studied[20].

3.5 Miscellaneous Techniques

A number of other techniques were used to assist with the characterisation of the materials prepared. Thermal gravimetric analysis was carried out using either a Netzsch STA449C TGA/DSC-TGA/DTA or a TA Instruments SDT2960 TGA/DSC. Solution phase ^{1}H NMR experiments were conducted on either a Varian Gemini 2000 or a Bruker Avance 300, with a Bruker AM300 used to record ^{29}Si data. X-ray powder diffraction was carried out using a Stoe Stadi-P Diffractometer. Mass spectroscopy was recorded on a VG Autospec using electron impact ionisation and X-ray fluorescence measurement recorded using a Spectro X-Lab Energy Dispersive Polarised X-ray Fluorescence (EDPXRF) Analyser.

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4 Preparation and Characterisation of POSS Copolymers

4.1 Aims and Objectives

First synthesised by Harrison and Kannengiesser[1] copolymers based upon cubic silsesquioxane building blocks, are readily obtained by means of a platinum catalysed hydrosilation reaction between vinyl- and hydrido- silane species. The synthesis and characterisation of these materials has been attempted, with particular emphasis upon the product arising from the reaction of octavinylsilsesquioxane and octahydridosilsesquioxane.

4.2 Hydridosilsesquioxanes

4.2.1 Introduction

The term hydridosilsesquioxane applies to a number of different possible conformations, each possessing the general formula $(HSiO_{3/2})_{2n}$, where n has a lowest possible value of 3. These compounds were first observed by Müller and co-workers in 1959[2]. However, their reported yields were initially very low (less than 1%). The preparation of these compounds has since been improved upon, firstly by Frye and Collins[3] and then more recently by Agaskar[4]. The method described by the latter enables the possibility of preparing pure samples of octahydridosilsesquioxane (***figure 4.1***).

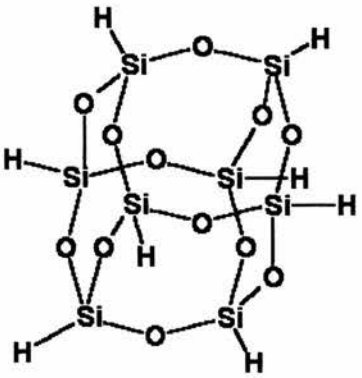

Figure 4.1: Structure of octahydridosilsesquioxane, $(HSiO_{3/2})_8$

In addition to the formation of the above species, the reaction allows for the possible formation of larger units. Most notable of these is decahydridosilsesquioxane, $(HSiO_{3/2})_{10}$. Structurally it differs from the octahydridosilsesquioxane by possessing a double-five ringed structure, therefore having D_{2h} symmetry as opposed to the cubic O_h.

Both of these two products can be formed via the same procedure based upon the hydrolysis of trichlorosilane. However, the conditions need to be carefully controlled to prevent rapid condensation and the formation of an insoluble polymeric material. This is obtained by the employment of a biphasic system, thereby resulting in a minimal contact of the reactant silane with the small quantity of water present. The silane is added slowly over a period of time thereby cyclisation is increasingly favoured.

4.2.2 Synthesis

Adapting the method described by Agaskar[4], a mixture of iron (III) chloride (anhydrous, 50g), concentrated hydrochloric acid (20ml), methanol (40ml), *n*-hexane (350ml) and toluene (50ml) were stirred together in a one litre three necked flask fitted with a condenser. Over a period of about seven hours a solution of trichlorosilane (25ml) in *n*-hexane (150ml) was added dropwise, the rate being controlled by using a tubing pump (operating at approximately 0.5ml/min). When addition of the silane had been completed, the solution was allowed to continue stirring overnight.

Following stirring the organic layer was decanted off, allowing some of the yellow solid which was suspended within the liquid to be removed, and dried by stirring in the presence of potassium carbonate (14g) and calcium chloride (10g) for a period of four hours. The waste solids were then removed by filtration.

This resulting solution of *n*-hexane and toluene was partially evaporated using a rotary evaporator until a white solid started to precipitate out. At this point the solid is redissolved, with the addition of additional *n*-hexane if required. Then allowed to crystallise out of solution whilst cooled at -30°C. The crystals formed from this were white needles and recovered by filtration, then washed with *n*-hexane. After being allowed to dry at room temperature, the resulting solid was generally found to weigh approximately 2g, corresponding to a yield of approximately 20%.

The washings recovered from this previous stage could then be further reduced by evaporation as before, and a further sample of the white solid was obtained in lower yields.

The reaction could be repeated immediately by reusing the remainder of the iron chloride, with the addition of fresh hydrochloric acid together with the organic solvents. This could be repeated several times, although never more than four consecutive repetitions were conducted. For the final batch prepared the whole biphasic mixture was filtered, before a separating funnel was used to remove the inorganic layer.

Any product obtained was allowed to dry in air after filtration. For these materials drying under vacuum was not used, this was due to the tendency of hydridosilsesquioxanes to sublime at low temperatures under such conditions.

4.2.3 Analysis

All samples produced resulting from the above procedure were examined by ^{1}H NMR spectroscopy ($CDCl_3$, 300MHz), which was able to identify the two potential products. In both instances these only possess a single peak with a chemical shift around 4.2ppm, the deca- product having a slightly higher shift than the octa- equivalent. Crystals which precipitated out after the first evaporation of the solvent generally showed only one peak, which can be assigned to octahydridosilsesquioxane. If two peaks were observed the size ratio between them enables a determination to be made as to the relative quantities of the different hydridosilsesquioxanes.

Infra red spectroscopy was additionally used in some cases to characterise the octahydridosilsesquioxane. The IR spectrum consisted of (cm^{-1}, KBr disc) 2295 (s), 1115 (s), 905 (w), 855 (s), 565 (w), 535 (w), 460 (m). This is in close agreement with the result obtained by Frye and Collins[3].

4.2.4 Observations

If the product of this reaction was found to be a mixture of both the octa- and decahydridosilsesquioxanes, it was possible to try to remove the latter through washing again with *n*-hexane, it being slightly more soluble in this solvent in comparison with the cubic product.

This reaction could also be scaled both up or down as required. The scale used here proved to be the most convenient, leading to a yield which was significantly large enough to use as a reactant in subsequent reactions.

4.2.5 Alternative Synthesis

In addition to the synthesis described above, a second alternative preparation outlined by Desu and co-workers[5] was attempted as a possible preparation for these compounds. Unlike the previous method, toluene was not present within the reaction mixture, instead *n*-hexane was used as the sole solvent.

Iron (III) chloride (anhydrous, 50g), concentrated hydrochloric acid (20ml), methanol (40ml), sodium dodecylsulphate (1.5g) and *n*-hexane (400ml) were mixed together forming a biphasic system. To this a solution of trichlorosilane (20ml) in *n*-hexane (200ml) was added from a dropping funnel over a period of approximately six hours.

The organic layer was decanted off and dried with potassium carbonate (14g) and calcium chloride (5.5g) for four hours. The solids were then filtered off and the product recovered using the previous method above.

The yield obtained by this alternative method was consistently lower than for the previous preparation of octahydridosilsesquioxane, based on trichlorosilane used a yield of no higher than 10% conversion was obtained after several attempts.

4.3 Octavinylsilsesquioxane

4.3.1 Introduction

Olsson[6] initially studied the condensation reactions of trichlorovinylsilane during the 1950's, with the reaction further refined at a later date by Voronkov and co-workers[7,8]. They investigated variables such as the volume of water present within the reaction mixture and its effects upon the silsesquioxanes formed. They successfully managed to obtain both octavinylsilsesquioxane (***figure 4.2***) as well as the deca- equivalent.

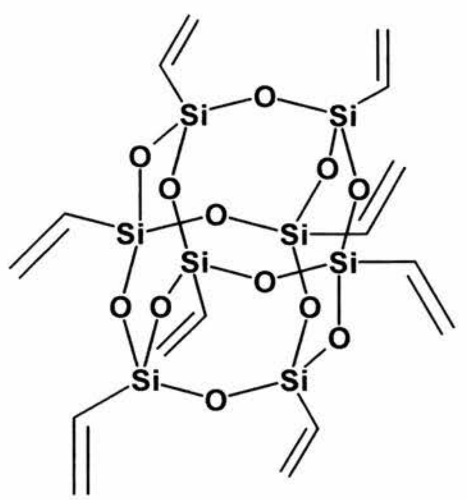

Figure 4.2: Octavinylsilsesquioxane

It is from the method of Voronkov that the preparation used here has been derived. As the condensation of trichlorovinylsilane proceeds at a significantly slower rate than in the case of trichlorosilane, a similar biphasic reaction system need not be employed. Even in the presence of larger relative quantities of water, the formation of a polymeric species in preference to discrete monomeric units is disfavoured.

4.3.2 Synthesis

A mixture of acetone (1,500ml) and distilled water (450ml) was cooled with an ice bath. To this, whilst continually stirring, trichlorovinylsilane (40ml) was added slowly using a dropping funnel. Upon completion of this addition, the reaction flask was sealed and left to stir for a period of up to two months.

Over this period a white power gradually precipitated out of solution.. This was obtained by filtration before being washed with acetone previously cooled in an ice bath. Following this the product was dried under vacuum (80°C, 2 hours, 0.2mmHg). The resulting yield obtained tended to be approximately 10g, which represents a percentage yield based on trichlorovinylsilane used of 40%.

4.3.3 Analysis

All samples were analysed using ^{1}H NMR spectroscopy ($CDCl_3$, 300MHz), which showed a single multiplet centred around 6.0ppm. This indicates the presence of the vinyl group, as expected, within the product.

The most suited method to determine that the product was indeed the cubic octavinylsilsesquioxane was mass spectroscopy. The solid produced from this reaction showed the molecular ion peak to be at m/z 632, which is to be expected from octavinylsilsesquioxane. The peaks at m/z 605 (loss of vinyl group) and m/z 577 (loss of vinyl group and attached silicon atom) also indicate this to be the cubic silsesquioxane.

Infra red spectroscopy was carried out on several of the samples showing (cm^{-1}, KBr disc) 3065 (w), 2960 (w), 2355 (w), 1605 (m), 1410 (m), 1280 (m), 1105 (s), 1005 (m), 970 (m), 775 (m), 580 (s), 460 (w). This also shows a strong correlation between the observed absorbances for the silsesquioxane core recorded by Frye and Collins[3,9], together with addition absorbances detected for the vinyl groups noted by Voronkov and co-workers.

4.3.4 Observations

Similarly to the preparation of octahydridosilsesquioxane, this reaction procedure could be conducted on a scaled up or down basis. Using double the quantities of the reactants involved resulted in a yield comparable to the 40% conversion observed earlier.

The duration for which the silane was allowed to condense for was also subject to some variation. The two months stated represents a good compromise between obtaining the product relatively quickly whilst maximising the potential yield. By removing the precipitate slightly earlier or later the yield would be altered accordingly.

Reuse of the acetone solvent also proved successful. To acetone (2250ml, recycled from an earlier experiment) additional acetone (375ml, previously unused) and distilled water (450ml) were cooled prior to the addition of trichlorovinylsilane (40ml). The reaction was then conducted using the method described previously.

4.3.5 Alternative Synthesis

The preparation of octahydridosilsesquioxane has been carried out via the method of Agaskar[4]. An attempt was made to apply this reaction using trichlorovinylsilane instead of the trichlorosilane used in that procedure.

In a round bottomed flask iron (III) chloride (anhydrous, 50g), concentrated hydrochloric acid (20ml), methanol (40ml), *n*-hexane (350ml) and toluene (50ml) were mixed together forming a biphasic mixture. To this a solution of trichlorovinylsilane (24ml) in *n*-hexane (150ml) was added dropwise from a dropping funnel.

This was allowed to stir overnight before the organic layer was separated off and stirred together with potassium carbonate (14g) and calcium chloride (10g) for four hours. After the solid was filtered off, the solvent was removed using a rotary evaporator. The soluble residue was recrystallised from an acetone/water mixture (3:1, 100ml). This resulted in 0.662g of a white solid being deposited.

Comparison of the material produced as a result of this procedure to the product of the original method was conducted by thin layer chromatography (*n*-hexane used as solvent). This indicated that the products of the two methods were identical. However, the yield obtained was significantly lower, this reaction resulting in 4.4% octavinylsilsesquioxane formed in relation to the mass of trichlorovinylsilane used.

4.4 Silsesquioxane Copolymers

4.4.1 Introduction

The silsesquioxane cubes as already noted possess an organic group on each of the eight silicon atoms present within the structure. To use the functionality these possess in order to form polymers is therefore a possibility. Using two individual types of POSS cubes, the octahydrido- and octavinyl- structures, through a hydrosilation reaction it is possible to link the two species together, with the eventual aim to use these as catalytic supports.

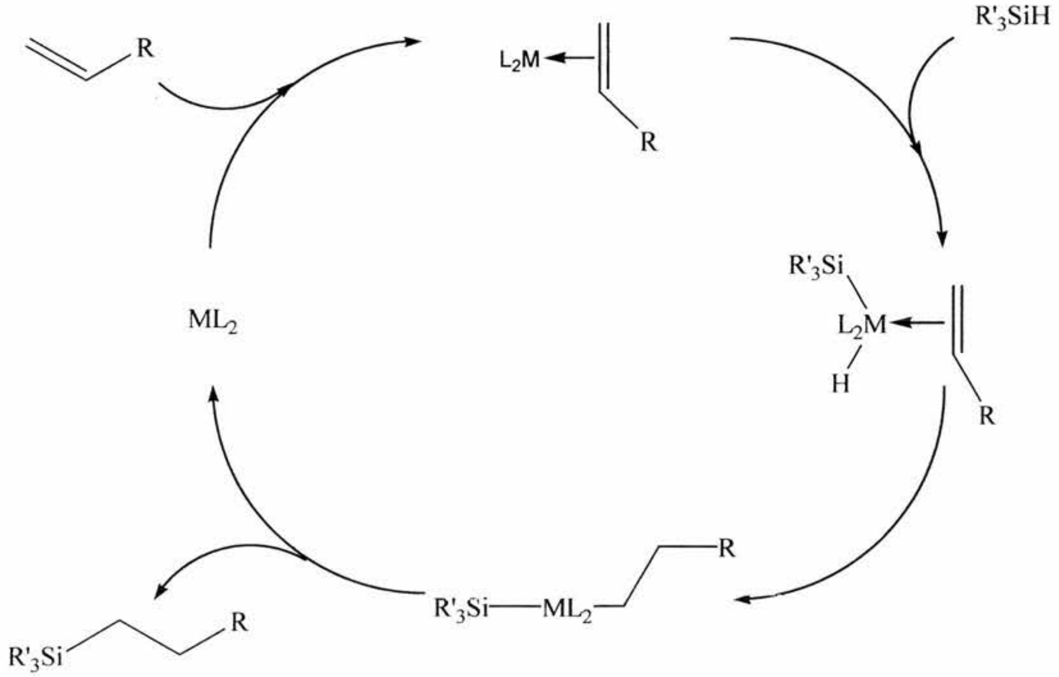

Figure 4.3: Schematic of catalytic hydrosilation reaction

The hydrosilation[10] reaction (***figure 4.3***) is in this case catalysed by a platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylenes, which is also referred to as Karstedt's catalyst. Due to the presence of the bulky silsesquioxane cages, it is to be expected that the reaction will proceed as a terminal addition to the vinyl group, as this position is the least hindered.

4.4.2 Synthesis

Based upon the method of Laine and co-workers[11], octahydridosilsesquioxane (0.4g) and octavinylsilsesquioxane (0.6g) were placed in a Schlenk tube, and purged with argon three times. Dry toluene (30ml) was added by syringe, before the solids allowed to dissolve whilst being stirred. After all of the material had been dissolved, the solution was cooled down to -77°C. After purging with argon a further three times, the solution was allowed to warm up to room temperature. Following further cooling to 0°C, a solution of Karstedt's catalyst (0.1ml, 3%wt solution in xylenes) was added.

The solution was left stirring at room temperature until gelation occurred. Typically this occurred overnight. The gel was removed by filtration, and any excess catalyst removed by washing with toluene. The solvent was removed firstly by leaving to dry slowly by exposure to the atmosphere, before further drying under vacuum (80°C, 2 hours, 0.2mmHg). After the resulting copolymer was dried, the material was crushed, the yield of which was typically found to be almost 100%, based upon the total mass of the two monomeric silsesquioxanes used.

4.4.3 Analysis

X-ray powder diffraction was carried out to observe if the structure possessed any long range order. It was clear that the pattern obtained (***figure 4.4***) shows no sharp peaks, which indicates that the structure is amorphous, with no long range order in the system.

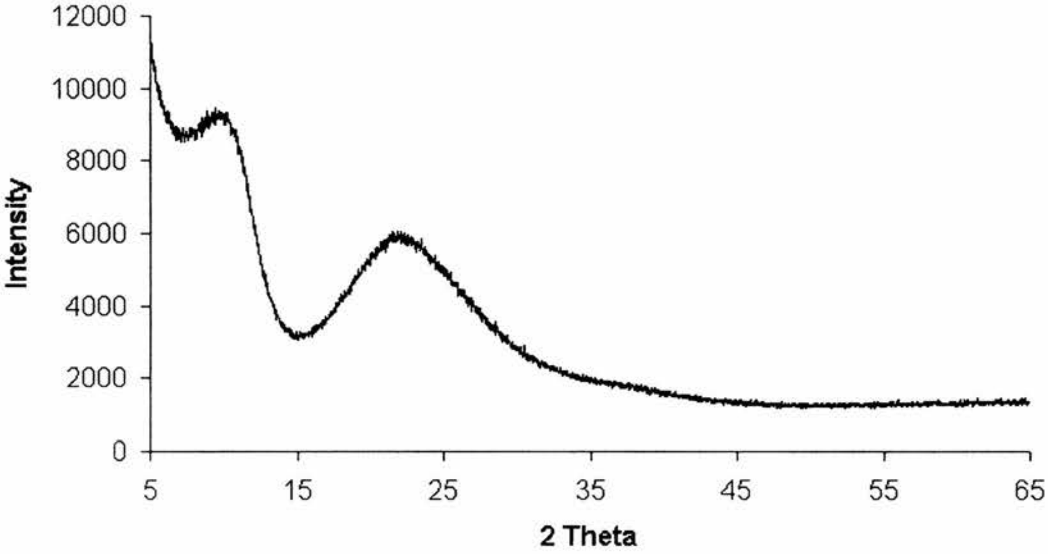

Figure 4.4: Powder x-ray diffraction pattern of POSS copolymer

The infra red spectrum of the copolymer was recorded as (cm^{-1}, KBr disc) 3425 (w), 2960 (w), 2355 (w), 1410 (w), 1115 (s), 885 (m), 765 (m), 705 (w), 565 (m).

4.4.4 Observations

On the occasional instance where this reaction failed to produce any gelation overnight, addition of extra Karstedt's catalyst (0.1ml, 3%wt solution in xylenes) was used in an attempt to promote the reaction further. The problem can be attributed to degradation of the catalyst with time, as when recently opened gelation inevitably occurred relatively quickly.

4.4.5 Alternative Synthesis

As a slight variation on the above procedure, it is also possible to prepare the copolymer at higher temperatures. In a round bottomed flask fitted with a condenser octavinylsilsesquioxane (0.3g) and octahydridosilsesquioxane (0.2g) were dissolved in dry toluene (20ml). The system was sealed and purged with argon, before addition of Karstedt's catalyst (0.1ml, 3%wt solution in xylenes) was added. The mixture was stirred under an atmosphere of argon whilst being heated to a temperature of 80°C, and left until gelation was observed. The copolymer was then filtered and dried as previously.

4.5 Solid State NMR Studies Of POSS Copolymers

4.5.1 Introduction

Whilst it has been clearly shown that these copolymers possess no long range ordering, owing to the regular inorganic cages within the material, techniques that look at a much smaller range, such as solid sate NMR, will be of use. These compounds contain two suitable nuclei for this; ^{29}Si and ^{13}C.

4.5.2 ^{29}Si NMR

The silicon NMR spectrum of the POSS copolymer shows three separate peaks (***figure 4.5***). They can be assigned to the three silicon environments to be expected within the material. The peak observed at -66ppm is that attached to the organic bridging group formed during polymerisation, whilst the other two peaks found at -80ppm and -84ppm are as a result of silicon atoms attached to the unreacted vinyl and hydrido groups respectively.

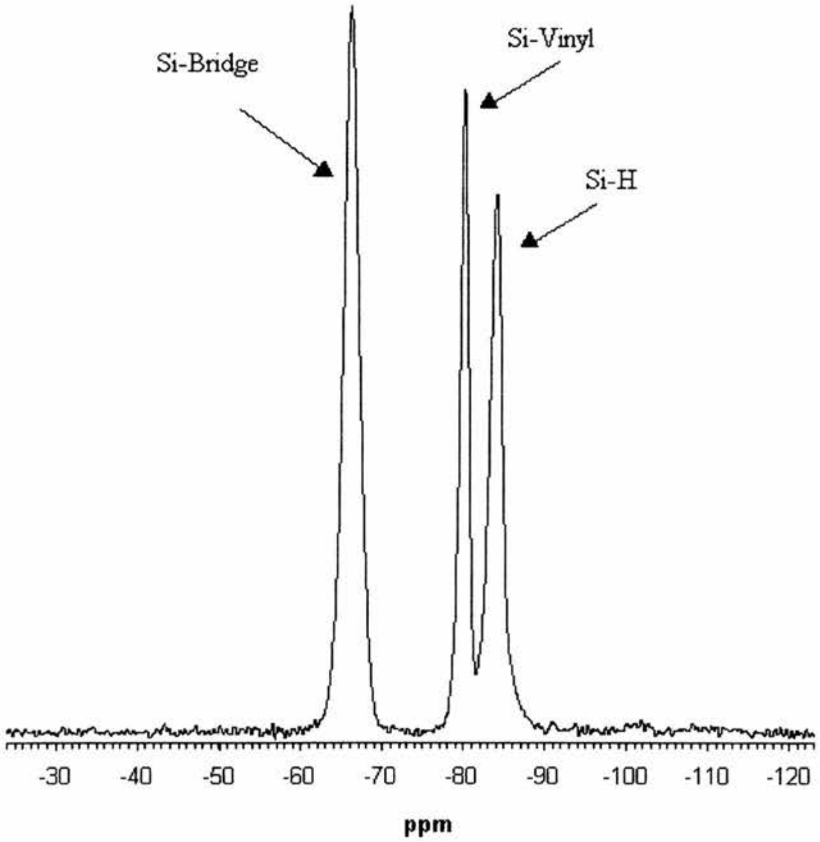

Figure 4.5: ^{29}Si MAS NMR recorded for POSS copolymer, showing peak assignments

4.5.2 ^{13}C NMR

The carbon NMR spectra of the silsesquioxane copolymer (***figure 4.6***), reveals three peaks at 135ppm, 129ppm and 3ppm. The latter peak corresponds to the carbon atoms found within the bridging group, where the polymerisation has successfully occurred. The remaining two peaks arise from the vinyl groups that have not been involved with the polymerisation process. The terminal carbon is seen at 129ppm, with the carbon bonded to the silicon in the central core appearing at 135ppm.

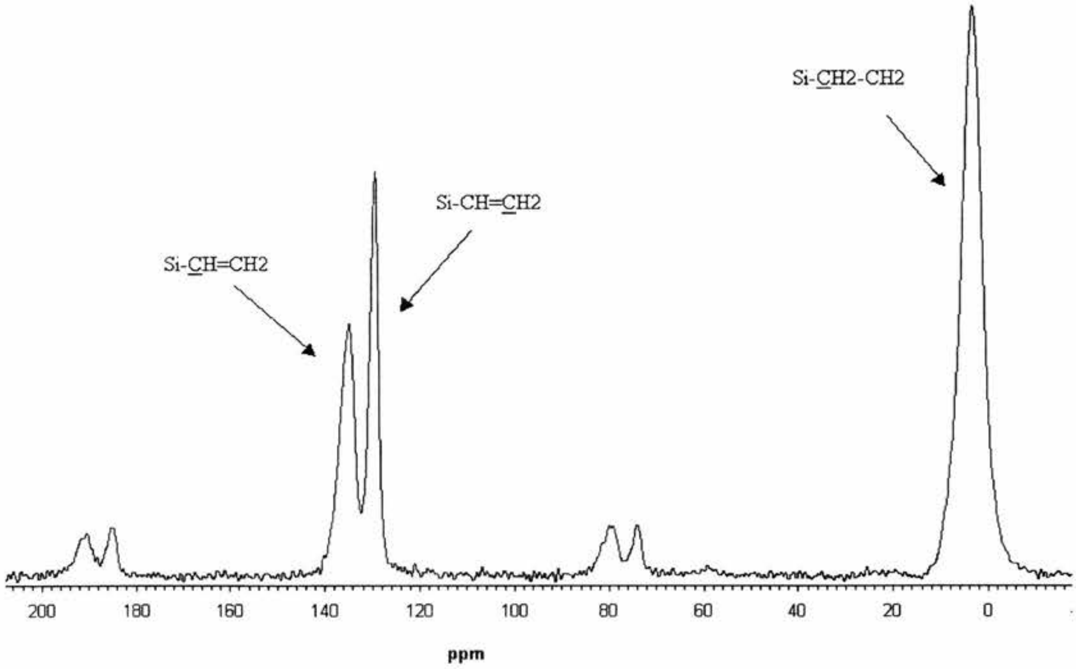

Figure 4.6: ^{13}C MAS NMR, with assignments of POSS copolymer

The satellite peaks observed are likely to be spinning side bands. It is likely these arise from the vinyl monomers having a higher chemical shift anisotropy than the ethylene bridge carbons, therefore faster spinning would be needed to remove these side bands.

4.6 Nitrogen Adsorption Studies Of POSS Copolymers

4.6.1 Introduction

The surface area and pore size can be derived from nitrogen adsorption BET experiments. To be potentially useful as catalytic supports, it is a requirement that these materials should have a high surface area, together with pore sizes that allow potential reactants to pass through the framework. Due to the copolymers lacking a crystalline structure, the pores found within the structure are likely to vary, and cannot be easily calculated from a predicted conformation.

Calculating the surface area of the compounds is the major factor in characterising the prepared silsesquioxane copolymers. Providing the polymerisation has been completed successfully, all the copolymers prepared through a specific method, should exhibit a relatively small range of surface areas.

4.6.2 Experimental

Taking care to ensure all samples were thoroughly ground before testing, approximately 30mg was used on each occasion. For purposes of calculating only the surface area of the copolymers, only a limited number of points needed to be obtained. The samples were heated under vacuum at 125°C prior to recording data. Starting at a pressure of 10mbar nitrogen, results were recorded at 50mbar intervals until exceeding 500mbar, whilst keeping the sample cooled with liquid nitrogen to 77K. For the purposes of consistently assigning the surface area, the slope used for calculating the BET[12] surface area was used only between relative pressures (p/p_o) of 0.05 and 0.20.

To view the adsorption and desorption of the compounds, data at a wider range of pressures was used, still maintaining a temperature of 77K with liquid nitrogen as a coolant. Adsorption starting at a pressure of 10mbar, and following an initial step size of 20mbar, until reaching 870mbar. Desorption was started with a pressure of 850mbar, decreasing the pressure in 50mbar steps, before recording a final reading at 30mbar.

All points recorded were taken with a confidence level set at 95%, using a time out of one hour, where the mass recorded has not completely stabilised These constraints allowed sufficient time for most points taken to equilibrate, although those that failed to did not show any significantly anomalous results.

4.6.3 Analysis

The surface areas obtained using this method resulted in reasonably consistent figures obtained from a number of different samples of the silsesquioxane copolymer. From a series of ten samples, the lowest recorded value was noted to be 399m^2/g, with the upper limit of 597m^2/g. The other results showed a relatively even spread throughout this range. The mean value for all ten was calculated to be $500m^2/g$.

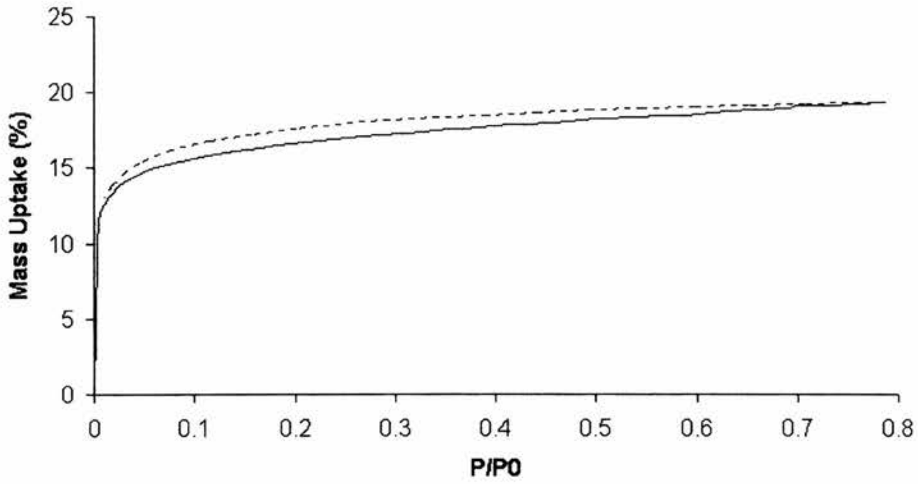

Figure 4.7: Nitrogen adsorption and desorption isotherm for silsesquioxane copolymer

The isotherm seen for the adsorption and then desorption of nitrogen onto the copolymer (***figure 4.7***), reveals an adsorption isotherm of type I[13], with only a very slight hysteresis on desorption. This would suggest that the pores within the structure are only slightly hindered by having a narrower neck.

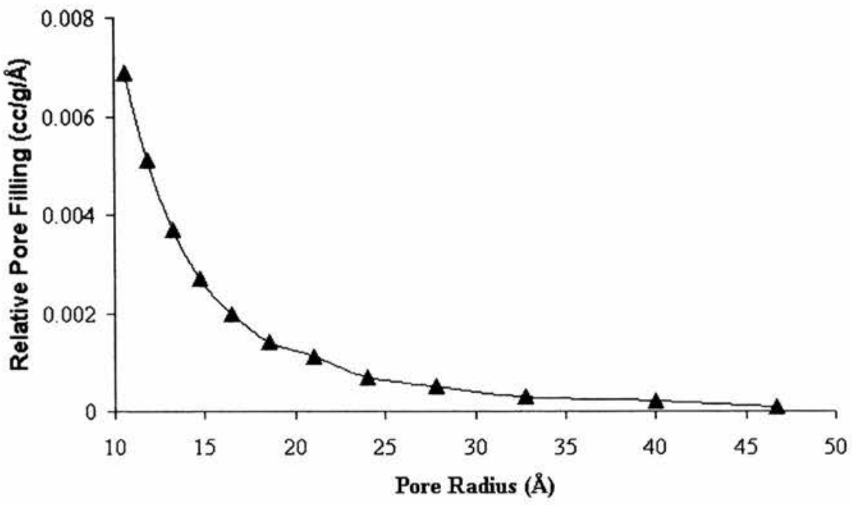

Figure 4.8: Pore size distribution of silsesquioxane copolymer

Cylindrical BJH treatment[14] (***figure 4.8***) of the adsorption/desorption data using the theory of de Boer[15,16], shows the relative quantity of pore radii to be highest around 10Å, with a continual decrease with increasing pore radius. A ten fold decrease in relative quantity of these pore radii is observed from 10Å to 25Å, with the amounts of pores with radii larger than these figure is very low.

4.7 Adsorption Of Gases Other Than Nitrogen

4.7.1 Introduction

The adsorption of nitrogen is very useful for gaining information regarding the nature of the substance onto which it is adsorped. However, adsorption does not have to be limited to only the use of this gas, and others can help to give an indication of the surface of the copolymer.

As a large molecule cyclopentane in comparison to nitrogen, then the behaviour upon adsorption could be expected to differ accordingly. Although the pore size distribution for the copolymer above with nitrogen only records values above 10Å, it is not unfeasible that some adsorped nitrogen would be in sites it would be impossible for a cyclopentane molecule to fit cleanly into, as it is relatively inflexible.

4.7.2 Experimental

Unlike nitrogen adsorption, the sample was cooled by water to a temperate of 5°C, with readings taken at an initial pressure of 0.1mbar, 0.25mbar, then 0.25mbar intervals up to 1mbar, 2mbar from this point rising to 5mbar, before points at 5mbar to 20mbar, finally increasing in step sizes of 10mbar up to 160mbar. At this high point this corresponds to a partial pressure of almost 0.9, which is comparable to the point reached for adsorption and desorption of nitrogen.

4.7.3 Analysis

Using the same relative pressure values to calculate a surface area for cyclopentane adsorption resulted in a significantly lower surface area for the silsesquioxane polymer. For a sample initially observed to possess a surface area of 475m^2/g, which is fairly typical of the material using nitrogen, the corresponding figure with cyclopentane was only 323m^2/g.

This figure is as expected lower than obtained with nitrogen, but it does indicate that the majority of pores are sufficiently large enough to accommodate more bulky molecules, such a this which is approximately 5Å in diameter. Although capable of fitting into the pores, it's bulk would hinder attempts to get it to cover as much of the available surface as nitrogen.

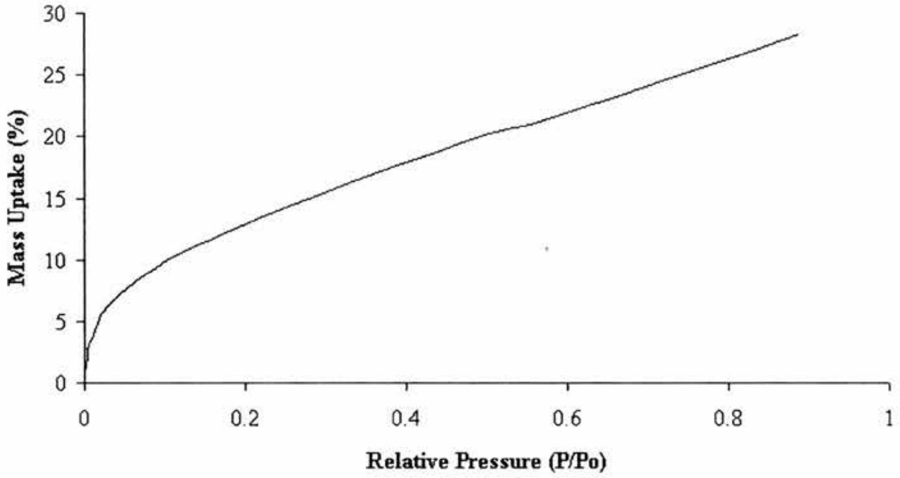

Figure 4.9: Isotherm obtained from adsorption of cyclopentane on silsesquioxane copolymer

The isotherm (***figure 4.9***) is of type I[13], which is the type observed with nitrogen, which would indicate a similar adsorption pattern, again suggesting that the pores do not feature a narrower bottleneck opening, which could potentially hinder larger molecules such as this. The curve does not level off as the cyclopentane can continue to adsorb onto the molecules already upon the surface.

4.8 Thermal Behaviour Of Silsesquioxane Copolymers

4.8.1 Introduction

With the intention that these polymers might have possible applications within the field of catalysis, the thermal behaviour of the copolymers is therefore of importance. Thermal gravimetric analysis was used to determine the effects of heating upon the materials under atmospheres of flowing nitrogen and oxygen.

4.8.2 Experimental

For each of the two gases used (oxygen and nitrogen), a sample of approximately 20mg, was allowed to heat up at a rate of 10°C per minute rising to 800°C. The temperature was then held constant for a further 15 minutes. A sample of alumina was used to provide a reference.

4.8.3 Oxygen

The TGA recorded for the sample heated up under oxygen (***figure 4.10***) shows only a minimal weight loss up to 170°C, due to a small residual amount of water present, following this however a slight increase is observed. The weight gain is equivalent to 1.5% increase over the initial mass, and can be attributed to initial process of oxidation of the copolymer.

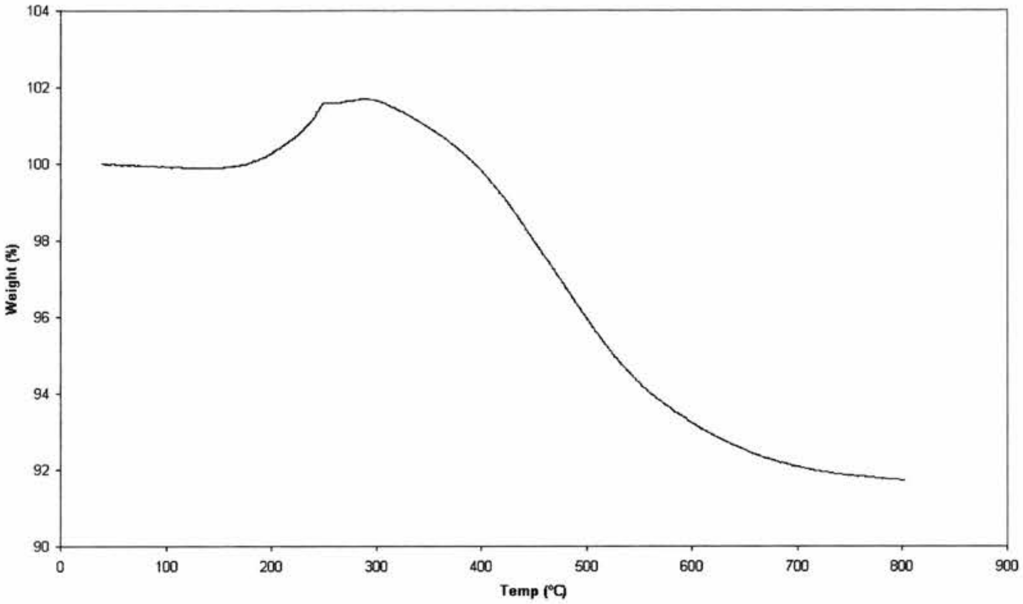

Figure 4.10: TGA obtained from sample of POSS copolymer under oxygen

As heating continues the weight loss is observed to decrease, as the organic bridging groups are lost in the form of carbon dioxide and water. The loss of these outweighs the additional oxygen as the silicon present is oxidised to silica.

The overall mass loss was seen to be 8.3% relative to the initial weight of the sample. This corresponds well with the theoretical value expected of 9.1%. This value is derived from the equation:

$$Si_{16}O_{24}C_{16}H_{32} + 26O_2 \rightarrow Si_{16}O_{32} + 16CO_2 + 16H_2O$$

The formula $Si_{16}O_{24}C_{16}H_{32}$ represents one unit of the copolymer, and is equivalent to the combined formula of one octahydridosilsesquioxane molecule and one octavinylsilsesquioxane molecule, which is valid for the copolymer due to their being no overall loss or gain of atoms during polymerisation. The molecular mass of this unit is calculated to be 1057.8, with the corresponding figure for the sixteen SiO_2 units a combined 961.3.

4.8.4 Nitrogen

Unlike the TGA recorded for oxygen, that seen under nitrogen (***figure 4.11***) shows the copolymer to be thermally stable to a temperature of about 400°C. This is significantly higher than recorded under oxygen, which started to show signs of oxidation around 170°C.

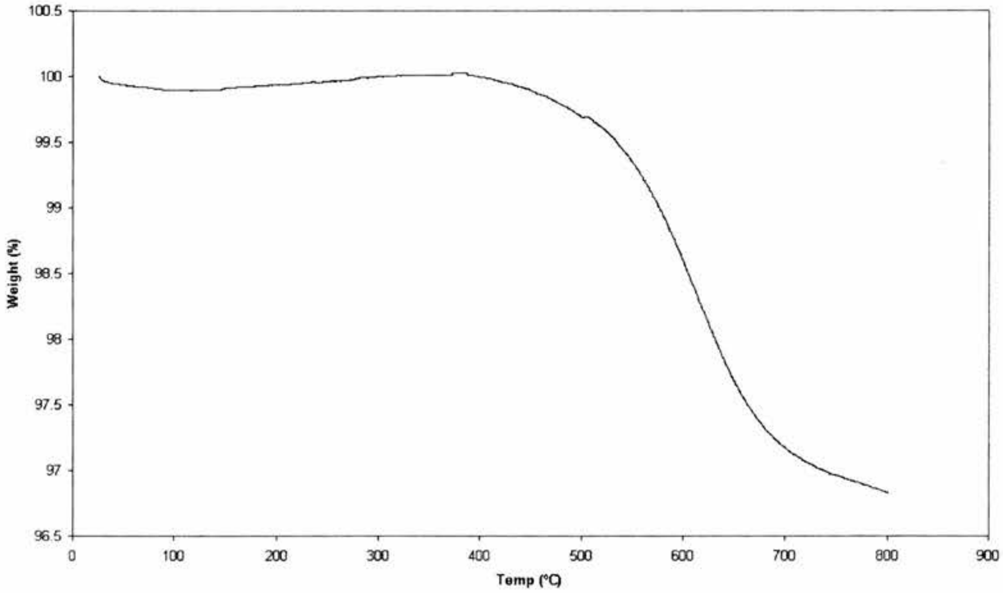

Figure 4.11: TGA obtained from a POSS copolymer under nitrogen

After this point the compound starts to degrade, losing the organic groups present. It is not likely to be excess solvent due to the sample run under oxygen showed a weight loss as expected if converted to silica, leaving too small a margin for significant quantities of solvent to remain, in this case over 3% of the weight is lost by heating to 800°C.

4.9 Calcination Of Silsesquioxane Copolymers

4.9.1 Introduction

Thermal gravimetric analysis has shown that upon calcination the copolymer loses the organics present within the structure as it is heated. That experiment simply looked at the mass of the material over time. Whilst the initial structure might not be retained as it undergoes the calcination, it is plausible that the structures found after calcining will still exhibit a high degree of porosity.

4.9.2 Experimental

Samples of silsesquioxane copolymer (0.3g, preparation above) were calcined under a steady flow of oxygen to temperatures of 150°C, 200°C, 250°C and 450°C. These values are taken from the TGA obtained for the sample as being before oxidation occurs, just after oxidation occurs, when the mass of the compound is at it's highest and midway through the weight loss. All samples were heated at a rate of 10°C/min, and held at the appropriate temperature for 200 minutes.

4.9.3 Analysis

The surface area for all samples was calculated from nitrogen BET analysis (***table 4.1***) , including the figure for the copolymer used before calcination for comparison. Prior to the onset of oxidation the surface area recorded in comparison to the initial sample is sufficiently close enough to be considered unchanged as expected.

Temp Calcined (°C)	Surface Area (m2/g)
Not calcined	539
150	524
200	448
250	441
450	356

Table 4.1: Surface area of calcined silsesquioxane copolymers

As calcination proceeds it can clearly be observed that the surface area reduces, although even by 450°C, the surface area is still reasonably high.

4.10 Mixed Ratio Silsesquioxane Copolymers

4.10.1 Introduction

In their investigation into the polymerisation of combinations of four differing silsesquioxane monomeric species, Laine and co-workers[11] reported upon the degree of polymerisation. Likewise, the results obtained earlier from ^{29}Si NMR solid state spectroscopy, show that in the reaction between octavinylsilsesquioxane and octahydridosilsesquioxane only occurs with only an approximate average of half the organic groups being converted into the bridging chain, due to the steric problems encountered by the bulky inorganic core.
Additionally, as shown by x-ray powder diffraction, the copolymer is an amorphous solid. Therefore, with a large level of randomness in the structure, slight alterations in the composition should hopefully have minimal effect upon the overall properties, in particular the surface area of the materials and the preparation time involved.

This opens up several possibilities involving the use of changing the quantity of vinyl and hydrido groups present relative to each other in the reaction, yet still being able to form a copolymer. The initial step tried was to alter the ratio between the two reacting silsesquioxanes.

4.10.2 Synthesis

The preparation for the materials followed the same method outlined for the synthesis of the silsesquioxane copolymers described earlier. Octavinylsilsesquioxane and octahydridosilsesquioxane (***table 4.2***) were dissolved in dry toluene (15ml). The resulting solution was cooled to -77°C. When reaching this point, it was degassed under argon, and then allowed to warm up to room temperature. After cooling again to 0°C, and Karstedt's catalyst (0.1ml, 3%wt solutions in xylenes) added. The reaction was then allowed to proceed, being allowed to warm up again to room temperature, until a gel formed. This was removed by filtration, washed with toluene, and dried initially in air at room temperature and subsequently under vacuum (80°C, 2 hours, 0.2mmHg).

Polymer	Vinyl (g)	Hydrido (g)	Ratio (molar H:V)
A	0.37	0.13	0.5:1
B	0.33	0.17	0.75:1
C	0.30	0.20	1:1
D	0.29	0.21	1.125:1
E	0.25	0.25	1.5:1
F	0.22	0.28	1.875:1

Table 4.2: Quantities of octavinylsilsesquioxane and octahydridosilsesquioxane used in copolymerisation reaction

With the exception of polymer A, all reactions were found to gel overnight. Addition of additional Karstedt's catalyst (0.1ml) after three days failed to show any evidence of gelation occurring within an additional two days. Upon repetition of this particular experiment the reaction mixture left to stir for forty days. When examined after this period it was discovered a gel had been formed.

4.10.3 Analysis

Unlike the polymers obtained from the copolymers obtained from the reaction of equimolar amounts of the two silsesquioxane monomers (one of which was prepared here for comparison), these samples were only analysed by BET surface area. Excepting polymer A, the gelation period observed was comparable to those found for copolymers prepared with a 1:1 ratio of the two different monomeric cubes. The surface areas recorded for these polymers varied slightly (***table 4.3***), as has always been observed, yet in all cases was noticed to be of a high porosity.

Polymer	BET Surface Area (m^2/g)
A	355
B	224
C	478
D	464
E	600
F	591

Table 4.3: BET surface area measurements for copolymers with varying ratios of monomeric species used

In all cases the observed surface areas from these copolymers indicate that they are highly porous, and approximately within the range that might be expected for the 1:1 ratio copolymers, although with a higher octavinylsilsesquioxane content resulted in a slightly lower surface area than for those prepared with relatively higher octahydridosilsesquioxane content.

Thermal gravimetric analysis conducted upon copolymer F under oxygen (***figure 4.12***), using the same conditions (heating up to 800°C at 10°C per minute) as used for the 1:1 ratio copolymer. Similarly to that particular copolymer, a slight weight loss was observed to 170°C, before a slight increased as oxidation starts to occur.

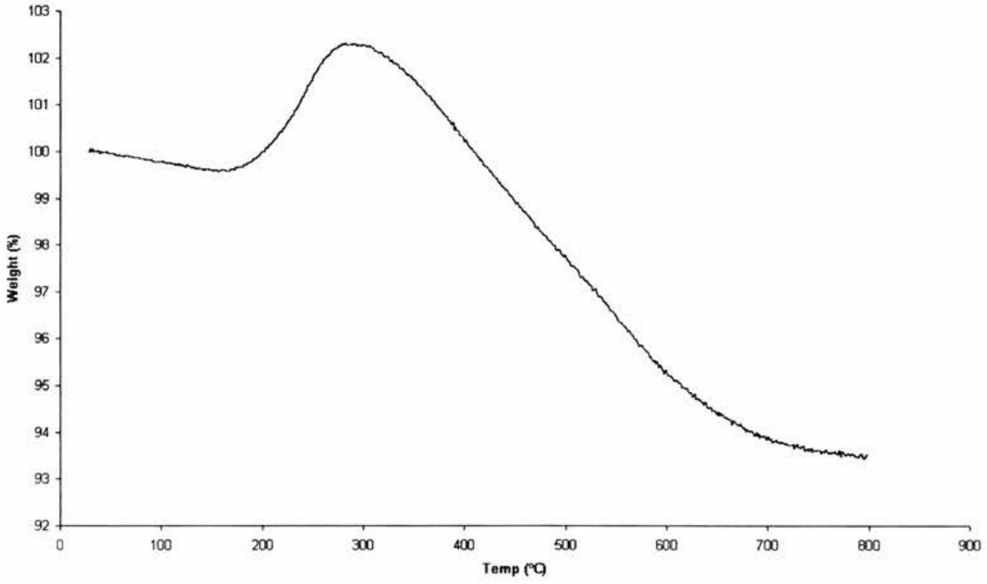

Figure 4.12: TGA obtained from mixed ratio POSS copolymer F under oxygen

At 800°C a weight loss of 6.5 % was observed, as might be expected this is lower than observed previously, as there is a smaller quantity of organics present in this copolymer. The equation for the reaction undergone in this case can be simplified to assume $Si_{23}O_{34.5}C_{16}H_{39}$ (equivalent to one octavinylsilsesquioxane and 1.875 octahydridosilsesquioxanes) converts to $Si_{23}O_{46}$.

However this only equates to an expected weight loss of 3.3%, which is clearly different to the experimental value. The most likely explanation for the difference is that due to the large excess of octahydridosilsesquioxane it is not possible for all to be involved with copolymerisation and so any excess left unreacted is removed when the sample is washed. This would then leave an increased organic content in the copolymer.

4.10.4 Observations

Unless as already noted, the alterations used within this reaction resulted in the reaction proceeding with no recognisable difference to the unchanged ratio copolymer, only when relatively large differences in the ratio of monomers used was a changed observed, but the TGA analysis on one of these samples would suggest that not all of the monomers are used in the polymerisation.

4.11 Mixed Octa-/Decahydridosilsesquioxane Based Copolymers

4.11.1 Introduction

As observed, and hypothesised, during the preparation of copolymers with varying ratios of octahydrido- and octavinylsilsesquioxanes, it is clear that there is some degree of leeway possible during the preparation away from the standard copolymer formation that will still allow the resulting product to have a similar degree of porosity. To follow this another possible simple modification has been tried, in this case using a mixture of octahydrido- and decahydridosilsesquioxane instead of a pure sample of the former.

As an x-ray powder diffraction has shown the materials to have an amorphous structure, it follows that by introducing monomers which are relatively similar in size to the cubic units, will result in a similar copolymer. Specifically, the preparation of octahydridosilsesquioxane results in the formation of a quantity of decahydridosilsesquioxane. Instead of consisting of two double four rings of silicon atoms, this material has two double five rings. Whilst it is a relatively simple process to obtain the cubic product from this procedure, if this can successfully be used without removing the major decahydridosilsesquioxane, which contains the same $HSiO_{3/2}$ units, it will effectively increase the useful yield of the hydridosilsesquioxane preparation.

4.11.2 Synthesis

The preparation for these polymers followed the preparation used for the reaction to prepare the copolymers containing only the octahydridosilsesquioxane. Into a Schlenk tube octavinylsilsesquioxane (0.6g) and a mixture of hydridosilsesquioxanes (0.4g, 30% by weight decahydridosilsesquioxane). Dry toluene (25ml) was added, and the solution degassed at -77°C three times with argon, before being allowed to warm up to room temperature. Karstedt's catalyst (0.1M, 3%wt solution in xylenes). The solution was stirred until gelation occurred, before being filtered, washed with toluene and then dried, firstly in air, then under vacuum (80°C, 2 hours 0.2mmHg). The resulting copolymer was ground with a pestle and mortar, leaving a white powder in approximately 100% yield.

4.11.3 Analysis

The important feature of these polymers in comparison to the standard copolymers previously prepared, is their surface area and porosity. Nitrogen adsorption and subsequent BET surface area analysis was conducted upon samples deriving from this preparation.

The three surface area results obtained were found to be 541m^2/g, 481m^2/g and 502m^2/g. This results in a mean value of 508m^2/g, which is extremely close to those copolymers obtained earlier by preparation from only octahydridosilsesquioxane (500m^2/g, mean of ten samples). Additionally all of these results fall within the range expected from the cubic based copolymers.

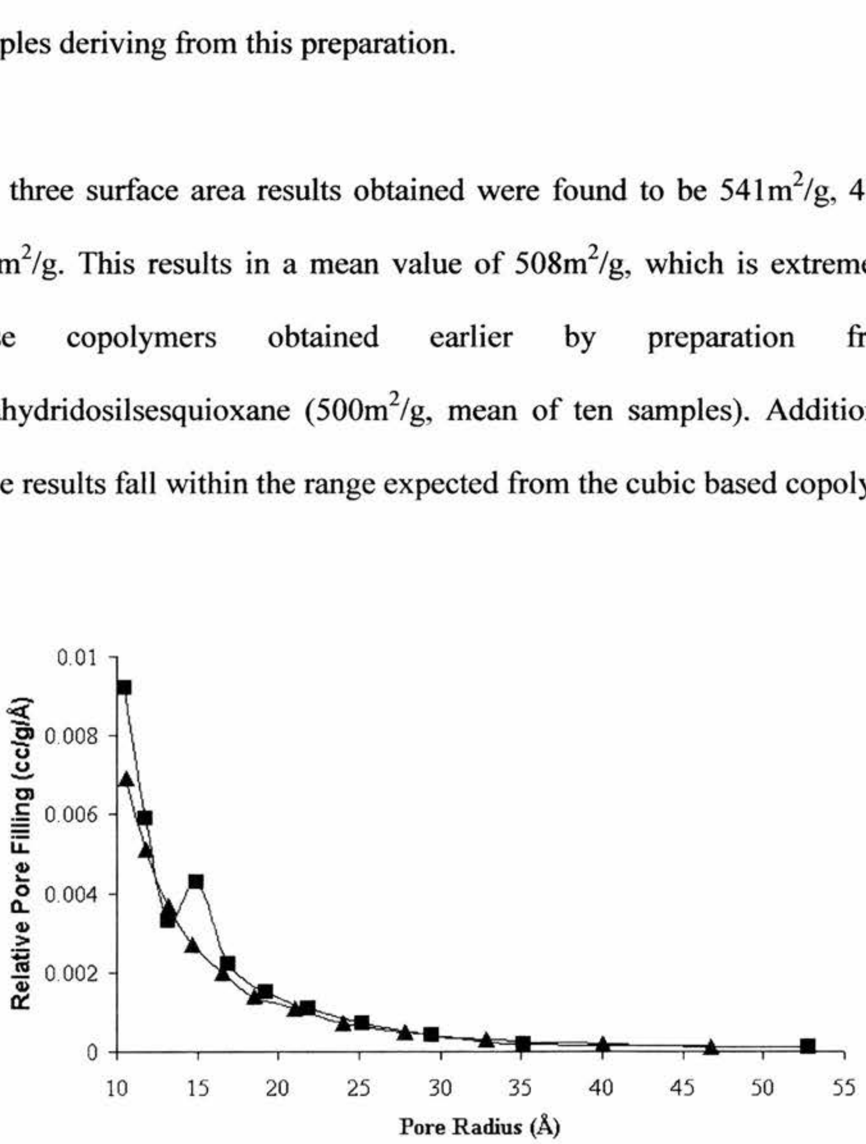

Figure 4.13: Comparison of pore size distribution of silsesquioxane copolymers with cubic monomers only (▲) and containing decahydridosilsesquioxane (■)

A comparison of the pore size distribution with the copolymer formed from entirely cubic monomers shows a high degree of correlation (***figure 4.13***), between samples of similar surface area.

The only significant difference between the two curves is the peaks around 15Å observed with the decahydridosilsesquioxane containing copolymer, but the overall trend is similar, thereby indicating that the randomness of the structure renders the exact shape of the monomers largely insignificant.

4.11.4 Observations

As might be expected no visible differences were noted between this reaction and than for the copolymer prepared using only cubic monomers. Gelation time was not distinguishable from the original materials.

4.12 Conclusions

Two distinct types of monomeric silsesquioxane have been prepared and characterised. Vinylsilsesquioxane is observed to be prepared as a cubic species only, whereas the hydridosilsesquioxane species can be prepared readily in two different conformations.

The two cubic monomeric species were polymerised using a hydrosilation reaction to produce a highly porous, non-crystalline solid. Analysis by nitrogen absorption upon this reveal a typical surface area of approximately $500m^2/g$, and a pore size distribution recorded at 10Å and above indicating the larger pores to be increasingly unlikely. The absorption of a larger organic molecule, cyclopentane, shows a noticeably reduced surface area. This is an indication of the presence of some pores which would be too small to fit this larger molecule.

The thermal behaviour of these silsesquioxane copolymers has been studied under both nitrogen and oxygen. When heated under nitrogen the compound is observed to be stable up to around 400°C. However with oxygen this stability is severely reduced, around 200°C the reaction leading to the eventually breakdown of the polymer and formation of silica can be seen. Calcination of the copolymer indicated that as the structure is oxidised and broken down, the resulting material still retains a high, but reduced porosity.

Due to a high element of randomness within the structure, and the possession of no long range ordering, a number of slight variations to the preparation were considered. By altering the relative quantities of the cubic silsesquioxanes, or by use of non-cubic hydridosilsesquioxane, highly porous copolymers were formed. The surface areas and pore size distributions of these materials were similar to those found using only cubic monomers. The notable exception observed was indicated by the behaviour of materials prepared without using the 1:1 octavinylsilsesquioxane to octahydridosilsesquioxane ratio. In this instance not all the excess monomer would be used within the reaction.

4.13 References

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5 Transition Metal Loaded Silsesquioxanes

5.1 Aims And Objectives

For a silsesquioxane copolymer to be used to support a transition metal, there is a requirement of finding ways to incorporate these within the structure. Whilst many monomeric and dimeric transition metal containing discrete silsesquioxanes have been characterised, the same cannot be said regarding polymeric species.

The preparation of such species has been attempted, with several different methods investigated as potential procedures for synthesising such compounds. Two different general approaches have been made, either to have the transition metal present on the monomer, or alternatively insert it within an already created copolymer.

The silsesquioxane copolymers are initially not capable of accepting a transition metal within the structure, therefore prior to this being able to occur, a suitable site must be prepared. This is to be achieved by partial opening of the ring structure of the silsesquioxanes, leaving a silanol functional group whereby in the presence of a weak base the insertion of a transition metal chloride can be attempted.

As well as preparing polymeric ring opened silsesquioxanes, monomeric species have been prepared using the same metal compounds, hopefully to provide a structural comparison around the metal centre.

The alternative method for the formation of metal containing silsesquioxane species is to attempt to prepare monomeric silsesquioxanes with the metal already present prior to polymerisation. The ring opening reactions have been attempted on monomeric species, in addition to reactions upon the functional groups of the silsesquioxanes, in order to replace these with either cobalt or zirconium. Provided these modifications are only carried out with a equal molecular ratio of the reactant species, on average addition would only occur upon an average of one corner per monomer. As the polymerisation has already been observed to show a significant degree of randomness, this should not prevent the process from occurring

Additionally using silsesquioxanes as the basis for forming transition metal containing species, despite not actually retaining the initial polymer based structure has been attempted. This was investigated by the dispersion of a transition metal species within the porous copolymers, before calcining to removed the organic material present, hopefully leaving a metal containing silicate.

Samples prepared have been characterised, in particular in comparison with the properties of the copolymers prepared without metallic elements attached.

5.2 Ring Opened Silsesquioxane Copolymers

5.2.1 Introduction

Silsesquioxane rings have been shown to be capable of being opened under basic conditions[1]. The degree as to which this occurs is dependent upon the conditions used within the reaction. The first step would be the opening of one side of the silsesquioxane (***figure 5.1***).

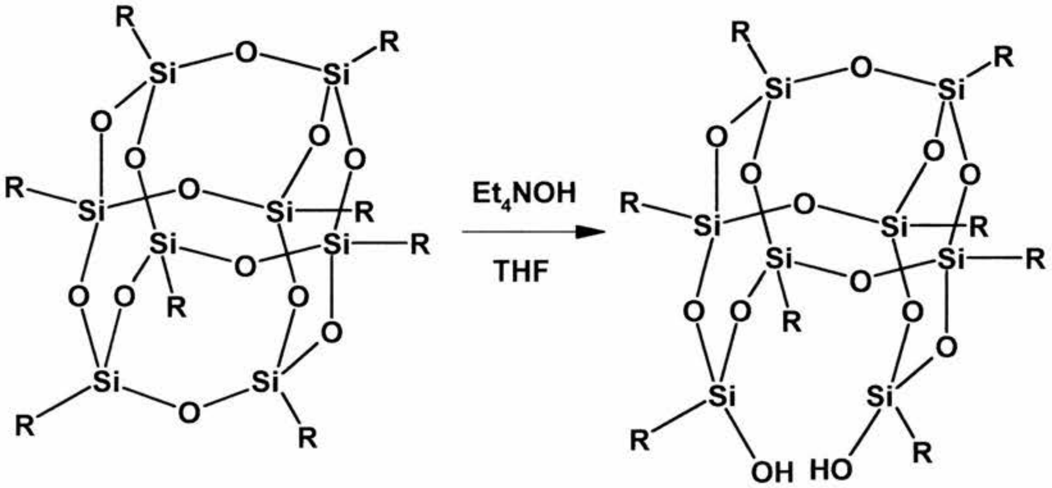

Figure 5.1: Representation of a disilanol resulting from a ring opening reaction of a silsesquioxane cube, R = H, C_2H_3 or C_2H_4 bridge

The desired products of the ring opening reactions are either this disilanol, or the trisilanol, which would be expected if a silicon 'corner' is removed in the presence of additional base (***figure 5.2***). Both of these structures would then have possibilities for later introducing a transition metal into the vacancy created within the central inorganic cage.

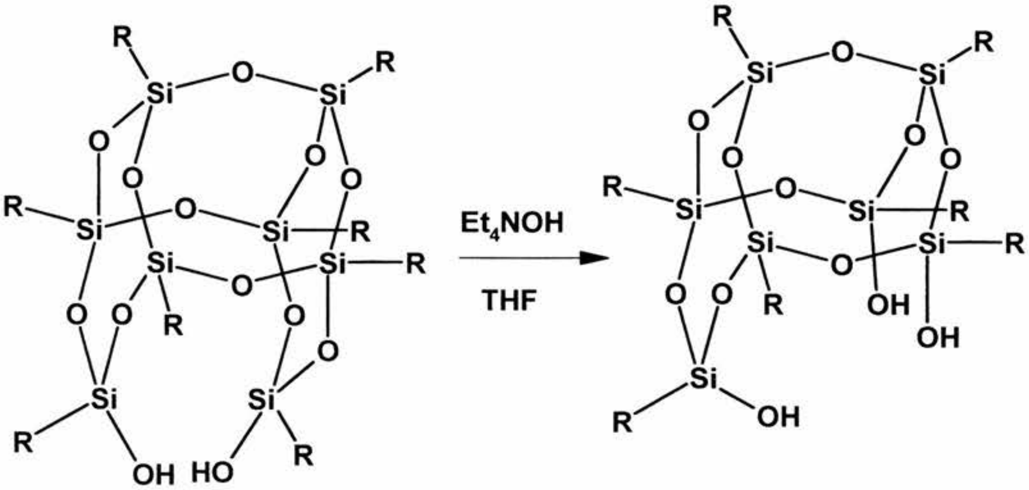

Figure 5.2: Representation of a trisilanol resulting from a ring opening reaction of a silsesquioxane cube, R = H, C_2H_3 or C_2H_4 bridge

It is known that if a strong base were used, the structure of the copolymers could be lost altogether. For these copolymers to act as suitable supports for transition metals, it is therefore required that the ring opening reaction is carried out under relatively mild conditions.

5.2.2 Synthesis

A sample of silsesquioxane copolymer (0.5g) was added to either MIBK (25ml) or THF (25ml) and allowed to stir. Sodium hydroxide solution (2.23ml, 0.986M) was added and allowed to continue stirring.

After one hour hydrochloric acid (2.5ml, 1.0M) was added to the mixture. After a short period the copolymer, still present as a solid, was recovered by filtration, before being washed with acetone. This was then dried under vacuum (80°C, 2 hours, 0.2mmHg). The resultant copolymer retained its white coloration, and was obtained in virtually 100% yield based on the initial copolymer.

5.2.3 Analysis

IR spectroscopy was used to determine whether the ring opening reaction had proved successful. This showed (cm^{-1}, KBr disc) 3455 (s), 2920 (w), 2360 (w), 1635 (w), 1375 (s), 1080 (s), 765 (m), 550 (w). The introduction of an O–H bond into the structure results in the appearance of a significant band recorded at $3450cm^{-1}$ which is not present in the initial silsesquioxane copolymer. Otherwise the two spectra are very similar to each other. This indicates that ring opening has occurred as expected.

5.2.4 Observations

This reaction offered several variables that could be altered to investigate their effects. The time scale for which the copolymer is exposed to the base is reasonably short, and it is possible that this could be increased. Leaving the copolymer for up to four days under such conditions still resulted in a similar yield. This reaction is also observed to not be dependant upon the copolymer used, and produces silanols with both entirely cubic monomer based species, and those prepared using decahydridosilsesquioxane.

In contrast addition of a significantly increased quantity of sodium hydroxide (5.69ml, 0.968M), resulted in significant breakdown of the copolymer. This was immediately obvious as the reaction resulted in a significantly very low yield of a remaining solid product, slightly below 50%, whilst on evaporation of the MIBK solvent resulted in a white solid being produced.

5.3 Nitrogen Adsorption Studies Of Ring Opened Copolymers

5.3.1 Introduction

After the ring opening of the silsesquioxane copolymers, and prior to attempting the insertion of a transition metal, the porosity of the copolymers would need to be retained. If the attack by the base resulted in a non-porous structure, any addition of a metal within the copolymer would be likely to prove unfeasible.

Ideally the surface area would remain consistent with the starting copolymer as the base should only be leading to limited breakdown of the structure leaving silanol groups present.

5.3.2 Experimental

For comparative purposes, it was important to keep the conditions the same as readings taken for the copolymers upon which these materials are based. After degassing under vacuum for 2 hours at 125°C, all readings were obtained with a confidence level of 95% and a time out of one hour.

From an initial nitrogen pressure of 10mbar, results were taken in 50mbar intervals until reaching past 500mbar. In analysing the data obtained for calculating the BET[2] surface area, partial pressures (p/p_o) between 0.05 and 0.20 were considered.

5.3.3 Analysis

Running BET analyses on samples under which ring opening was conducted using each of the two solvents attempted resulted in surface areas within the same range as found for the unopened copolymers, with a figure of $506m^2/g$ obtained with a sample in THF and $432m^2/g$ for a sample prepared in MIBK. In both these instances the porosity of the sample can be considered to be retained, and the possibility of inserting a transition metal species within the copolymer remains.

5.4 Ring Opened Silsesquioxane Monomers

5.4.1 Introduction

The ring opening of the copolymers has been shown to work, resulting in the presence of silanol groups within the structure. Whilst these have the potential for metal insertion reactions, it could be seen as preferable to insert the transition metal as part of the silsesquioxane cage prior to copolymerisation. It is possible that some of silanol groups observed within the ring opened copolymer might be too hindered to enable the transition metal complexes used to react at those sites.

However, if the insertion reaction could be attempted upon the monomer, this specific difficulty would not arise. As it has been shown earlier, the copolymerisation will still proceed even with varying the actual composition of reactants used, it is feasible that this could apply to a situation such as this.

Feher and co-workers have shown such a reaction to be possible for several cubic silsesquioxanes[1]. However, none of those they successfully prepared would be suitable for copolymerisation.

5.4.2 Synthesis

Octavinylsilsesquioxane (1.00g) was dissolved in THF (25ml) together with tetraethylammonium hydroxide (1.03ml, 35wt% solution in water). The solution was allowed to stir for one hour at room temperature before hydrochloric acid (2.5ml, 1.0M) was added. Extraction with ether (3 x 75ml) was used, before partial evaporation, then crystallisation, to leave a white solid (**A**).

Alternatively sodium hydroxide (2.23ml, 0.986M) was used a the base in this reaction, with conditions otherwise as above. This also upon evaporation and crystallisation resulted in a white solid (**B**).

All samples were dried under vacuum (80°C, 2 hours, 0.05mmHg).

5.4.3 Analysis

^{1}H NMR was used with the intention of identifying a peak due to the expected silanol group present, predicted to appear around 7ppm. However, whilst this was clearly present in sample B, appearing at 7.11ppm, the complete lack of a vinyl proton peak around 6ppm, indicates that complete breakdown of the compound has occurred. Therefore this is not going to be suitable to base a metal containing monomer around.

For sample A, however, shows a complete lack of a potential silanol peak, but does still show a clear vinyl peak centred at 5.96ppm. Conversely this indicates that no ring opening has been occurring, and that conditions are possibly too weak.

5.4.4 Observations

Slight variations were attempted for this reaction, including the solvents used for both the reaction and extraction. Substituting MIBK for THF appeared to make no distinguishable difference to the outcome, as did substituting acetone for ether to extract the products. As significant quantities of inorganic material were present this step was a necessity.

Although the attempted reaction is essentially the same as successfully used for the copolymers, the nature of the reactant here is shown to have a significant difference to the outcome. Conditions under which the copolymer is seen to undergo ring opening are capable of destroying the whole nature of the monomer, whereas using milder conditions appears not to even show signs of breaking down the cage.

5.5 Preparation Of Cyclopentyl Silanols

5.5.1 Introduction

Whilst it has been shown that silsesquioxane copolymers can be successfully be ring opened to form silanols, this has been shown not to be the case when a similar reaction is conducted upon octavinylsilsesquioxane. The preparation of a small number of such incompletely condensed silsesquioxanes have, however, been reported in the literature. These might serve to show how transition metals are bonded into the silsesquioxanes more clearly than the copolymers.

Unfortunately all such examples prepared are unsuitable for polymerisation, which prevents this being a viable route to synthesis transition metal loaded silsesquioxane copolymers. However, it is possible that such compounds could prove useful in determining the structure involved with inserted transition metals.

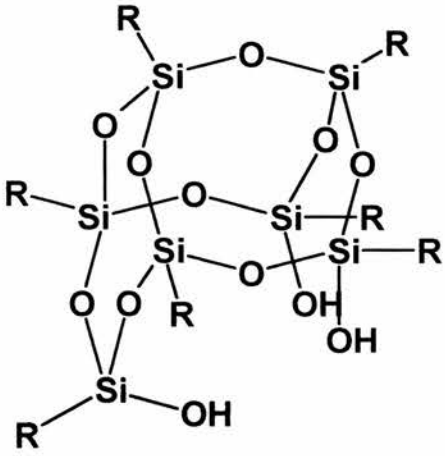

Figure 5.3: Trisilanol potentially deriving from the condensation reaction of cyclopentyltrichlorosilane, R = c-C_5H_9

The condensation reaction exhibited by cyclopentyltrichlorosilane, as identified by Feher and co-workers[3], is one example of this type of reaction. One of the expected products (***figure 5.3***) is the trisilanol, although it is conceivable that other silanols could be formed, such as a disilanol (***figure 5.4***) whereby the silane has undergone further condensation reactions. These are then hopefully capable of acting as a support for a transition metal.

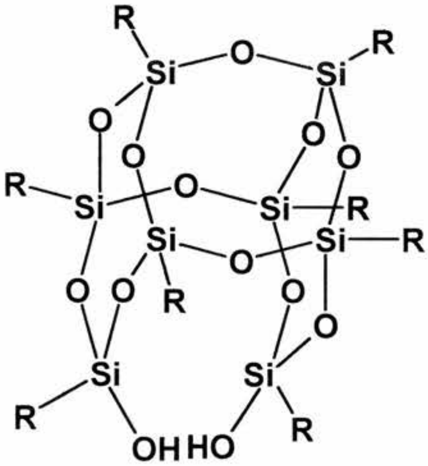

Figure 5.4: Example of a disilanol potentially deriving from the condensation reaction of cyclopentyltrichlorosilane, R = c-C_5H_9

5.5.2 Synthesis

To a solution of cyclopentyltrichlorosilane (18ml) in acetone (440ml), distilled water (120ml) was added dropwise, whilst stirring. Upon addition of the water the resultant mixture was headed to reflux and allowed to continue for 65 hours.

Upon completion the solution was observed to contain a white precipitate, which was obtained by filtration, and washed with acetone. The sample was then allowed to dry under air (**A**).

An additional product was obtained from this reaction by collecting the washings from the filtration and evaporating down the solvent until a precipitate started to form. This was allowed to redissolve, and recrystallise out. The white crystals that were formed were removed by filtration and washed with acetone (**B**).

5.5.3 Analysis

The samples were analysed using ^{1}H NMR ($CDCl_3$, 300MHz), in particular attempting to see any silanol groups present within their structures. These are the groups which will later be involved in the reaction to insert the transition metals.

In the spectrum obtained for sample A, a peak due to the silanol was observed at 6.10ppm. Also observed were three peaks arising from the cyclopentyl groups as expected. Seen at 1.67ppm, 1.41ppm and 0.89ppm (tertiary carbon), these are found to be in the expected 2:2:1 ratio. In comparison with the silanol peak the ratio of the solitary hydrogen found on the tertiary carbon within the cyclopentyl ring is approximately 5:1, which is much higher than would be found had the trisilanol been formed. This indicates that the condensation process has continued to a higher degree than expected, and would suggest that a disilanol is the major product.

For sample B, the ^{1}H NMR spectrum, the same four peaks were observed. However the ratio between the tertiary carbon and silanol peaks was recorded at approximately 10:1, which indicated that near complete condensation has occurred. Again a disilanol is likely to be the major silanol product present, but it is possible that there are significant quantities of a completely condensed silsesquioxane.

5.6 Preparation Of Cyclohexyl Silanols

5.6.1 Introduction

As noted in the preparation of cyclopentyl silanols, there are preparations known for a number of other incompletely condensed silsesquioxanes. The synthesis of the cyclohexyl equivalent has also been described by Feher and co-workers[4], but despite the similarity of the reacting silane, the procedure required noticeably differs.

Likewise this procedure isn't limited to producing one individual silanol. The expected products are likely to include the trisilanol as well as disilanolic species (***figure*** *5.5*). Another possibility is the formation of a double-three ring completely condensed silsesquioxane (***figure 5.6***).

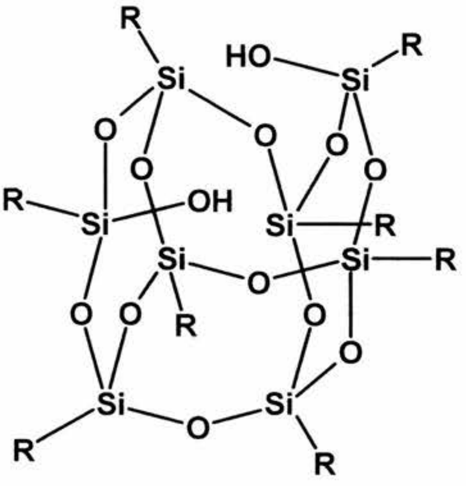

Figure 5.5: Example of a disilanol deriving from the incomplete condensation of cyclohexyltrichlorosilane, R = *c*-C_6H_{11}

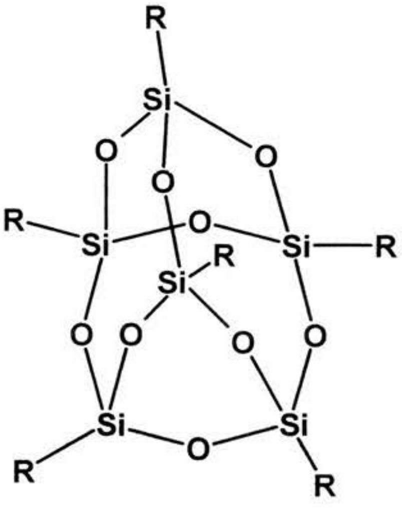

Figure 5.6: Structure of completely condensed silsesquioxane with a double-three ring structure, R = *c*-C_6H_{11}

5.6.2 Synthesis

Using the method of Feher and co-workers as a guideline[4], a solution of cyclohexyltrichlorosilane (25ml) in acetone (569ml) was prepared. To this distilled water (151ml) was added slowly, whilst continually stirring, avoiding any potential excessive heating. Upon completion of this addition the reaction flask was sealed and left to stir.

A precipitate gradually formed, and after a two month period the white solid was obtained by filtration. The solution was recovered and allowed to continue stirring, as this reaction should be capable of producing deposited silsesquioxanes over a period of up to three years. The filtrate was washed with acetone and allowed to dry in air before dried under vacuum (50°C, 1 hour, 0.2mmHg, then 80°C, 1 hour, 0.2mmHg).

5.6.3 Analysis

The product was analysed using ^1H NMR ($CDCl_3$, 300MHz) to show a peak deriving from the silanol at 6.47ppm, and three peaks arising from the cyclohexyl groups at 1.66ppm, 1.17ppm and 0.77ppm, all in the expected ratio of 3:2:1. The size of the silanol peak in relation to the hydrogen on the tertiary carbon atom was 1:15. This indicates a large degree of complete condensation.

^{29}Si NMR ($CDCl_3/CHCl_3$, 60MHz) was able to give a clearer idea as to the nature of the mixture of products present, a peak at -56.60ppm corresponds well to the results of Feher and co-workers obtained for the completely condensed double-three ring structure. The three remaining peaks, appearing in the spectra at -60.15ppm, -68.22ppm and -69.66ppm can be similarly assigned to the incompletely condensed trisilanol.

5.7 Insertion Of Transition Metals Within Ring Opened Copolymers

5.7.1 Introduction

The silsesquioxane copolymers have been shown to successfully undergo a ring opening reaction in the presence of a base. This provides a site whereby the insertion of a transition metal into the polymeric framework can be achieved.

A variety of insertion reactions have been noted for monomeric species by various researchers[5-7], often resulting in the formation of dimers[8-11]. Using a ring opened copolymer is likely to affect the insertion reactions. As these polymers are not soluble any insertion reaction will need to be allowed to run long enough to enable sufficient dispersion of transition metal within the pores.

The addition of four different transition metals has been attempted. Titanium in the form of cyclopentadienyltitanium trichloride, together with the equivalent zirconium complex. The use of the trichloride as opposed to the similar dichloride complexes is favoured as it should allow addition within both trisilanol and disilanol groups present. However, bis(cyclopentadienyl)molybdenum dichloride was used, as opposed to the trichloride, as the latter species is more difficult to prepare[12]. The final transition metal considered was cobalt, using cobalt (II) chloride. This species differs greatly from those used for the other three elements, possessing a crystalline structure, and without the attached cyclopentadienyl group(s).

The reaction, that the compounds are expected to undergo, and shown for titanium (***figure 5.7***)[13], is conducted in the presence of a weak base to prevent further attack on the copolymer, other than at the silanol groups.

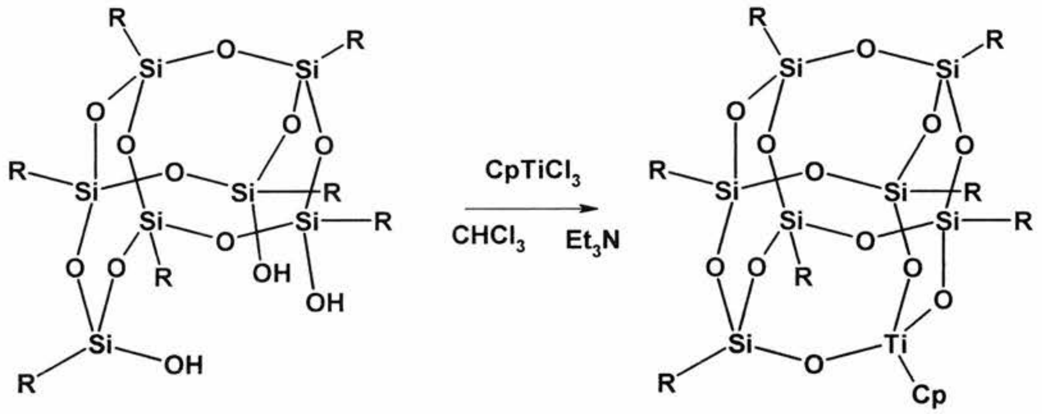

Figure 5.7: Possible insertion of titanium within incompletely condensed silsesquioxane copolymer, R = H, C_2H_3 or C_2H_4 bridge

The above diagram does, however, only represent one possible case scenario, assuming a disilanol to be present, then it might be expected that a chlorine atom will remain bonded to the metal. As a dichloride it could be expected that the molybdenum species leaves the remaining free disilanol group close to the metal (***figure 5.8***).

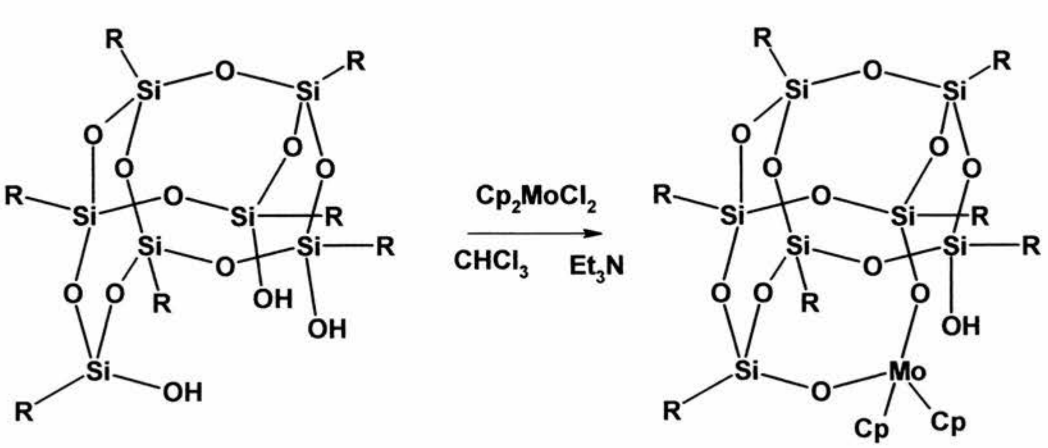

Figure 5.8: Possible insertion of molybdenum within incompletely condensed silsesquioxane copolymer, R = H, C_2H_3 or C_2H_4 bridge

5.7.2 Synthesis

A previously ring opened silsesquioxane copolymer (0.1g, prepared from octahydridosilsesquioxane or a mixture of the two hydridosilsesquioxanes) and a transition metal complex (varying quantities, ***table 5.1***) were placed in a Schlenk tube. After degassing three times with argon, dry chloroform (10ml) was added to the tube, and left to stir for 24 hours to enable the transition metal to disperse into the suspended copolymer.

After this period was over, dry triethylamine (1.25ml) was added to the mixture, before leaving to stir for a minimum of a further three days. The copolymer was easily separated off as it remained the only solid present, and was subsequently washed with dichloromethane. This transition metal loaded copolymer was then dried under vacuum (0.2mmHg, 2 hours, 80°C).

Transition Metal Compound	Weight Used (g)
$CpTiCl_3$	0.06
$CpZrCl_3$	0.13
Cp_2MoCl_2	0.15
$CoCl_2$	0.04

Table 5.1: Quantities of transition metal compounds used for insertion reaction with 0.1g of ring opened silsesquioxane copolymer

The materials obtained from these additions tended to show a slight coloration upon completion of the transition metal insertion. Titanium loading of samples resulted in a pale yellow compound. Addition of zirconium gave an off white colour, not too dissimilar to that exhibited by the initial copolymer. Cobalt lead to a pale blue coloured solid and molybdenum resulted in the formation of a grey product.

Yields of all products were noted to be almost 100% based upon total weight of copolymer and transition metal reactants.

5.7.3 Analysis

Although all samples prepared showed some visual evidence of the presence of the metals inserted, a practical method to determine the level to which this had occurred was XRF. Each of these four different species was observed by this technique, obtaining values which differed with the metal concerned (***table 5.2***).

Transition Metal	Content (%)
Ti	11.0
Zr	3.3
Mo	5.0
Co	18.0

Table 5.2: Summary of XRF data for the insertion of transition metals into ring opened silsesquioxane copolymers

Although it can be seen for all of the metal containing species that a noticeable quantity has been obtained within the copolymer, it can be clearly seen that this was more effective when considering the insertion of titanium and cobalt.

Additionally, to determine the structures of these materials, all samples were also analysed by EXAFS, with the intention of noting the differences between the metals.

5.7.4 Observations

Ring opened copolymers were also used whereby the initial polymerisation was carried out using decahydridosilsesquioxane as part of the reaction mixture. There appeared to be no difference with the copolymers based wholly on cubic monomers.

5.8 Insertion Of Transition Metals Within Incompletely Condensed Silsesquioxanes

5.8.1 Introduction

Having prepared incompletely condensed silsesquioxane monomeric species to act as models for the ring opened copolymers, transition metals were similarly to be inserted into these compounds. The same general procedure was used as for the copolymer insertion reaction, with the only notable difference being the solubility of the silsesquioxanes in solution.

5.8.2 Synthesis

The synthesis used for the insertion reactions into the copolymers was followed with a transition metal complex (***table 5.3***) and either cyclohexyl (0.31g) or cyclopentyl (0.28g) incompletely condensed silsesquioxanes in a Schlenk tube. After degassing the tube three times with argon, dry chloroform (15ml) was added and the mixture was allowed to stir for 24 hours, allowing time for the solids to dissolve and disperse.

Transition Metal Compound	Weight Used (g)
$CpTiCl_3$	0.11
$CpZrCl_3$	0.18
Cp_2MoCl_2	0.21
$CoCl_2$	0.08

Table 5.3: Quantities of transition metal compounds used for insertion reaction with incompletely condensed silsesquioxanes

Dry triethylamine (2.5ml) was added to the solution, before leaving to stir for a further period of at least three days. The solvent was removed in vacuo, and the solid product deposited washed with dichloromethane, before dried under vacuum (0.2mmHg, 2 hours, 80°C). An approximate yield of 40% based upon the weight of the initial reactants was obtained, showing similar, but darker, colours to the products of the metal insertion into the copolymer reactions.

5.8.3 Analysis

As samples prepared using this synthesis were not polymeric, the surface area of the compounds was not determined. All samples were analysed using EXAFS, in particular as a comparison to the polymeric species.

Transition Metal	Cyclohexyl- Content (%)	Cyclopentyl- Content (%)
Ti	5.8	22.0
Zr	9.8	9.4
Mo	2.8	0.8
Co	Not recorded	Not recorded

Table 5.4: Summary of XRF data for the insertion of transition metals into cyclohexyl- and cyclopentyl- incompletely condensed silsesquioxanes

The metal contents were determined by XRF (***table 5.4***), and for the incompletely condensed silsesquioxanes studies differed for the three elements concerned. The behaviour of each is observed to vary significantly with comparison for the results obtained in the polymeric species. The zirconium insertions into the incompletely condensed silsesquioxanes are significantly higher than the copolymer, the reverse is true in the case of molybdenum and then these two values differ widely for titanium, with values higher and lower than the previous value obtained.

5.8.4 Observations

The noticeable difference between attempting this procedure upon these monomeric silsesquioxanes is the solubility of the material. The process of washing the product is likely to be responsible for the majority of the poor yield of this experiment.

5.9 Zirconium Addition To Octavinylsilsesquioxane

5.9.1 Introduction

Schwartz's reagent, is a compound used as a source for the addition of zirconium to vinyl groups[14,15]. Therefore, it offers the possibility of being utilised as a means of preparing a monomer that contains a transition metal, without requiring need of a ring opening reaction.

As has been shown before, with the copolymerisation not necessarily in need of a straight mixture of the two cubic products, it seems feasible that with the addition of zirconium to one corner of the octavinylsilsesquioxane, that this might still be able to form a copolymer.

With the central inorganic cage separating the eight vinyl groups, there is no steric or chemical reason as to why the reaction cannot proceed on more than one corner of the same cube. As a result of reacting an approximately equimolar quantity of the two reactants, it is therefore likely that the number of corners upon which zirconium is added to vary to some degree.

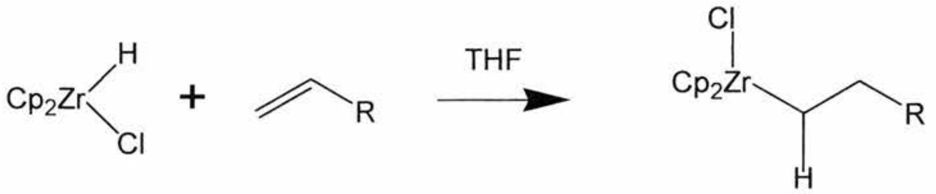

Figure 5.9: Addition of zirconium to a vinyl group using Schwartz's reagent as a source of zirconium

The addition of the zirconium proceeds (**figure 5.9**) through the insertion of the vinyl group into the zirconium to hydrogen bond. The reaction is noted to be strongly influenced by steric effects, resulting in the addition of the zirconium to the least hindered position. In this instance, as the inorganic cage is very bulky, addition would be expected on the terminal carbon.

5.9.2 Synthesis

Octavinylsilsesquioxane (1.0g) and Schwartz's reagent (0.45g) were placed in a Schlenk flask with a magnetic stirrer bar. The flask was sealed and degassed three times with argon. The reaction vessel was cooled in an ice bath, and dry THF (30ml) was added. Whilst maintaining the ice bath for a further two hours, the mixture was then allowed to continue stirring. After this point the ice bath was removed.

Upon stirring overnight approximately half the solution was removed, with the solvent then slowly evaporated off in vacuo. The white solid (**A**) recovered was subsequently dried further under vacuum (80°C, 2 hours, 0.2mmHg).

The solution remaining in the Schlenk flask was stirred for an additional four days, before the solvent was also evaporated off under vacuum to give a dirty white solid (**B**), which was dried as before.

5.9.3 Analysis

A ^{1}H NMR spectrum of ($CDCl_3$, 300MHz) on sample B showed peaks at 6.24ppm (s, 10H), 5.94ppm (m, 30H) and 1.51ppm (b, 4H). The ratios of the three peaks indicates that addition has occurred after this period of time on only half the octavinylsilsesquioxane units present, whereas the expected amount based upon the molar ratios of reactants should be approximately 1:1.

The corresponding 1H NMR spectrum ($CDCl_3$, 300MHz) for sample A possessed peaks at 6.24ppm (s, 10H), 5.94ppm (m, 36H) and 1.55ppm (b, 4H). This indicates only a slightly smaller conversion than the sample which had been allowed to continue reacting for a further four days, at slightly below 50%.

5.9.4 Copolymerisation

Using the general method prepared for the standard copolymers prepared in the previous chapter, the zirconium compound (sample A) prepared above (0.42g) and octahydridosilsesquioxane (0.20g) were placed in a Schlenk tube with a magnetic stirrer bar, and degassed three times under argon. Dry toluene (20ml) was added and after allowing the solids to dissolve, the reaction mixture was cooled down to -77°C using a dry ice/acetone bath. The tube was again degassed three times with argon.

After being left to warm up to room temperature, Karstedt's catalyst (0.1ml, 35%wt solution in xylenes) was added whilst cooling to 0°C. After leaving overnight gelation had failed to occur, so a further addition of Karstedt's catalyst (0.2ml, 35%wt solution in xylenes) was added, under the same conditions as the first addition. When this still proved unsuccessful at causing a gel to form after a further six days, a final addition of Karstedt's catalyst (0.5ml, 35%wt solution in xylenes) was carried out. This eventually produced the formation of the expected gel.

The solvent was removed in vacuo, before dried further (80°C, 2 hours, 0.2mmHg). The copolymer was then ground down, and the surface area calculated from nitrogen adsorption measurements.

Analysis of the resultant copolymer by nitrogen adsorption, using partial pressures up to 0.02 indicated this to have a surface area of 529m^2/g. This value is almost identical in comparison with the materials obtained without any metal inserted, indicating that it is possible to prepare metal containing silsesquioxane species in possession of a large surface area.

5.9.5 Alternative Synthesis

A slight variation on preparation of the eventual copolymer required was achieved by means of conducting the zirconium addition and copolymerisation processes in the same solvent, with no attempts made to separate out the intermediate product from the solution.

Initially octavinylsilsesquioxane (0.50g) and Schwartz's reagent (0.22g) placed along with a stirrer bar into a Schlenk flask, which upon sealing was purged three times with argon. After cooling down with an ice bath, dry toluene (15ml) was added, and the ice bath removed after two hours. Whilst continually stirring, the mixture was left for twenty four hours.

At this point octahydridosilsesquioxane (0.33g) was added and allowed to dissolve. After being cooled with a dry ice/acetone bath to -77°C, the flask was again degassed with argon three times. After allowing to warm up and then cooled with an ice bath, Karstedt's catalyst (0.3ml, 35%wt solution in xylenes) was added, and after stirring overnight resulted in gelation being observed.

The gel was filtered off from the solvent, and washed with acetone. After being allowed to dry in air and room temperature, drying was completed under vacuum (80°C, 2 hours, 0.2mmHg). The resulting polymer was then crushed into a powder.

XRF conducted upon a sample of the copolymer prepared using this method recorded a zirconium content of 2.9%, which represents a similar loading in comparison with the insertion into the ring opened copolymer studied previously.

5.10 Cobalt Addition To Octahydridosilsesquioxane

5.10.1 Introduction

With the addition of zirconium to octavinylsilsesquioxane successfully forming transition metal loaded copolymers, there is naturally the possibility to attempt the same idea with other metals.

The addition of cobalt onto octahydridosilsesquioxane is one such option. An example has already been identified by Calzaferri and co-workers[16], using octacarbonyldicobalt as the transition metal source. Their method (***figure 5.10***) sees the silsesquioxane and cobalt complex used in a 2:1 ratio, in order to see addition occurring on one vertex only.

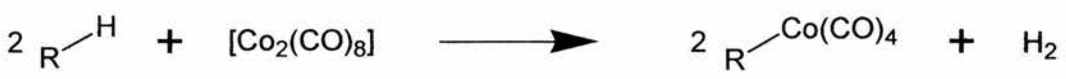

Figure 5.10: Addition of cobalt to octahydridosilsesquioxane

Their preparation was conducted at 50°C in toluene, but subsequently Rattay and co-workers[17] were able to synthesise the product with all eight vertices reacting with cobalt using four equivalents of octacarbonyldicobalt to one of octahydridosilsesquioxane at room temperature in hexane.

The latter procedure also results in the octa-substituted product precipitating out as crystals throughout the reaction, whereas those reacting on only one corner still remain soluble throughout. However, for the purposes of copolymerisation with octavinylsilsesquioxane, an eight substituted product is unsuitable.

As expected for the addition of zirconium, the exact numbers of cobalt atoms joined per monomer could be open to some degree of variation, as the reaction has been shown to proceed to completion with four equivalents of the cobalt species present under mild conditions. And pure one corner only addition would require separation of the products.

5.10.2 Synthesis

Octacarbonyldicobalt (0.40g) was placed in a round bottomed Schlenk flask (with the exclusion of light as the cobalt complex is light sensitive), with stirrer bar, after degassing three times with argon, dry hexane (50ml) was added. Separately octahydridosilsesquioxane (0.5g) was added to another Schlenk flask, which after also degassing three times with argon, was dissolved in dry hexane (140ml). The solution containing the silsesquioxane was transferred across to the flask with the cobalt solution by cannula. With argon allowed to flow continually over the solution to carry away evolved hydrogen, the reaction was allowed to continue with stirring for 72 hours.

The solvent was evaporated off under vacuum (0.2mmHg), with a liquid nitrogen trap present in case any products sublimed, as octahydridosilsesquioxane has a tendency to do under this vacuum, leaving a brown/black solid.

The solvent collected was then evaporated down under a lower vacuum, using a water pump (10mmHg, room temperature). Under these conditions any octahydridosilsesquioxane present should not sublime, and as any expected products are of a greater molecular mass, it would not be expected they do either. Upon completion of this evaporation no solid product was found.

The brown/black solid obtained as a result of the first evaporation needed to be separated and dried before it could be used to attempt preparation of a cobalt containing copolymer. The separation was attempted through means of a chromatography column of silica using a hexane with 10% ether solution as a solvent. A pale yellow coloured transparent liquid was obtained, but on evaporation failed to reveal and solids. Repeating the evaporation with the colourless solution also failed to deposit any solid product.

5.10.3 Observations

The difficulty with this reaction is seen to be the separation out of a cobalt containing silsesquioxane. Further efforts would be needed to obtain the desired species, which should be able to form a copolymer with octavinylsilsesquioxane.

5.11 Nitrogen Adsorption Studies Of Metal Loaded Silsesquioxanes

5.11.1 Introduction

Transition metals have been shown to capable of being successfully inserted into the silsesquioxane polymers, following a ring opening reaction. However, it is important that any transition metals remain accessible within the pores if such materials are going to be able to react further with the intention of possibly going on to consider such materials in catalytic applications.

Nitrogen adsorption studies can determine the surface area of these materials, and act as a comparison with the starting copolymers. Ideally following the properties should remain similar between the two.

5.11.2 Experimental

Using carefully ground samples, 30mg of which was degassed under high vacuum at 125°C for two hours prior to analysis. For consistency with the results obtained from the original copolymer all results were recorded at 77K, with readings recorded at pressures of nitrogen starting at 10mbar, increasing in 50mbar intervals until reaching 510mbar for determining surface area only. To determine pore size distributions a starting pressure of 10mbar, and following an initial step size of 20mbar, until reaching 870mbar was used. The desorption was started using a pressure of 850mbar, decreasing the pressure in steps of 50mbar, taking a final reading at 30mbar.

Data points were taken with a confidence level set to 95%, and with a time out of one hour. Relative pressures (p/p_o) with values between 0.05 and 0.20 were used to determine the BET[2] surface area.

5.11.3 Analysis

A sample loaded with titanium after the ring opening reaction, is observed to possess a surface area of $265m^2/g$, this is significantly reduced from the surface area of both the initial copolymer this particular samples was derived from recorded to be $597m^2/g$ and $503m^2/g$ after having the ring opened under basic conditions. This is significantly lower than either of these two readings, however, it still means the resultant material still retains a reasonably high porosity.

When attempting adsorption and desorption of nitrogen from this material (***figure 5.11***), it was observed that the adsorption and desorption isotherms under nitrogen showed a large similarity to the initial copolymer. It can be seen that the isotherm is again of type I, and shows virtually no hysteresis.

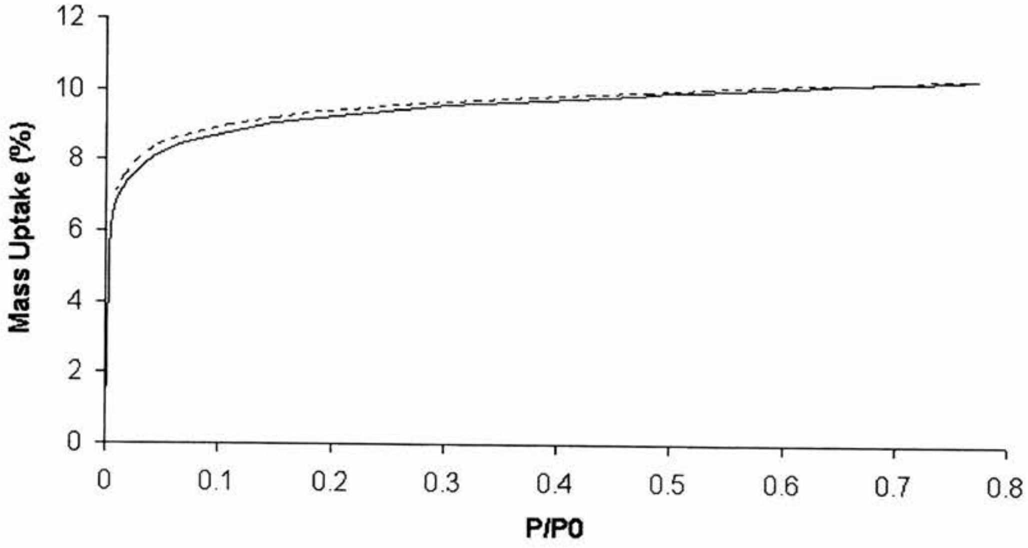

Figure 5.11: Nitrogen adsorption and desorption isotherms obtained from a titanium loaded silsesquioxane copolymer, noting the lack of any significant hysteresis

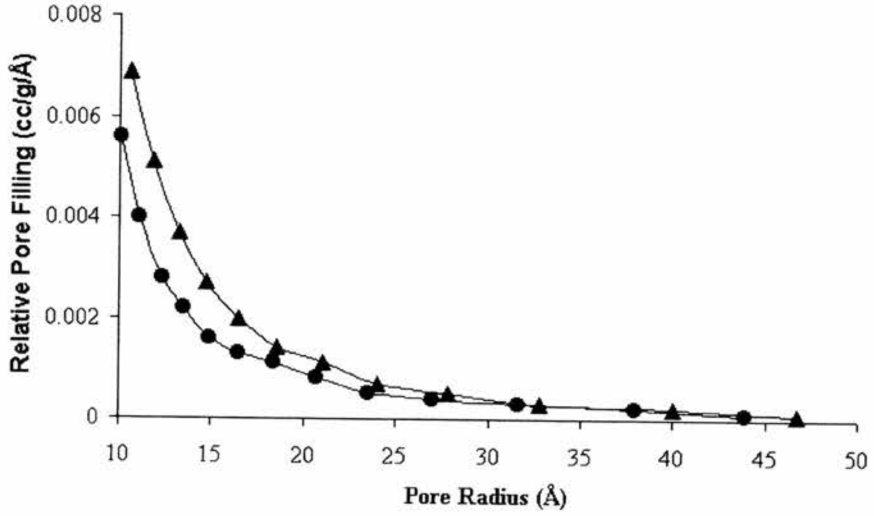

Figure 5.12: Comparison of pore size distribution between silsesquioxane copolymer (▲) and titanium loaded silsesquioxane (●)

Using de Boer's method[18,19] to produce a comparison of the pore size (***figure 5.12***) reveals a similar distribution pattern. Aside from the increased relative pore filling at any given radius, to be expected given the difference in surface areas, the shape of the distribution is identical, both possessing the majority of the distribution at smaller radii.

5.12 Solid State MAS NMR Studies Of Metal Loaded Silsesquioxanes

5.12.1 Introduction

Solid state MAS NMR has been used to aid determination of the structure of the silsesquioxane copolymers, with both ^{29}Si and ^{13}C proving suitable nuclei to gain information about this. After opening the silsesquioxane ring and inserting a transition metal into the resulting material, it is conceivable that the silicon spectra should show clear differences.

In the initial spectra three silicon peaks were clearly identifiable, corresponding to the three possible organic groups that could be bonded to the silicon atom. As a result of opening and insertion, further peaks would be expected arising from the presence of both titanium and some remaining silanol groups.

5.12.2 ^{29}Si NMR Of Titanium Loaded Copolymer

The solid state MAS ^{29}Si spectra for the titanium loaded ring opened copolymer (***figure 3.13***) shows an extra two peaks in comparison to that obtained for the unopened copolymer. Peaks seen at -69ppm, -81ppm and -100ppm correspond well to the values for the first material, although in this case small shoulders are in evidence on all three which can be assigned to some silanol groups remaining unreacted within the structure.

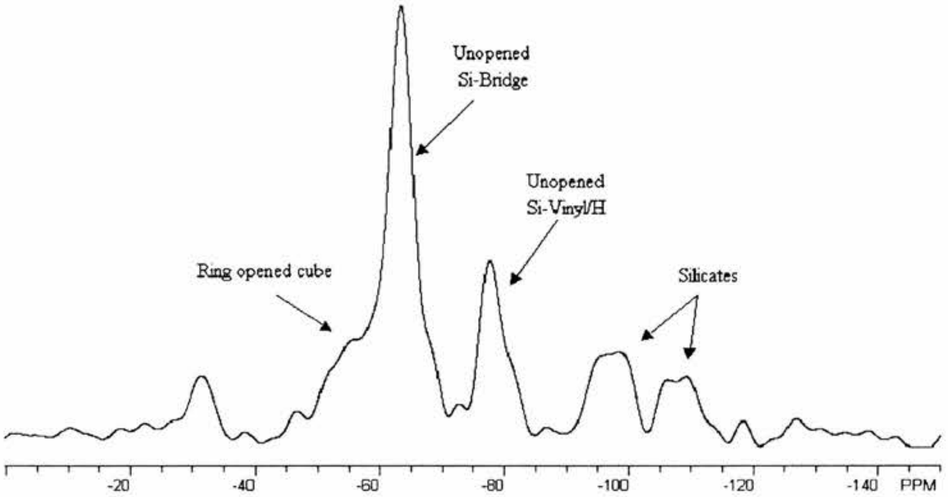

Figure 5.13: ^{29}Si solid state MAS NMR spectrum of titanium loaded ring opened copolymer, with peak assignments

Additional peaks are observed at -32ppm and -111ppm. The latter peak corresponds well with a quaternary silicate unit, possibly resulting from the base starting to break down the copolymer during ring opening (as noted if too much base was used the material was clearly observed to break down). The former peak is most likely to derive from the effects of a titanium atom through an oxygen bridge. A silicon to metal bond would expect to produce a upfield chemical shift, so it can be assume that the normal tertiary silicate shift will be moved in this direction somewhat.

5.13 Dispersion And Calcination

5.13.1 Introduction

So far the focus has been to produce metal containing species which retain the general skeleton structure of the initially prepared silsesquioxane copolymers. However, this is only one method by which these copolymers could be useful in preparing porous transition metal containing materials.

It has already been shown that when calcined, the resulting silicate materials still retain a large, but reduced, surface area. Therefore, by dispersing in a transition metal prior to calcination, it would be expected that the porosity would remain reasonably high.

5.13.2 Synthesis

Silsesquioxane copolymer (0.30g) and a bis(cyclopentadienyl) dichloride transition metal complex (***table 5.5***) were placed with a stirrer into a Schlenk tube. After sealing and purging with argon three times, dry chloroform (7.5ml) was added, leaving to stir for one week to allow for dispersion of the metal within the insoluble copolymer.

Transition Metal (Cp_2MCl_2)	Weight Used (g)
Ti	0.15
Zr	0.19
Mo	0.20

Table 5.5: Quantities of transition metal complexes to be dispersed with 0.3g of silsesquioxane copolymer

After a week the solvent was removed by filtration, and the solid removed dried under vacuum (0.2mmHg, 2 hours, 80°C). Yields of material obtained at this stage being higher than the copolymer being used, suggested that some of the metal complexes were to be found within the pores. A noticeable yellow and grey colour obtained from titanium and molybdenum respectively indicated the presence of these metals. The zirconium samples remained a similar colour to the initial copolymer.

The resulting samples were then calcined under a steady flow of oxygen, the temperature was increased to 550°C at 10°C per minute, before holding isothermal for a period of 200 minutes. After being allowed to cool down to room temperature.

5.13.3 Analysis

XRF was used to determine the metal content of the samples following dispersion (***table 5.6***), which upon calcination the relative concentration of which should be increased as the organics are removed.

Transition Metal	Metal Content (%)
Ti	5.1
Zr	1.7
Mo	4.2

Table 5.6: Average concentration of transition metal dispersed within silsesquioxane copolymer as determine by XRF

The XRF results show relatively little dispersion of zirconium within the pores in comparison with the other two metals.

Following calcination, nitrogen BET adsorption was used to determine the surface area of the materials prepared (***table 5.7***). Taking five readings up to a partial pressure of 0.2, after previously degassing samples at 125°C.

Transition Metal	Surface Area (m^2/g)
Ti	2.4
Zr	96.1
Mo	36.7

Table 5.7: Surface area measurements taken for calcined silsesquioxane copolymers containing dispersed transition metal complexes

In all cases the surface areas recorded are very low, especially in comparison to calcined copolymers prepared at 450°C, without transition metals dispersed into the structure.

5.14 Conclusions

A number of different methods have been attempted, with varying degrees of success, to insert one of four different transition metals into porous materials deriving from the silsesquioxane copolymers which have been prepared.

The ring opening reaction in particular has been useful to achieve the aims, enabling materials to be prepared containing either titanium, zirconium, molybdenum or cobalt, whilst still retaining a high porosity. Although the transition metal content of the species shows some variations, in all instances a noticeable quantity has been recorded. Additionally the pore size distribution of these compounds shows little change, which acts as an indicator that there has not been much breakdown of the silsesquioxane structure.

Solid state MAS ^{29}Si NMR studies of the metal containing copolymers show a strong resemblance to the spectra obtained before the insertion reactions. Peaks due to the silicon bonded directly to the three organic groups are still clearly visible, in addition to a small shoulder where the ring structure has been broken without later insertion of the metal occurring at that site. Finally peaks can be observed corresponding to a more silicate like structure, where the silicon is close to a transition metal.

The preparation of similar monomeric species has also been seen to occur. Unfortunately attempts to prepare an incompletely condensed vinyl silsesquioxane did not prove successful, which could provide another route to transition metal containing porous polymers.

The addition of transition metals to monomeric species prior to copolymerisation has shown some promise of being able to provide a route to obtaining such materials. Addition of cobalt to octahydridosilsesquioxane has proved difficult to isolate the required species, but the addition of zirconium to octavinylsilsesquioxane has successfully enabled production of a transition metal containing copolymer without the need for a ring opening reaction.

In attempting to prepare silicate materials, using the silsesquioxane copolymers to provide the means to disperse the transition metal, yet lose the organic material, did result in such materials being prepared, unfortunately these possessed significantly reduced surface areas when compared to the silsesquioxane copolymers.

5.15 References

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6 EXAFS Studies Of Transition Metal Containing Silsesquioxanes

6.1 Aims And Objectives

A number of different transition metal containing silsesquioxane based compounds have been synthesised, incorporating either titanium, zirconium, molybdenum or cobalt. These have been prepared using several different methods, and while it has been shown that the metals can be found within the materials, the structure is harder to determine.

As the materials do not form crystals, this limits the techniques that can be used to determine the structure around the transition metal atoms. However, EXAFS[1-6] does not require the samples to be crystalline, only looking at the local structure around an atom requiring no long range order, and therefore has been used to give an indication of these structures.

All EXAFS data has been collected at the synchrotron radiation source at Daresbury Laboratories, with the conditions under which this was collected varied depending on the element investigated. Raw data processing of the results was carried out using the program EXCALIB, background removal using EXSPLINE[7] and the theoretical and experimental EXAFS compared using EXCURV98[8]. Bond distances and structures obtained were compared for feasibility with known materials recorded in the Cambridge Structural Database[9] (CSD) and Inorganic Crystal Structure Database (ICSD)[10].

For all samples the EXAFS data was only modelled and compared to experimental data up to the point where the noise levels in the collected data still allowed the curves to be followed and therefore allow the refinement to attempt to replicate this, and for suggestions to be made as to possible structures.

6.2 Titanium EXAFS

6.2.1 Introduction

EXAFS measurements were conducted on several titanium samples using station 8.1 at Daresbury. This station was fitted with a double crystal Si(1,1,1) monochromator, which was used with harmonic rejection set at 50%. Prior to collecting results, the Ti K-edge position was calibrated using titanium foil.

Samples were analysed as pellets, these were prepared with the titanium loaded material (approx. 20mg) in either boron nitride (approx. 180mg) or fused silica (approx. 80mg). The solids were ground together and pressed into the pellet using a 20mm die, with 6 tons pressure. These were checked visibly to ensure even distribution of the compound.

Where possible transmission EXAFS was recorded, but generally, and in particular for weaker samples, fluorescence was used instead. All EXAFS data, together with its associated Fourier transform, is shown with both experimental (solid line) and calculated theoretical (dashed line) values for comparison.

6.2.2 Dispersed And Calcined Titanium

EXAFS can be used to view the dispersed titanium complex prior to calcination. The structure (***figure 6.1***) of bis(cyclopentadienyl)titanium dichloride has been studied using other techniques[11], to show a titanium to chlorine bond distance of 2.36Å and a titanium to carbon distance of 2.37Å.

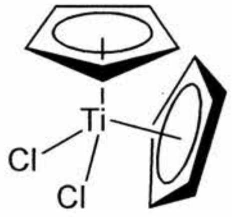

Figure 6.1: Structure of bis(cyclopentadienyl)titanium dichloride

In attempting to fit the dispersed material, given the similarity expected for the two atom types in terms of distance from the central titanium atom, during refinement the radii of these were kept identical to each other. The EXAFS (***figure 6.2***) and associated Fourier transform (***figure 6.3***) are shown for both experimental and theoretical data.

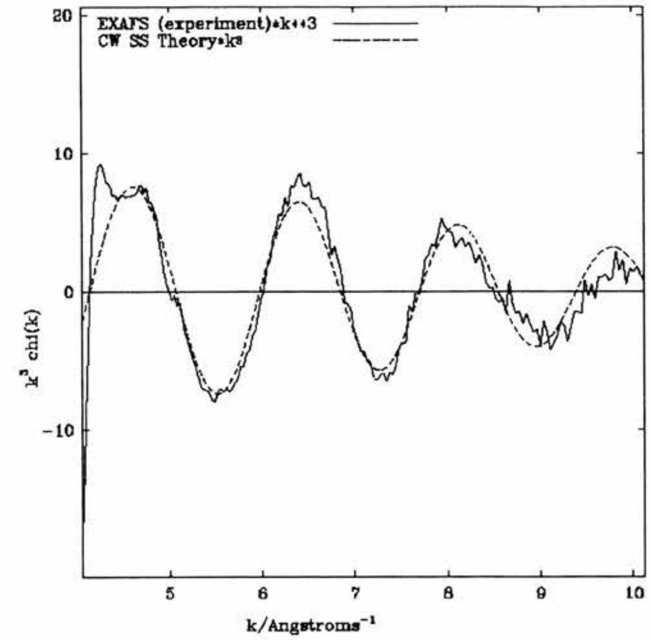

Figure 6.2: EXAFS data collected for bis(cyclopentadienyl)titanium dichloride in silsesquioxane copolymer

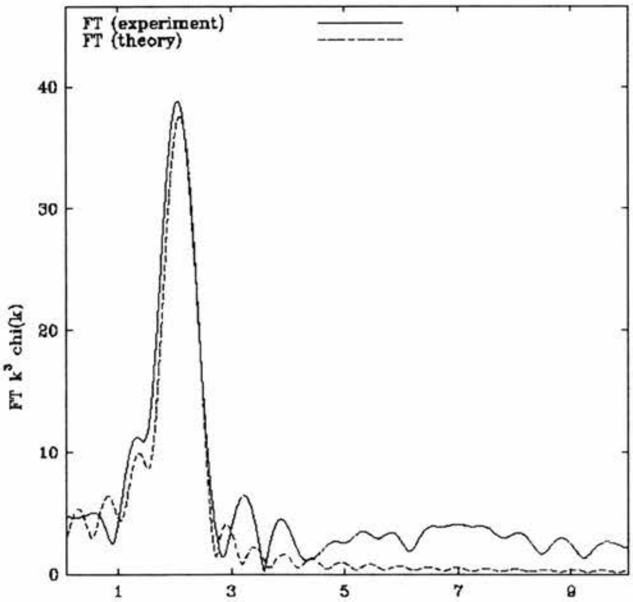

Figure 6.3: Associated Fourier transform of EXAFS collected for dispersed titanium

The refined bond distances calculated from the EXAFS data (***table 6.1***) differ from those expected from free bis(cyclopentadienyl)titanium dichloride.

	Ti–C	Ti–Cl
Refined EXAFS distances (*ca.* ±0.03Å)	2.21	2.19
Occupation numbers (N)	10	2
Debye-Waller factors (σ^2)	0.006	0.006

R(%)=30.99, AFAC=1.00

Table 6.1: Refined EXAFS data for dispersed bis(cyclopentadienyl)titanium dichloride in silsesquioxane copolymer

Additional peaks that can be observed around 3Å to 4Å on the associated Fourier transform, could possibly be a result of atoms within the surrounding copolymer. No attempt was made to try and fit another shell to these peaks. With the quality of the data a reasonable assignment would not be possible.

After dispersing bis(cyclopentadienyl)titanium dichloride into the silsesquioxane copolymer, the expected species upon calcination would be a titanium silicate. Therefore when attempting to fit the EXAFS obtained (***figure 6.4***), the first shell was initially assumed to be four oxygen atoms at an approximate distance of 1.8Å surrounding the titanium.

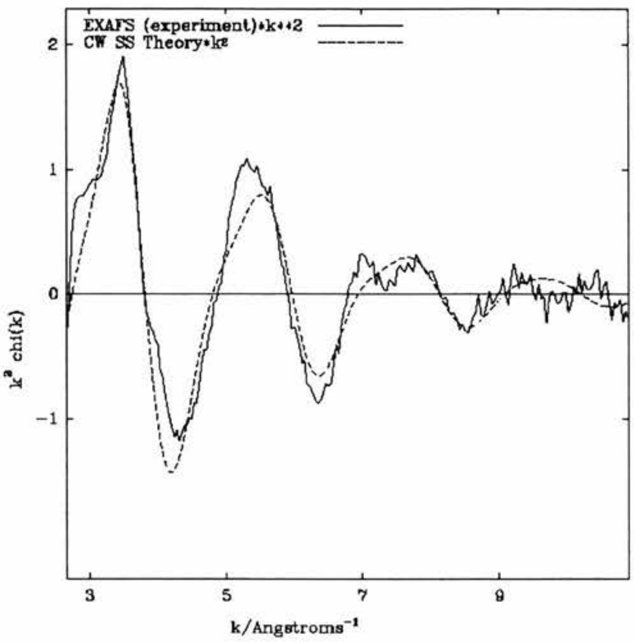

Figure 6.4: EXAFS of calcined silsesquioxane copolymer in the presence of dispersed titanium

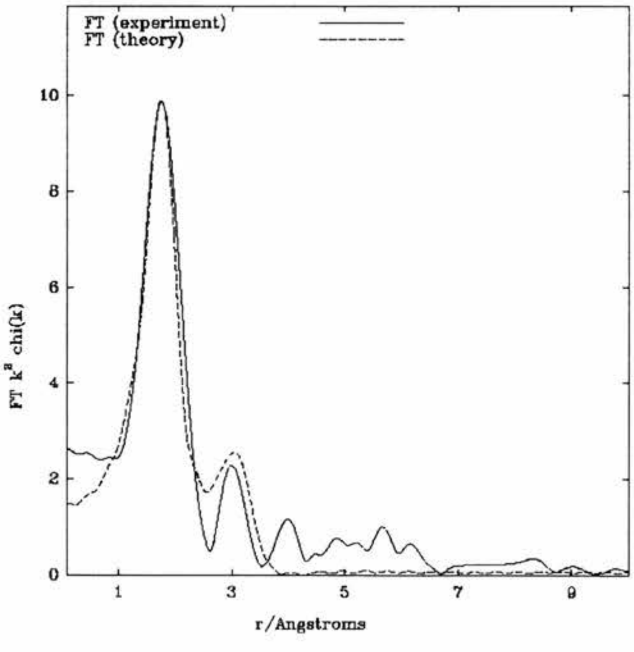

Figure 6.5: Associated Fourier transform from EXAFS obtained from a calcined silsesquioxane copolymer in the presence of dispersed titanium

With these four oxygen atoms proving a good fit, the second shell would be expected to be four silicon atoms around a distance of 3.2Å, each bonded to one of the four oxygen atoms assumed to be present. After refinement the R value was brought down to 33.83, which as seen from the EXAFS, together with its associated Fourier transform (***figure 6.5***) represents a reasonably good fit.

The bond distances produced as a result of the refinement (***table 6.2***) are consistent with values obtained for such bonds in other materials. Assuming a silicon to oxygen to titanium bond angle of 120° then a rough calculation gives the titanium to oxygen bond as 1.9Å.

	Ti–O	Ti–Si
Refined EXAFS distances (*ca.* ±0.03Å)	1.83	3.19
Occupation numbers (N)	4	4
Debye-Waller factors (σ^2)	0.008	0.016

R=(%)33.83, AFAC=0.70

Table 6.2: Summary of refined EXAFS data for calcined titanium loaded species

The structure around the titanium atom (***figure 6.6***) is therefore close to what was expected, although be changing the AFAC value to 0.70 there will be some doubt as to the actual structure present.

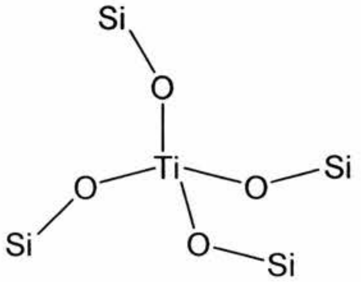

Figure 6.6: Structure surrounding titanium as determined from EXAFS data.

6.2.3 Titanium Insertion In Ring Opened Copolymer

After the insertion of cyclopentadienyltitanium trichloride within a ring opened copolymer, the structure involved should result in chlorine atoms lost as the titanium bonds to the oxygen atoms of the silanol groups, whilst the cyclopentadienyl ring remained uninvolved with any reaction. A third shell would be silicon atoms attached to the oxygen. One possible variation would be only partial reaction of the chlorine, rather than to completion.

Initially trying to fit the EXAFS (***figure 6.7***) with a shell of three oxygen atoms about 1.9Å followed by a second shell of five carbons at 2.4Å, upon refinement resulted in a good fit around these values. Attempts to use only three oxygen atoms at this distance and adding a chlorine atom around the distance of the carbons failed to result in an improved fit, favouring the ideal configuration outlined above.

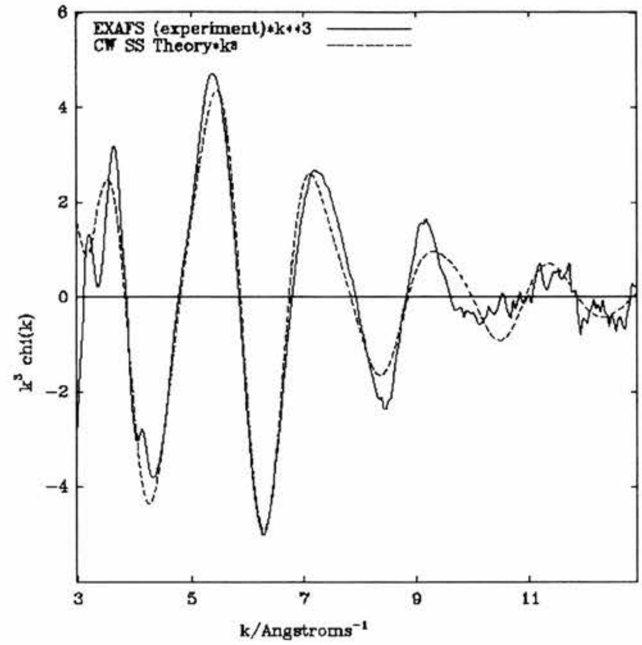

Figure 6.7: EXAFS data for titanium inserted into ring opened silsesquioxane copolymer.

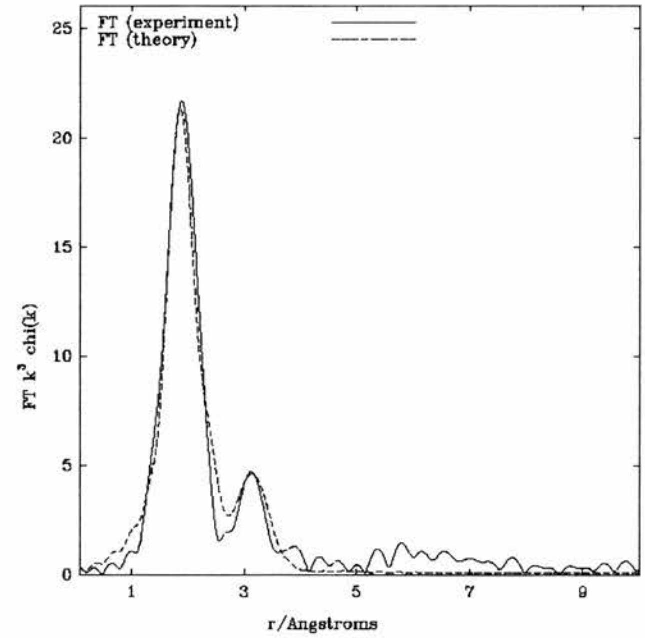

Figure 6.8: Associated Fourier transform for the EXAFS collected from the insertion of cyclopentadienyltitanium trichloride into a ring opened silsesquioxane copolymer

From the associated Fourier transform (***figure 6.8***) a further peak can be observed slightly above 3Å, given the assignment of three oxygen atoms previously, this would be expected to refine to three silicons. This is indeed seen to be the situation.

All bond distances (***table 6.3***) collected from this refinement, offer realistic values that are comparable to other compounds. The structure that this represents (***figure 6.9***)

	Ti–O	Ti–C	Ti–Si
Refined EXAFS distances (*ca.* ±0.03Å)	1.87	2.45	3.19
Occupation numbers (N)	3	5	3
Debye-Waller factors (σ^2)	0.009	0.015	0.017

R(%)=29.81, AFAC=0.88

Table 6.3: Summary of refinement of EXAFS from titanium loaded copolymer.

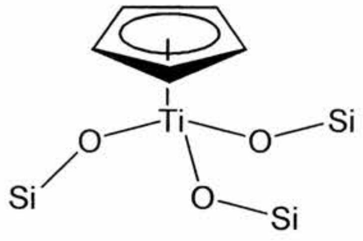

Figure 6.9: Structure surrounding titanium as determined from EXAFS

6.2.4 Titanium Insertion Into Incompletely Condensed Silsesquioxanes

Although EXAFS data was collected for both cyclohexyl and cyclopentyl incompletely condensed silsesquioxanes upon which the attempted insertion of titanium had been conducted, only the latter resulted was suitable to try to refine theoretical parameters to identify the structure.

For the cyclohexyl silsesquioxane the EXAFS (***figure 6.10***) there appeared to be too many large oscillations in the collected data, which even following background subtraction failed to result in data that could readily be assigned to shells of atoms that might be reasonably contained within the structure of the product.

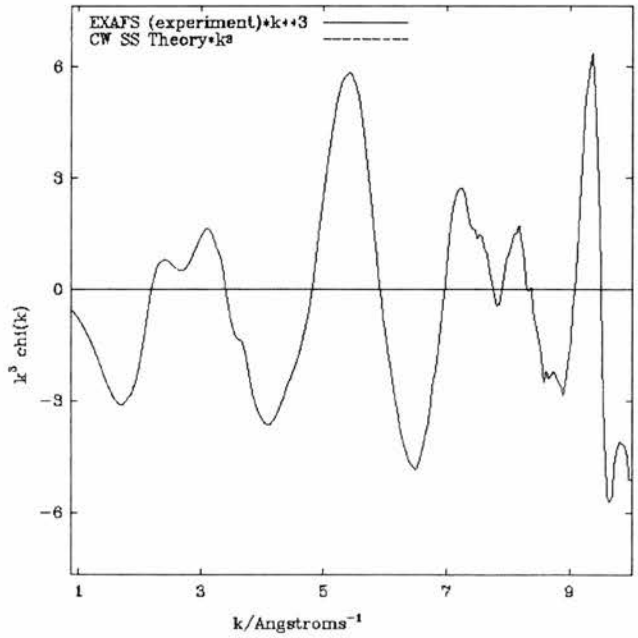

Figure 6.10: EXAFS of the attempted insertion of titanium into incompletely condensed cyclohexyl silsesquioxane

However, the EXAFS of the insertion within the cyclopentyl equivalent ***(figure 6.11)*** showed a strong resemblance to the result of the same reaction with the ring opened copolymer. As can be seen from the associated Fourier transform ***(figure 6.12)***, there appear to be shells corresponding approximately to the oxygen and carbon shells observed with the copolymer.

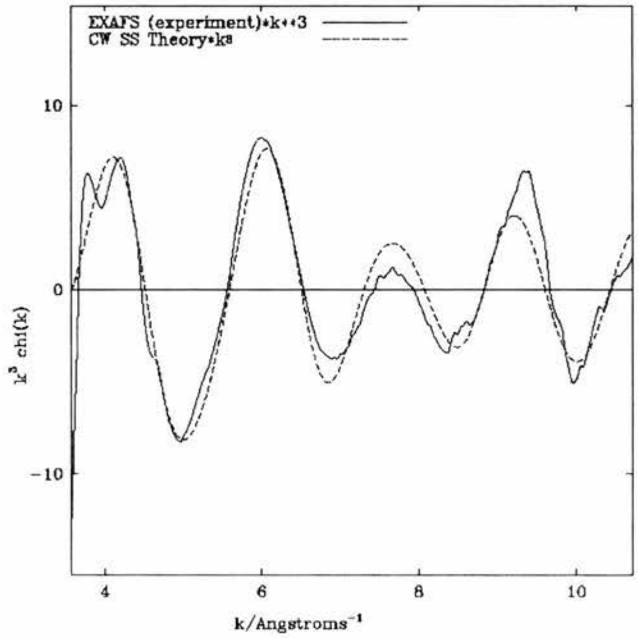

Figure 6.11: EXFAS showing the insertion of titanium within incompletely condensed cyclopentyl silsesquioxane

The most notable difference between this species and that of the copolymer is the separation of two separate peaks rather than one around where the first two shells would be expected. However, trying to refine these as shells of three oxygen and five carbon atoms respectively, does give a reasonable fit, although the distances to the titanium are slightly affected. In both cases being slightly shorter.

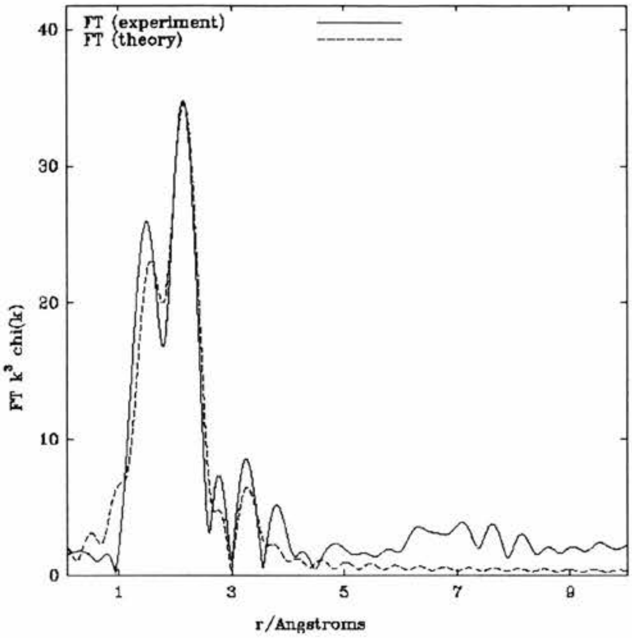

Figure 6.12: Associated Fourier transform of titanium insertion within cyclopentyl silsesquioxane

Attempting to assign a silicon shell around 3.5Å, did not significantly increase the quality of the fit, and the best fit was obtained with the occupancy of this set to two (***table 6.4***). However, assuming this to be correct, that would most likely imply an identical number of oxygen atoms to this figure, plus one extra chlorine, with approximately the same distance to titanium as the five carbons from the cyclopentadienyl ring.

Although this data does not entirely result in an acceptable configuration of the atoms, it does seem reasonable to suggest that it is indicative of the titanium being inserted into the silsesquioxane, although it is a possibility that the insertion has not gone to completion, the result of which would be some chlorine atoms being present.

	Ti–O	Ti–C	Ti–Si
Refined EXAFS distances (*ca.* ±0.03Å)	1.66	2.27	3.47
Occupation numbers (N)	3	5	2
Debye-Waller factors (σ^2)	0.015	0.002	0.012

R(%)=31.12, AFAC=1.00

Table 6.4: Summary of refined EXAFS data from the insertion of titanium within incompletely condensed cyclopentyl silsesquioxane

6.3 Zirconium EXAFS

6.3.1 Introduction

EXAFS data for all zirconium samples was collected on station 9.2 at Daresbury. This was fitted with a double crystal Si(2,2,0) monochromator, which was used with the harmonic rejection set to 50%. Before any results were collected, the position of the Zr K-edge position was calibrated with the use of zirconium foil.

As with the titanium containing samples, these were prepared for analysis by producing 20mm diameter pellets pressed at 6 tons containing zirconium loaded material (approx. 20mg), with either boron nitride (approx. 180mg) or fused silica (approx. 80mg). The pellets needed to have a uniform distribution, so the solids were ground together and mixed with a pestle and mortar, and after they had been prepared viewed to check for an even coloration across the surface of the compound.

Due to generally relatively low zirconium content in some of these materials, in all cases fluorescence EXAFS was used to collect data. With all the EXAFS data shown, and for the associated Fourier transforms, the experimental (solid line) and calculated theoretical (dashed line) are shown together for comparison.

6.3.2 Dispersed And Calcined Zirconium

The zirconium complex prior to calcination can be viewed by EXAFS, the structure of this species (***figure 6.13***)[12] should closely resemble that for titanium, with two chlorine atoms and ten carbon atoms to fill the first two shells.

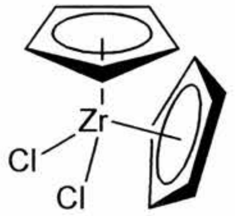

Figure 6.13: Bis(cyclopentadienyl)zirconium dichloride

Attempting to refine the expected values, as being similar to the titanium equivalent, to the EXAFS (***figure 6.14***) collected refined results in values (***table 6.5***) which are close to those expected.

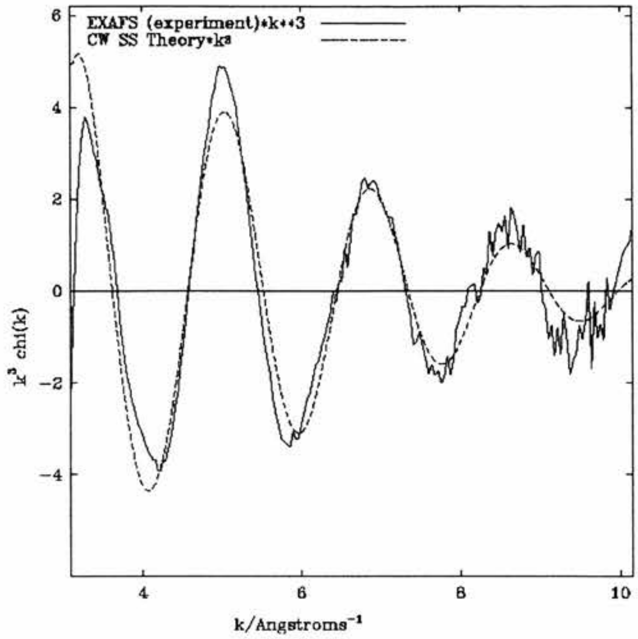

Figure 6.14: EXAFS obtained from bis(cyclopentadienyl)zirconium dichloride dispersed into silsesquioxane copolymer

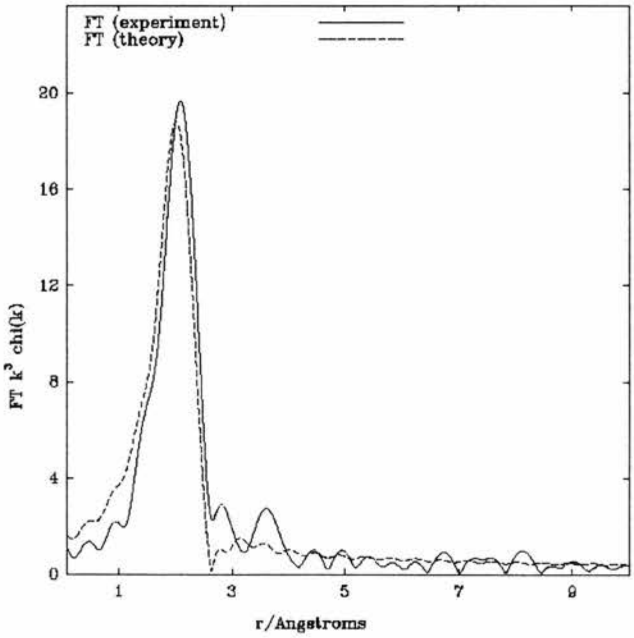

Figure 6.15: Associated Fourier transform from EXAFS of dispersed zirconium

The associated Fourier transform for this data (***figure 6.15***) can be seen to show some smaller peaks which whilst they may largely be due to noise within the

EXAFS, the peak in particular around 3.5Å could derive from the surrounding copolymer.

	Zr–C	Zr–Cl
Refined EXAFS distances (*ca.* ±0.03Å)	2.23	2.19
Occupation numbers (N)	10	2
Debye-Waller factors (σ^2)	0.015	0.017

R(%)=33.18, AFAC=0.80

Table 6.5: Summary of values refined from EXAFS data for the dispersion of zirconium within silsesquioxane copolymer

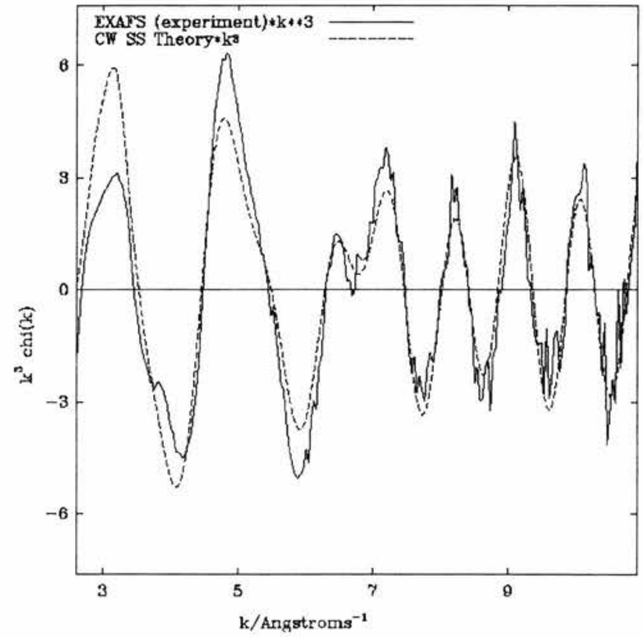

Figure 6.16: EXAFS of calcined zirconium containing silsesquioxane

The zirconium EXAFS (***figure 6.16***) obtained after calcination of dispersed bis(cyclopentadienyl)zirconium dichloride into the silsesquioxane copolymer, would be expected to show some similarities with that exhibited by titanium. An initial look at the associated Fourier transform (***figure 6.17***) reveals peaks around 2Å and 3.5Å.

When attempting to fit the data, the first peak was assumed to be oxygen, and with zirconium being capable of forming up to six co-ordinate species, this number was used, and refined parameters seemed to agree with this. However, a slightly better fit was obtained with the oxygen atoms split into two slightly different environments, with two oxygen bonds a little shorter than the other four.

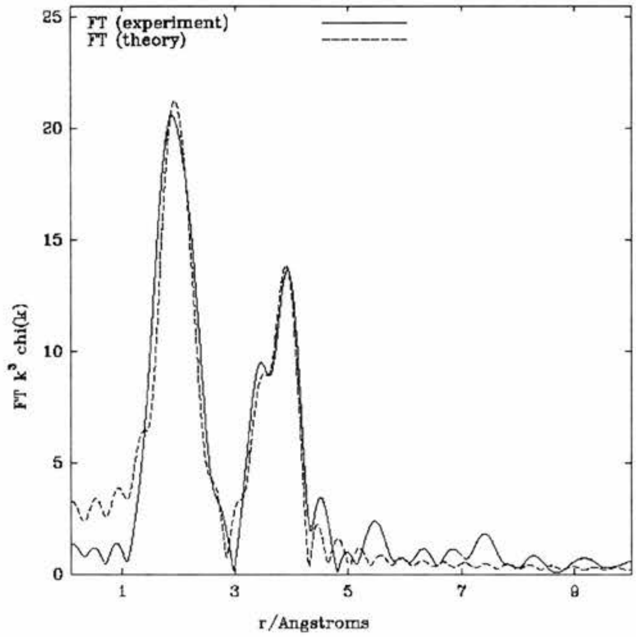

Figure 6.17: Associated Fourier transform of zirconium containing calcined silsesquioxane

Attempting to fit for six silicon atoms as a single shell, failed to refine to give sensible values, even by splitting up into two different environments led to negative Debye-Waller factors. Something which is not possible. Additionally trying to have shells of six oxygen then six silicon atoms around a single zirconium would not be in all likelihood feasible.

To properly fit these higher shells it was therefore assumed some heavier element must be present at this distance. The only such metal present could be zirconium itself. Refining third and fourth shells to two zirconium atoms and four silicon atoms resulted in acceptable parameters (***table 6.6***).

	Zr–O	Zr–O	Zr–Zr	Zr–Si
Refined EXAFS distances (*ca.* ±0.03Å)	2.01	2.15	3.61	3.91
Occupation numbers (N)	2	2	2	4
Debye-Waller factors (σ^2)	0.006	0.012	0.005	0.011

R(%)=37.05, AFAC=0.90

Table 6.6: Summary of refined EXAFS data for calcined zirconium containing silsesquioxane copolymer

A single structure explaining this refined data is not going to be physically possible, one possibility would be for two different zirconium containing species being present. One of these could be a zirconium silicate, possibly a four co-ordinate (***figure 6.18***). This would have to have a tetrahedral zirconium to allow for a regular silicate structure.

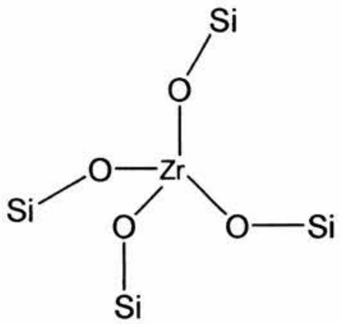

Figure 6.18: Possible zirconium silicate structure

A second compound present is could be a zirconium oxide (***figure 6.19***), with oxygen bridges between two zirconium atoms. This can explain the refined zirconium to zirconium distances to be smaller than to silicon, through the requirement of having a smaller angle at the intervening oxygen.

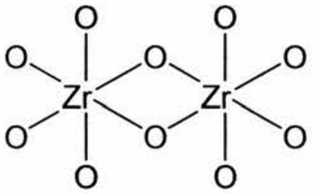

Figure 6.19: Possible zirconium oxide resulting from calcination

The oxygen atoms from the refinement don't exactly equate to those used in either structure suggested, but it is difficult to determine a ratio between the two types of material as refining to a single oxygen environment would not decrease the R factor too significantly.

After the EXAFS were collected for this sample, it was subsequently dried under vacuum (1.0 mmHg, 2 hours, 235°C). Whilst still keeping the sample under vacuum, EXAFS was collected again to view the effects of the drying process.

Although slight differences were noticed, there didn't appear to be anything significantly changed from the above example, and inputting the variables from this gave a low R value, which could only be slightly refined. Removing an extra oxygen does not give an improved fit, as might be expected if the copolymer had some co-ordinated water present.

6.3.3 Zirconium Insertion In Ring Opened Copolymer

The insertion of zirconium within the structure of the ring opened copolymer involves the addition of cyclopentadienyl zirconium trichloride. As this resembles the titanium species used for a similar reaction, it is expected that any product should possess a similar structure.

When attempting to refine a fit for the EXAFS (***figure 6.20***) obtained for the product of this reaction, initially three oxygen atoms around 1.9Å were used to try and model the first peak seen in the associated Fourier transform (***figure 6.21***), followed by five carbon atoms around 2.2Å.

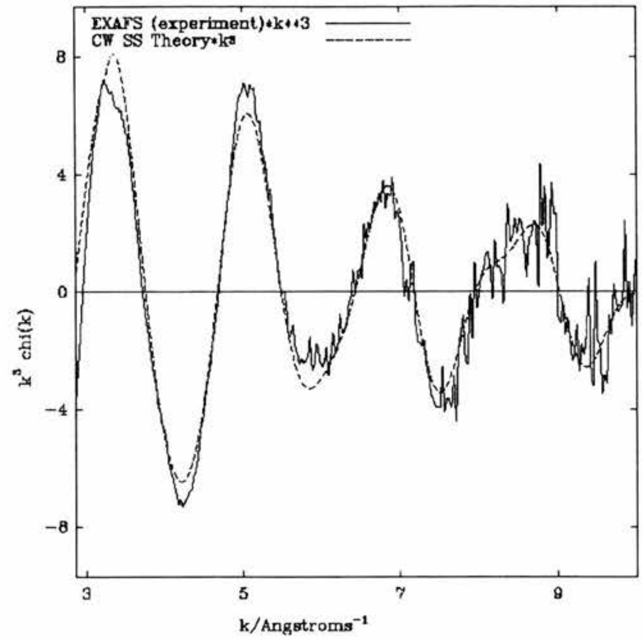

Figure 6.20: Zirconium EXAFS obtained from the insertion of zirconium within ring opened copolymer, showing refinement with two oxygen atoms in the first shell

However, refinement of these values indicated that there were too many oxygen atoms in the first shell, and the second shell of carbon did not seem to lead to the best possible fit either. Assuming the carbons were present, and therefore as a shell of five atoms representing an unreacted cyclopentadienyl ring, the most likely solution was for only partial insertion to occur, leaving some chlorine remaining bonded to the zirconium.

Substituting one chlorine for one oxygen, and assuming the chlorine distance to be initially the same as the carbon shell, upon refinement lead to a significantly improved fit. After addition of a fourth shell of two silicon atoms, bonded to the oxygen present, the refinement gave a R value of 24.61, and acceptable parameters for all atoms (***table 6.7***).

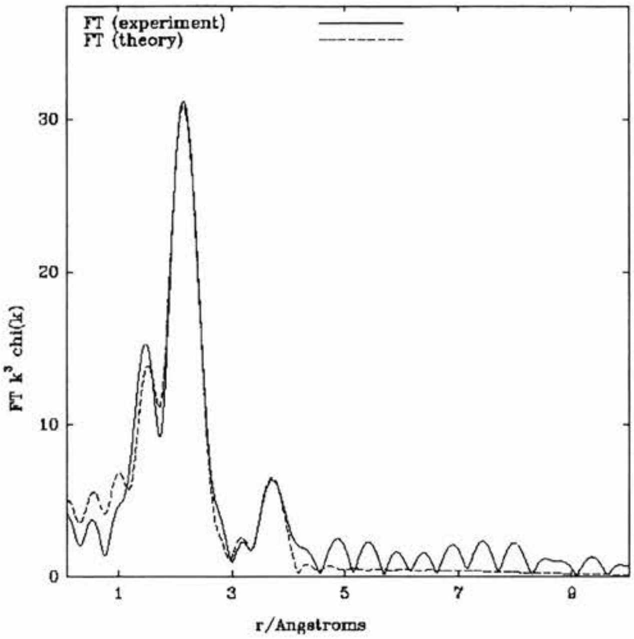

Figure 6.21: Associated Fourier transform for the insertion of zirconium species into a ring opened silsesquioxane copolymer, assuming a first shell of two oxygen atoms

The structure derived from this (***figure 6.22***) is something that would be acceptable from the reaction originally intended. However, it is also possible to assume from the EXAFS that perhaps only one oxygen atom is present in the first shell.

	Zr–O	Zr–C	Zr–Cl	Zr–Si
Refined EXAFS distances (*ca.* ±0.03Å)	1.87	2.13	2.39	3.70
Occupation numbers (N)	2	5	1	2
Debye-Waller factors (σ^2)	0.010	0.001	0.002	0.004

R(%)=24.61, AFAC=1.00

Table 6.7: Summary of refinement for zirconium in silsesquioxane copolymer, with two oxygen atoms assumed as first shell

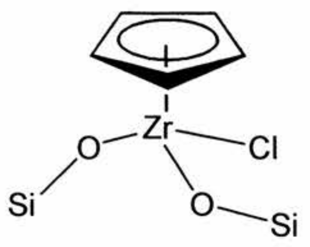

Figure 6.22: Possible structure resulting from the insertion of zirconium into ring opened silsesquioxane copolymer

In addition to trying to refine assuming the first oxygen shell to contain two atoms, this refinement was also conducted with one oxygen only, therefore implying the presence of two chlorine atoms as the third shell and only one silicon as the fourth (***figure 6.23***). This does lead to a slightly improved R value, but at the expense of making the Debye-Waller factor for the silicon to equal a negative number, which is clearly not a valid result.

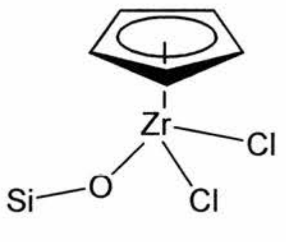

Figure 6.23: Zirconium structure used as an attempted fit, with only one bond to the copolymer

6.3.4 Zirconium Addition To Octavinylsilsesquioxane Based Copolymers

The EXAFS obtained for samples of materials prepared using this method failed to show any useful data through means of having too much noise present upon collection. As can be seen for the EXAFS (***figure 6.24***), even at 8Å^{-1} in k-space the noise oscillations are larger than some of those seen to be real data.

Using only the reasonable part of the data is too small to give valid results for the number of parameters to be refined for the predicted structure (***figure 6.25***). Attempts to do so anyway do not result in a good fit, the dashed line in figure 6.24 represents a refinement up to a maximum k value of 10Å^{-1}, but this results in a R value of over 60.

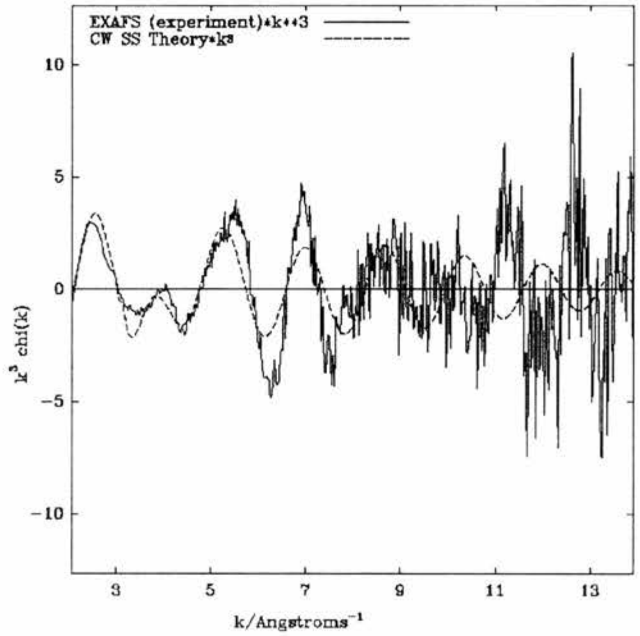

Figure 6.24: EXAFS of silsesquioxane copolymer with zirconium added to monomeric octavinylsilsesquioxane

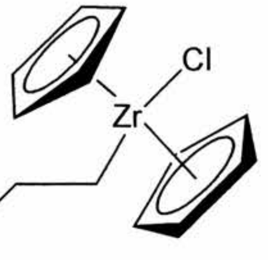

Figure 6.25: Expected zirconium environment after addition to octavinylsilsesquioxane

6.3.5 Zirconium Insertion Into Incompletely Condensed Silsesquioxanes

The EXAFS obtained from the attempted insertion of zirconium into the two types of incompletely condensed silsesquioxanes prepared have been collected, and analysed in comparison to the ring opened copolymer.

Using the cyclopentyl incompletely condensed silsesquioxane the EXAFS recorded (***figure 6.26***) and it's associated Fourier transform (***figure 6.27***) show a strong comparison with the material derived from the copolymer. A large peak around 2.3Å, with a small shoulder appearing around 1.9Å. A further shell can be observed above 3Å in both instances.

Given the resemblance to the copolymer, the values obtained for that species represented a reasonable starting point in attempting to refine the structure of this particular material. The relative number of oxygen and chlorine atoms in their respective shells was changed, although the fit obtained with the zirconium atoms bound to two of the silanol groups still resulted in the best fit of the EXAFS.

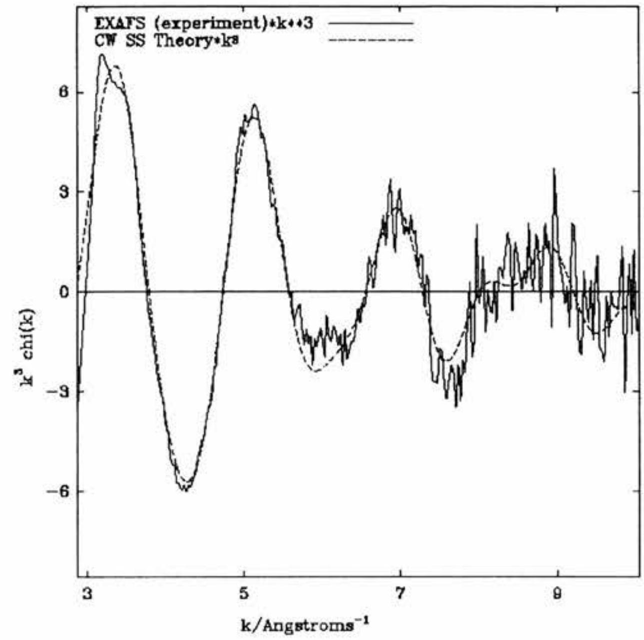

Figure 6.26: EXAFS obtained from the insertion of zirconium into a cyclopentyl incompletely condensed silsesquioxane

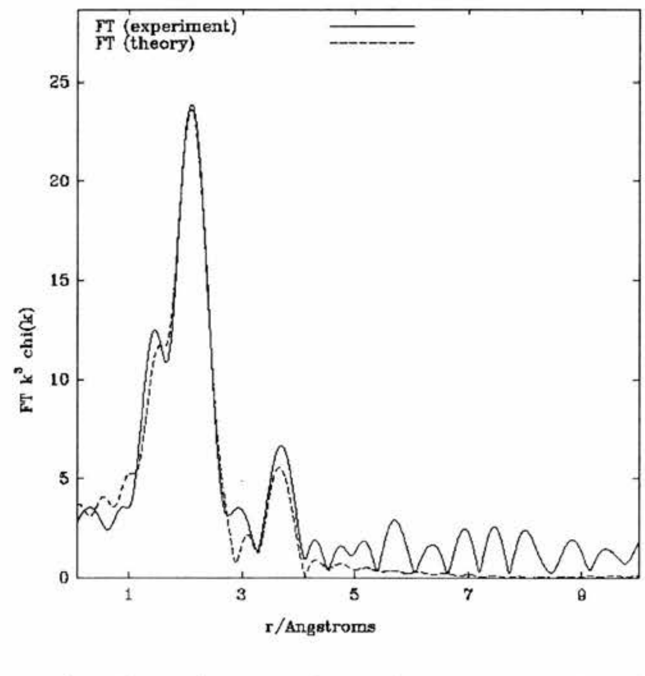

Figure 6.27: Associated Fourier transform of EXAFS obtained from zirconium insertion into incompletely condensed cyclopentyl silsesquioxane

The refined structure immediately surrounding the zirconium also differs little in the interatomic distances obtained (***table 6.8***), with none of the calculated values differing by 0.05Å.

	Zr–O	Zr–C	Zr–Cl	Zr–Si
Refined EXAFS distances (*ca.* ±0.03Å)	1.86	2.10	2.38	3.65
Occupation numbers (N)	2	5	1	2
Debye-Waller factors (σ^2)	0.011	0.003	0.004	0.005

R(%)=26.38, AFAC=0.90

Table 6.8: Summary of refined EXAFS data on zirconium insertion into cyclopentyl incompletely condensed silsesquioxane

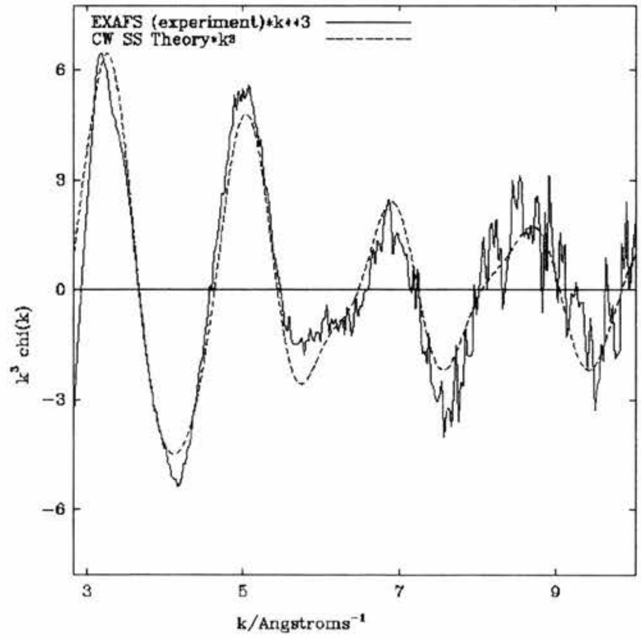

Figure 6.28: EXAFS obtained from the insertion of zirconium into incompletely condensed cyclohexyl silsesquioxane

The corresponding EXAFS obtained from the cyclohexyl incompletely condensed silsesquioxane (***figure 6.28***) and associated Fourier transform (***figure 6.29***) are also observed to show the same general pattern.

The refined distances (***table 6.9***) differ slightly from the values obtained for the other two similar species, but the occupation numbers remain the same. Attempting to either add or subtract a siloxane linkage to the zirconium in either case results in a less accurate fit.

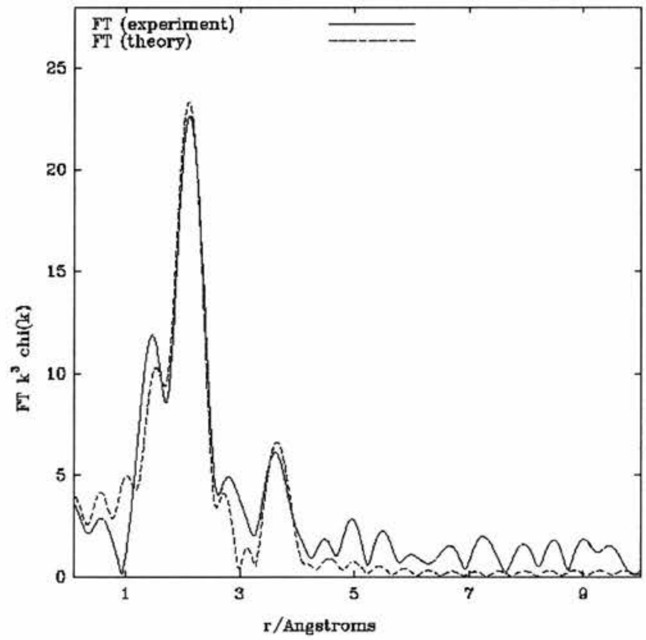

Figure 6.29: Associated Fourier transform from zirconium EXAFS with incompletely condensed cyclohexyl silsesquioxane

	Zr–O	Zr–C	Zr–Cl	Zr–Si
Refined EXAFS distances (*ca.* ±0.03Å)	1.91	2.16	2.45	3.68
Occupation numbers (N)	2	5	1	2
Debye-Waller factors (σ^2)	0.014	0.004	0.014	0.012

R(%)=33.90, AFAC=0.90

Table 6.9: Refined distances with zirconium insertion into incompletely condensed cyclohexyl silsesquioxane

6.4 Molybdenum EXAFS

6.4.1 Introduction

For all molybdenum samples, the EXAFS data was collected using station 9.2 at Daresbury. A double crystal Si(2,2,0) was fitted to this station, and used with a harmonic rejection of 50%. Prior to collection of data the position of the Mo K-edge position was first calibrated using molybdenum foil.

The samples were analysed as 20mm pellets with either silica or boron nitride prepared as for the zirconium samples. Transmission EXAFS was recorded for the dispersion and calcinated materials. When analysing the products of the insertion reactions fluorescence EXAFS was used instead.

All EXAFS and associated Fourier transforms are shown with both experimental (solid line) and theoretical refined data (dashed line).

6.4.2 Dispersed And Calcined Molybdenum

The dispersion prior to calcination has been examined under EXAFS (***figure 6.30***), which as the structure of the bis(cyclopentadienyl)molybdenum dichloride is already known[13], gives a good starting position when attempting to refine the structure.

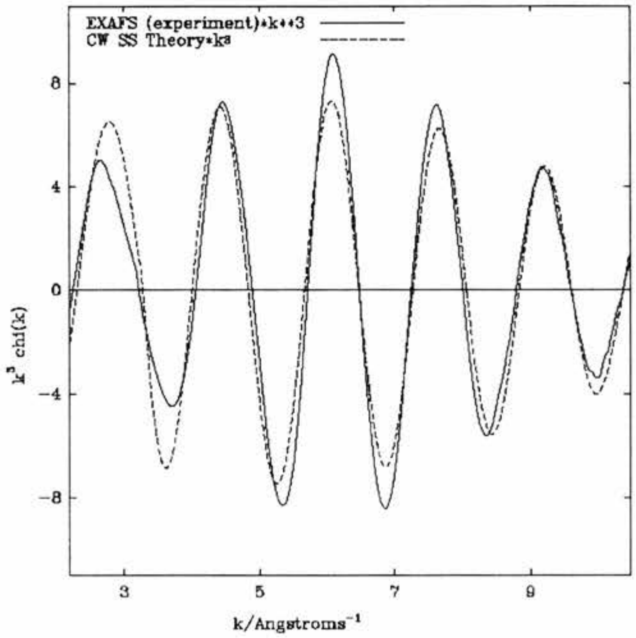

Figure 6.30: EXAFS of bis(cyclopentadienyl)molybdenum dichloride dispersed in silsesquioxane copolymer

The associated Fourier transform (***figure 6.31***) of the EXAFS shows the expected single peak, as the carbon and chlorine to molybdenum are almost identical. The refined distances obtained (***table 6.10***) are close to those obtained for the similar titanium and zirconium species, as well as confirming the expected unreacted structure (***figure 6.32***).

	Mo–C	Mo–Cl
Refined EXAFS distances (*ca.* ±0.03Å)	2.35	2.46
Occupation numbers (N)	10	2
Debye-Waller factors (σ^2)	0.007	0.005

R(%)=26.44, AFAC=1.00

Table 6.10: Summary of refined parameters for molybdenum dispersed in copolymer

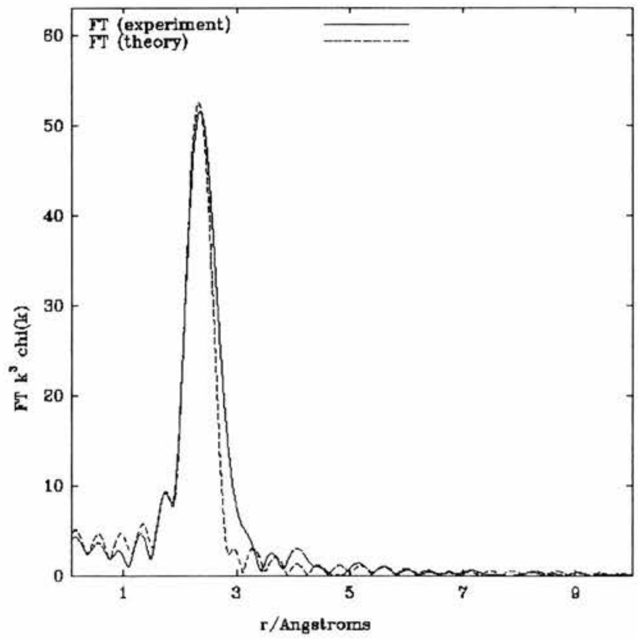

Figure 6.31: Associated Fourier transform of EXAFS taken with dispersed molybdenum in silsesquioxane copolymer

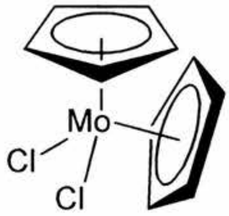

Figure 6.32: Structure of bis(cyclopentadienyl)molybdenum dichloride

Upon calcination of bis(cyclopentadienyl)molybdenum dichloride within the pores of a silsesquioxane copolymer, it would be expected that the organic material present to be completely removed, leaving only the metal with oxygen and silicon remaining in the resulting compound. EXAFS data ***(figure 6.33)***, shown with the associated Fourier transform ***(figure 6.34)*** appears to initially indicate three different shells around the central molybdenum.

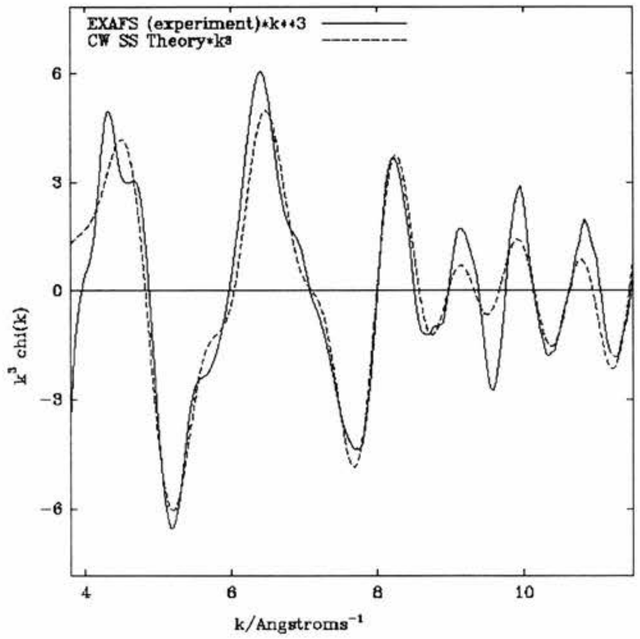

Figure 6.33: EXAFS of calcined silsesquioxane copolymer with molybdenum dispersed into the pores

Attempting to fit the large peak appearing on the associated Fourier transform around 2Å, initially tried four oxygen atoms, but this did not refine well, being too sharp for the peak shown. Splitting into two separate shells, one slightly below 2Å and one slightly above, enabled an improved fit to be made. The first such shell was determined to have a molybdenum to oxygen distance of 1.66Å, this indicates the likelihood of a double bond being present. The second shell resulted in a 2.15Å distance, which is more indicative of a single bond.

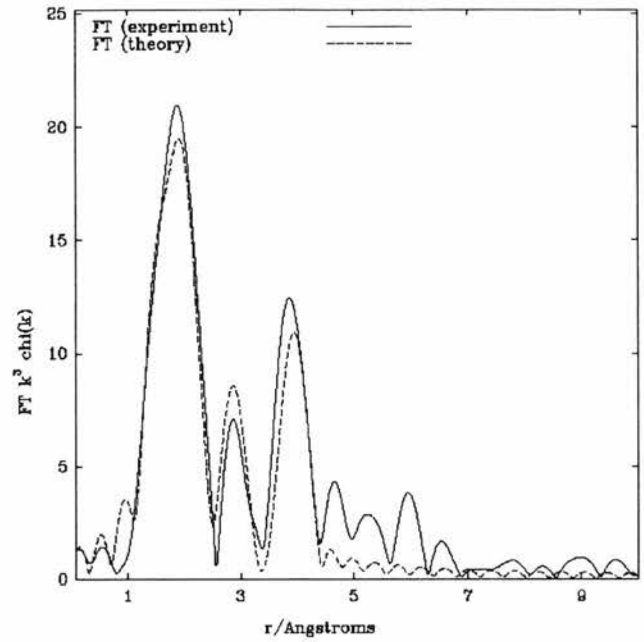

Figure 6.34: Associated Fourier transform of EXAFS for calcined molybdenum dispersed copolymer

The shell which appears around 3Å was considered to be a further oxygen shell. This distance is too long to be a direct bond to the molybdenum, yet too close to be a silicon or other atoms linked by an oxygen bridge. The most likely possibility would be further oxygen atoms, possibly in the form of water. This idea is reinforced by the lack of such a peak appearing when the material is dried further under vacuum. It can be refined easily to two oxygen atoms.

The larger peak around 3.5Å is most likely to represent silicon, and it refines well to four silicon atoms, although an extra one or two may be added without significantly affecting the overall quality of fit, to complete the attempted refinements (***table 6.11***).

	Mo–O	Mo–O	Mo–O	Mo–Si
Refined EXAFS distances (*ca.* ±0.03Å)	1.66	2.15	2.92	3.93
Occupation numbers (N)	2	2	2	4
Debye-Waller factors (σ^2)	0.009	0.003	0.001	0.003

R(%)=30.59, AFAC=1.00

Table 6.11: Summary of refined EXAFS data for molybdenum dispersed then calcined in silsesquioxane copolymer

Attempting to assign this data to a structure is slightly more difficult. The oxygen atoms and two silicons can be assigned to a structure (***figure 6.35***). This does not appear to as readily lend itself towards the formation of two products present as the zirconium does, through lack of the dimeric molybdenum with bridging oxygen atoms known to exist.

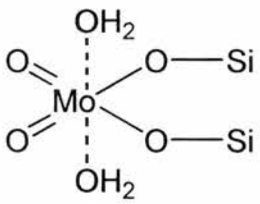

Figure 6.35: Possible molybdenum environment after calcination of the dispersed compound.

The calcined sample was further dried under vacuum (1.0 mmHg, 2 hours, 235°C), and whilst still retaining under the vacuum, EXAFS data was collected for a second time, with the intention of removing the shell assigned to the oxygen in water.

The EXAFS (***figure 6.36***), shown with associated Fourier transform (***figure 6.37***) at first glance appear to show this. However, upon attempting to fit and refine the oxygen atoms, the best fit obtained is for only two oxygen atoms at 1.7Å. A second shell can be refined to four silicon atoms at 3.72Å.

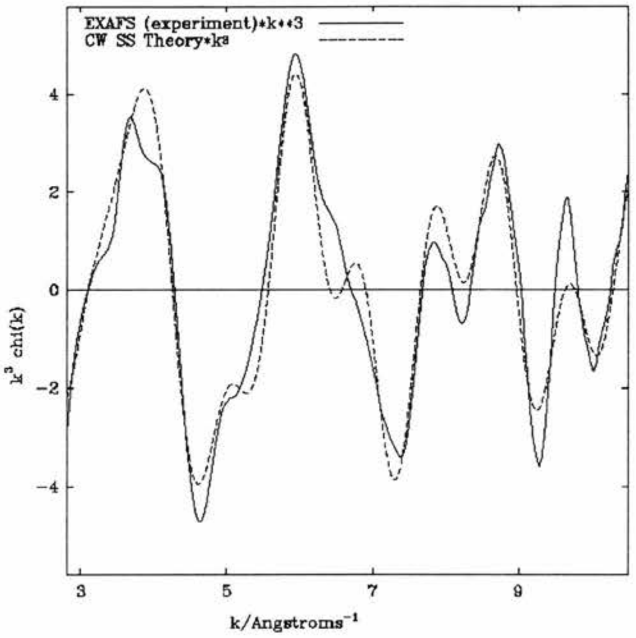

Figure 6.36: EXAFS obtained from calcined molybdenum dispersed silsesquioxane after drying under vacuum

Although the fit for this is reasonably good, the R value obtained is below 30, but this does not imply a sensible structure from the obtained data (***table 6.12***). One possibility would be that a molybdenum oxide is contained within a silicate structure, without any direct linkage to this material. Particularly with the short

Mo–O distances implying double bonds, there does not appear to be any connection to the material seen around 3.7Å.

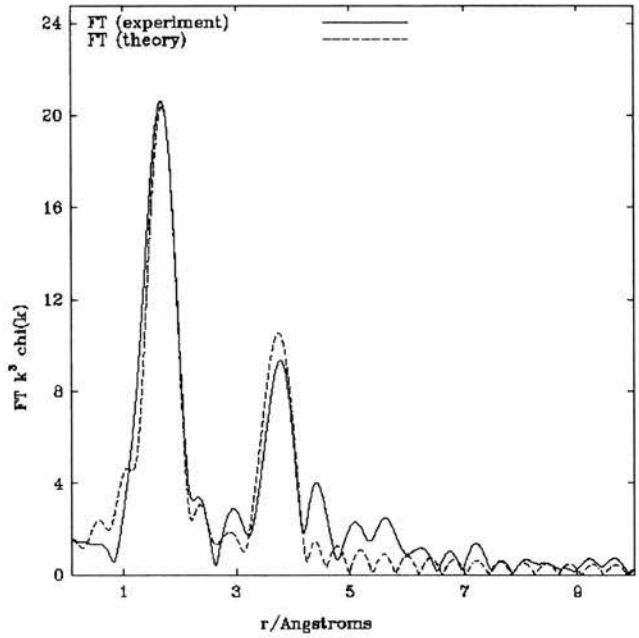

Figure 6.37: Associated Fourier transform after drying under vacuum

	Mo–O	Mo–Si
Refined EXAFS distances (*ca.* ±0.03Å)	1.75	3.72
Occupation numbers (N)	2	4
Debye-Waller factors (σ^2)	0.006	0.004

R(%)=29.44, AFAC=1.00

Table 6.12: Refined data for calcined molybdenum species after drying further under vacuum

6.4.3 Molybdenum Insertion In Ring Opened Copolymer

Although the insertion of molybdenum was conducted with only a dichloride metal complex, as opposed to the trichloride used for titanium and zirconium, the same type of reaction observed for those materials should be expected here.

However it is clear to see from the EXAFS (***figure 6.38***) and in particular its associated Fourier transform (***figure 6.39***), that this does not appear to have proceeded as for those two materials. The biggest comparison is with the dispersed molybdenum complex prior to calcination.

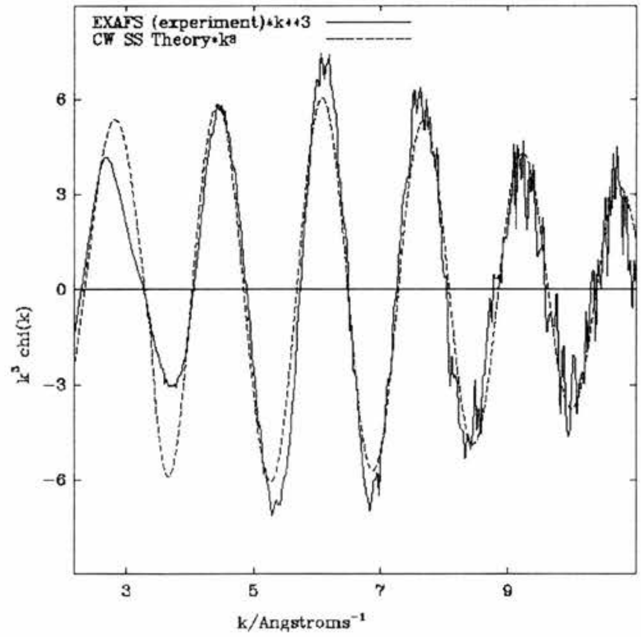

Figure 6.38: EXAFS of attempted molybdenum insertion into ring opened copolymer

From this the data was refined starting from a shell of ten carbon atoms and a shell of two chlorine atoms, both at 2.4Å. This resulted in a good fit (R=30.32) quite easily without resorting to these initial values being altered too significantly (***table 6.13***), and can be considered to still retain the bis(cyclopentadienyl)molybdenum dichloride unreacted (***figure 6.40***).

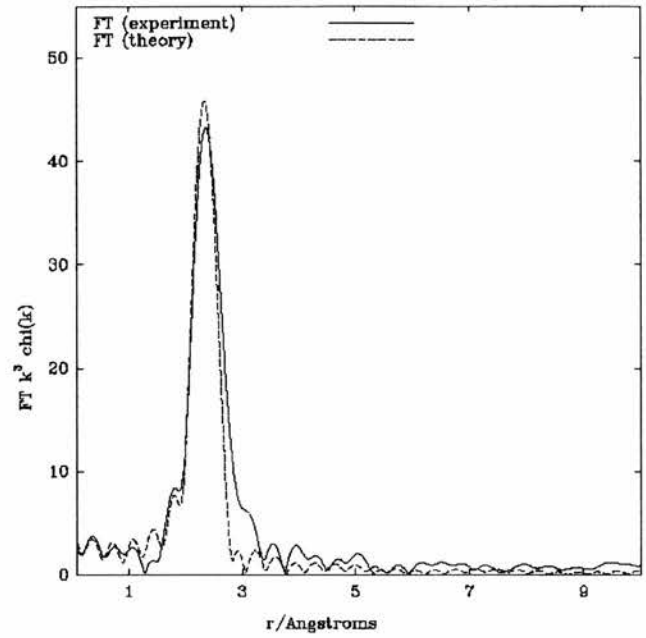

Figure 6.39: Associated Fourier transform from the attempted insertion of molybdenum.

	Mo–C	Mo–Cl
Refined EXAFS distances (*ca.* ±0.03Å)	2.36	2.45
Occupation numbers (N)	10	2
Debye-Waller factors (σ^2)	0.006	0.005

R(%)=30.32, AFAC=0.80

Table 6.13: Summary of refined fit resulting from the insertion of molybdenum into the ring opened silsesquioxane copolymer

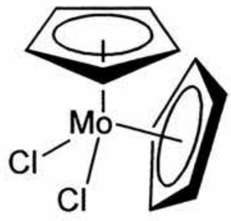

Figure 6.40: Molybdenum species still present after attempted insertion into copolymer

6.4.4 Molybdenum Insertion Into Incompletely Condensed Silsesquioxanes

The EXAFS obtained (***figure 6.41***) insertion of molybdenum into incompletely condensed cyclopentyl silsesquioxane immediately looked in close agreement with that obtained for the insertion within the ring opened copolymer. The associate Fourier transform (***figure 6.42***) showed this quite clearly, so the most likely fit appeared to be unreacted bis(cyclopentadienyl)molybdenum dichloride once again.

Whilst using the original molybdenum complex as a starting point for a refinement (***table 6.14***), which results in a good fit shown with the EXAFS and associated Fourier transform, it would appear possible that there could be a shell due to molybdenum to oxygen bonding. Assuming only limited bonding, only one oxygen atoms was considered, losing one chlorine from the relevant shell, the refined fit was approximately the same as previously, with the oxygen distance around 1.8Å.

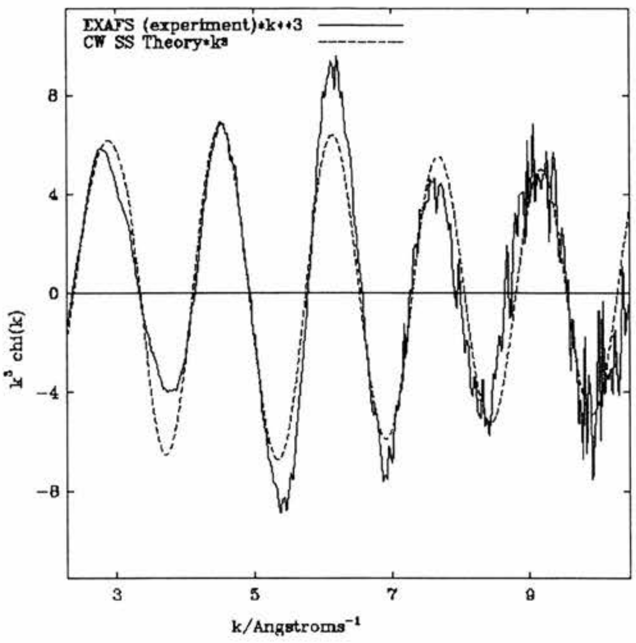

Figure 6.41: EXAFS obtained from attempted molybdenum insertion within incompletely condensed cyclopentyl silsesquioxane

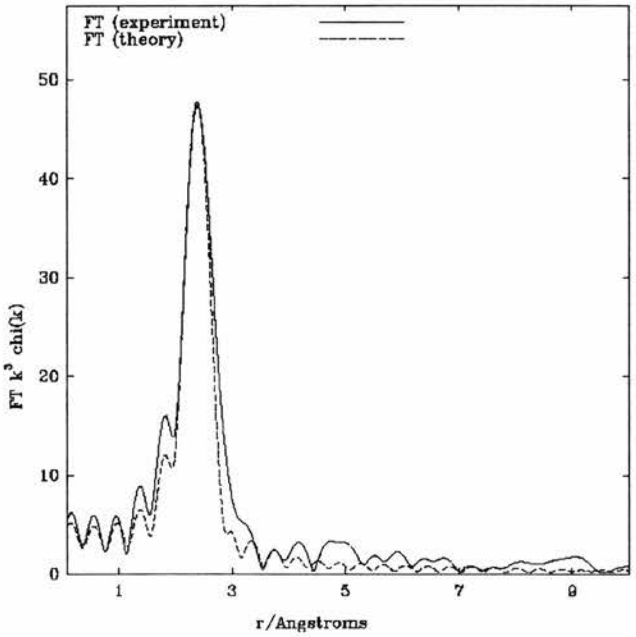

Figure 6.42: Associated Fourier transform from the EXAFS of molybdenum insertion into cyclopentyl silsesquioxane

Using the map function of the EXCURV98 program to find a balance between the number of oxygen and chlorine atoms present, resulted in more of the latter being the minimum. Although as a result of this it could imply limited insertion with respect to molybdenum.

	Mo–C	Mo–Cl
Refined EXAFS distances (*ca.* ±0.03Å)	2.31	2.47
Occupation numbers (N)	10	2
Debye-Waller factors (σ^2)	0.016	0.001

R(%)=32.45, AFAC=1.00

Table 6.14: Summary of EXAFS data for the attempted insertion of molybdenum into cyclopentyl incompletely condensed silsesquioxane

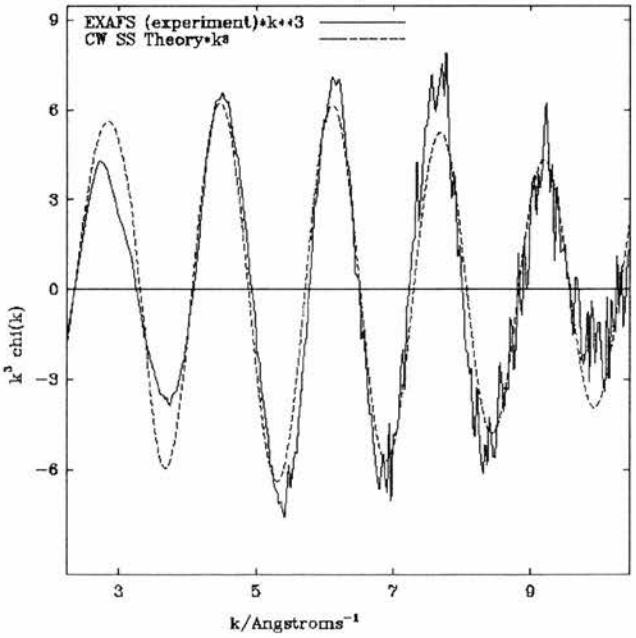

Figure 6.43: EXAFS of molybdenum in cyclohexyl incompletely condensed silsesquioxane

Similar data was collected for the insertion into the equivalent cyclohexyl species. Likewise the EXAFS (***figure 6.43***) and associated Fourier transform (***figure 6.44***) indicted that no reaction had occurred and the initial molybdenum structure is retained.

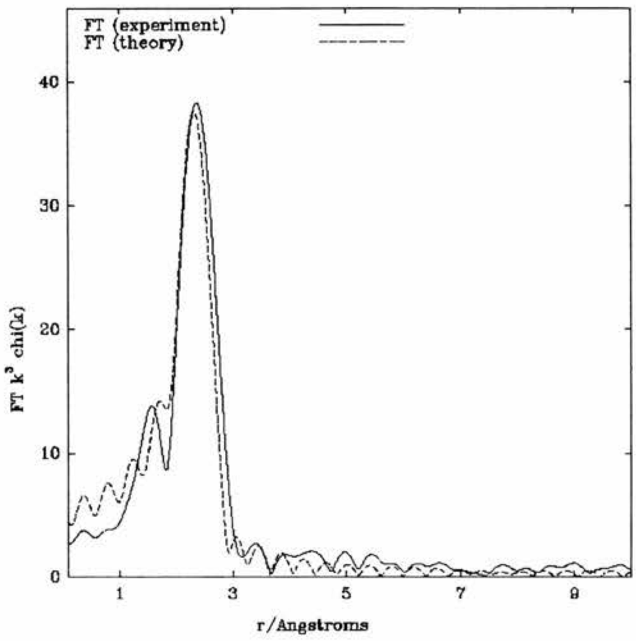

Figure 6.44: Associated Fourier transform of EXAFS resulting from cyclohexyl incompletely condensed silsesquioxane inserted with molybdenum

The refined values for this particular sample (***table 6.15***) were similar to the cyclopentyl equivalent, with the exception of attempting to fit a shell of a single oxygen atom. Even assuming only one to be present as a first shell, it was not possible to refine this to an acceptable fit. In this case using the EXCURV98 program to calculate the numbers of oxygen and chlorine resulted in values of approximately two for the latter and almost zero.

	Mo–C	Mo–Cl
Refined EXAFS distances (*ca.* ±0.03Å)	2.33	2.47
Occupation numbers (N)	10	2
Debye-Waller factors (σ^2)	0.013	0.002

R(%)=31.62, AFAC=0.90

Table 6.15: Summary of EXAFS data from the attempted insertion into cyclohexyl incompletely condensed silsesquioxane

6.5 Cobalt EXAFS

6.5.1 Introduction

The EXAFS obtained of cobalt containing samples were recorded using station 8.1 at Daresbury. Fitted with a double crystal Si(1,1,1) monochromator, and set to 50% harmonic rejection. Before data could be recorded, the position of the Co K-edge needed to be calibrated using cobalt foil.

Samples were analysed as 20mm pellets with either silica or boron nitride, prepared as for zirconium. Transmission EXAFS was used to collect data for the insertion into the copolymer, but proved unsuitable for gathering data on the insertions into the incompletely condensed silsesquioxanes, thus fluorescence EXAFS was used instead.

Similarly to the EXAFS of the other transition metals both experimental (solid line) and theoretical (dashed line) are shown together for comparison.

6.5.2 Cobalt Insertion In Ring Opened Copolymer

Unlike the insertion reactions of titanium, zirconium and molybdenum the insertion reaction of cobalt was not conducted with a cyclopentadienyl complex. However, if a reaction were to have been observed, it would appear likely that a similar addition had occurred.

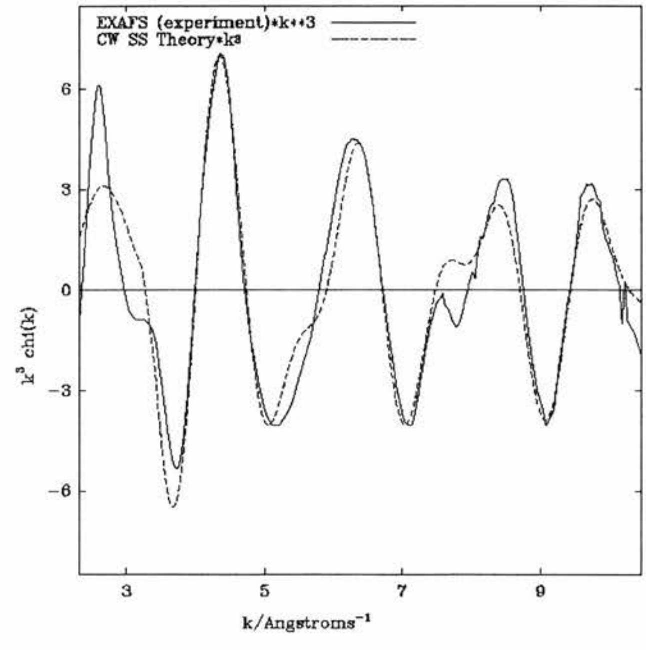

Figure 6.45: EXAFS obtained from insertion reaction of cobalt within silsesquioxane copolymer, fit shown with chlorine present

When looking at the EXAFS (***figure 6.45***) and its associated Fourier transform (***figure 6.46***) the first shell would appear around 2Å and a third shell slightly above 3Å. As this has been seen before for other materials, such as the titanium inserted ring opened copolymer, considering these to be three oxygen and three silicon atoms respectively. Trying to refine these two shells does indeed result in acceptable parameters for these two.

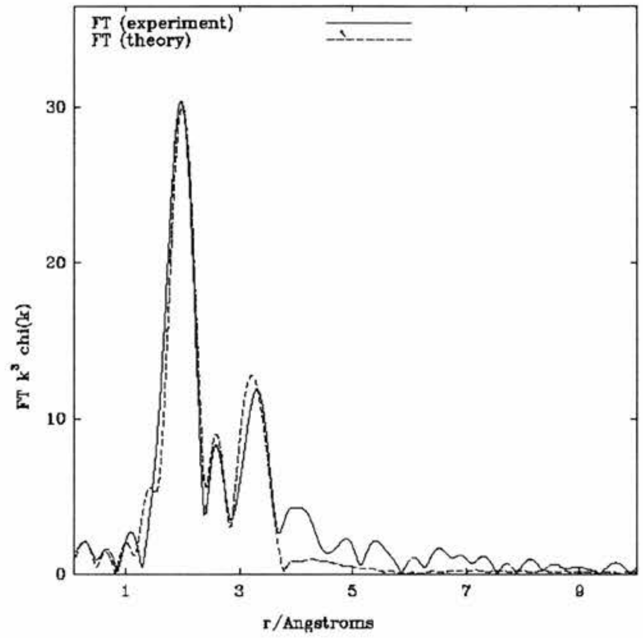

Figure 6.46: Associated Fourier transform of EXAFS for cobalt inserted copolymer, the clear second shell peak attempted refinement with chlorine

From the associated Fourier transform, there is clearly a shell in between these two and this could be assumed to be one of either two elements. Firstly would be chlorine remaining from the cobalt chloride, and secondly would be oxygen, either as co-ordinated water or possibly a hydroxide group.

With chlorine the EXAFS (***figure 6.45***) and associated Fourier transform (***figure 6.46***) show a good correlation between experimental and theoretic refined data. Leaving a cobalt to chlorine bond as being an acceptable figure of 2.48Å. The bond distances derived from this (***table 6.16***) lead to a four co-ordinate structure (***figure 6.47***).

	Co–O	Co–Cl	Co–Si
Refined EXAFS distances (*ca.* ±0.03Å)	2.05	2.48	3.29
Occupation numbers (N)	3	1	3
Debye-Waller factors (σ^2)	0.004	0.016	0.006

R(%)=30.15, AFAC=0.95

Table 6.16: Summary of refined EXAFS data for cobalt inserted into silsesquioxane copolymer, assuming chlorine to be present

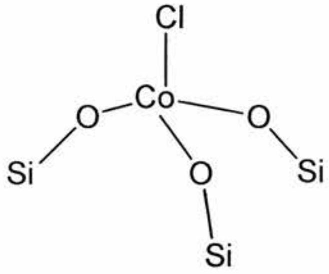

Figure 6.47: Possible structure derived from EXAFS data

However, also by substituting an additional shell of oxygen into the refinement, instead of the chlorine atom a similarly good fit can be obtained. The EXAFS (***figure 6.48***) and associated Fourier transform (***figure 6.49***) are close to that using chlorine in the refinement.

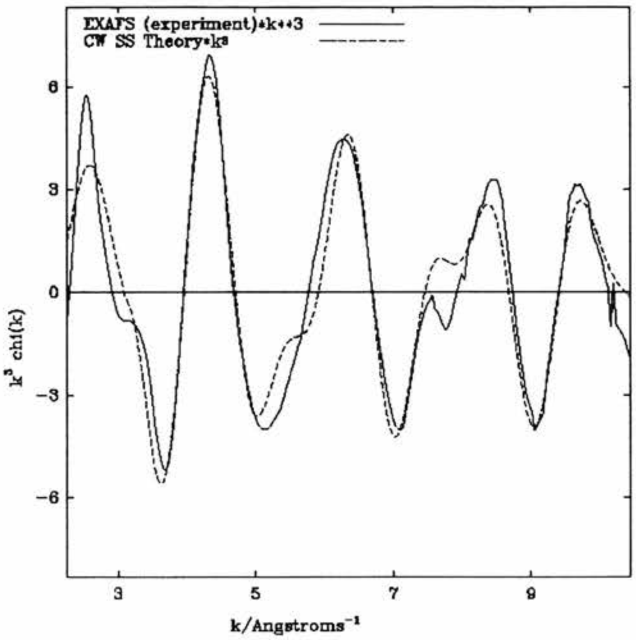

Figure 6.48: EXAFS of cobalt inserted silsesquioxane copolymer showing refined data using two shells of oxygen.

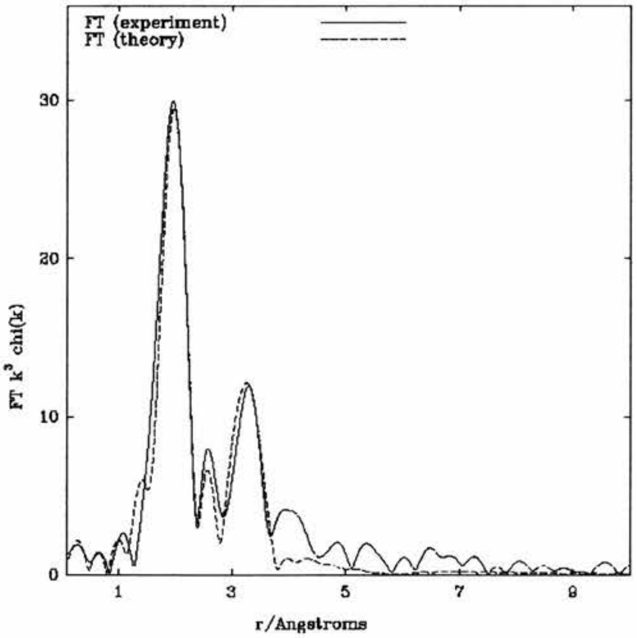

Figure 6.49: Associated Fourier transform assuming oxygen to be the second shell

In comparison with the example using chlorine, the bond distances of the first and third shells are as would be expected almost identical (***table 6.17***). The major difference in the bond distance of the second shell is smaller, but at 2.27Å this is suitable to be assigned to oxygen, leaving a structure (***figure 6.50***) which is essentially the same.

	Co–O	Co–O	Co–Si
Refined EXAFS distances (*ca.* ±0.03Å)	2.05	2.27	3.30
Occupation numbers (N)	3	1	3
Debye-Waller factors (σ^2)	0.003	0.008	0.006

R(%)=28.07, AFAC=0.95

Table 6.17: Summary of refined EXAFS data for cobalt inserted into silsesquioxane copolymer, assuming chlorine to be present

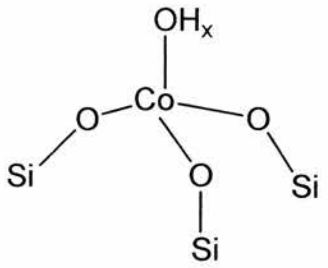

Figure 6.50: Structure deriving from refinement with oxygen as the second shell, hydrogen atoms assumed as silicon not likely to be bonded to fourth oxygen, x=1 or 2

Refinement of both possibilities shows a slight favouring towards the second structure, although this is not very significant. One possibility is that throughout the material both cobalt environments could be observed, the resulting collected EXAFS appearing as an average of the two.

6.5.3 Cobalt Insertion Into Incompletely Condensed Silsesquioxanes

The insertion of cobalt was only studied with EXAFS for the cyclohexyl incompletely condensed silsesquioxane. However, the data obtained (***figure 6.51***) suffered from excessive which prevented a reasonably valid fit to be made.

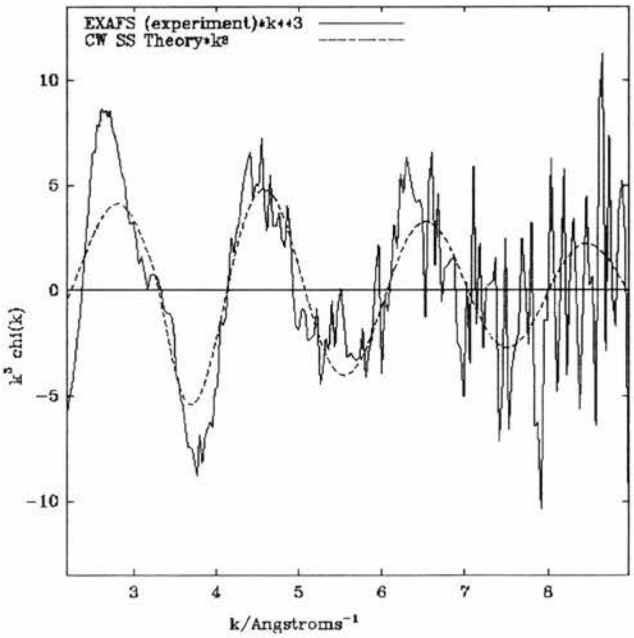

Figure 6.51: EXAFS from insertion of cobalt into cyclohexyl silsesquioxane

The dashed line appearing in the EXAFS and associated Fourier transform (***figure 6.52***) represents the theoretical values for an initial shell of three oxygen atoms refined to a distance of 1.98Å. These are shown as a example of the fit are what is to be expected judging from the polymeric equivalent. But as can be seen in k-space after 6.5Å^{-1}, the refinement is not capable of even generally following the trend of the EXAFS.

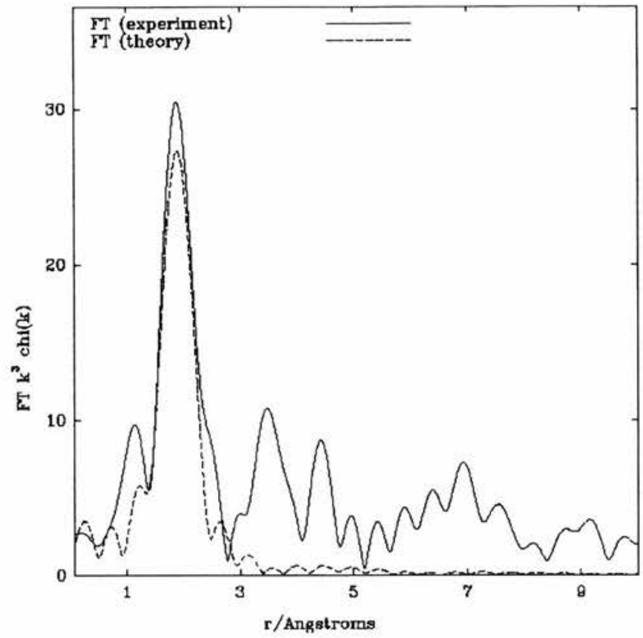

Figure 6.52: Associated Fourier transform derived from EXAFS of cobalt containing incomplete silsesquioxane

6.6 Conclusions

Using EXAFS as a means of determining the structure of transition metal containing species has proved somewhat successful, with some reactions giving reasonably conclusive results, whilst others have given data with sufficient lack of quality to even attempt an assignation of the identity of the material.

The EXAFS data collected is however seen as the average environment of the particular elemental type being studied. In cases where there is not just one unique environment, then the data obtained will be composed of contributions from each of these, which may therefore not have been possible to refine entirely satisfactory models.

Additionally the distances calculated between the central atom and those surrounding it are only interatomic distances, and do not imply the presence of a bond between the atoms, these have been inferred based on approximate likely values.

The insertion of transition metals into ring opened copolymers has resulted in reasonable EXAFS for all four transition metals. Although, however, there are noticeable differences between these. Despite using the equivalent complexes as a source of both titanium and zirconium, the former results in complete insertion, with no chlorine atoms remaining attached to the metal, whereas for zirconium this only gives partial insertion. However, in contrast, the molybdenum addition, albeit using a slightly different compound as a source of the metal results in no insertion occurring whatsoever. Finally cobalt also appears to show complete insertion, although as would be expected some chlorine is retained to give a four co-ordinate metal.

Comparison of these with materials with similar species prepared from the incompletely condensed silsesquioxanes, appeared to give similar results, although in some cases inconclusive EXAFS data was obtained to make a determination of the structure, notably in the case of cobalt. Molybdenum failed to react, and zirconium indicated only partial insertion. Both of which as in the situation of the copolymer. Titanium was the one notable difference, as the results of this hinted at the possibility of only partial insertion.

The results of dispersions of the three metals used for calcination showed the initial starting material quite clearly, but after the reaction with oxygen the structures were more difficult to determine. For titanium it appears reasonably likely that the material obtained is a titanium silicate, but the results of this reaction with zirconium and molybdenum appear to favour a mixture of compounds, as it is difficult to assign a single suitable structure to the data.

The other reaction studied, that of the addition of zirconium to the octavinylsilsesquioxane prior to copolymerisation unfortunately resulted in data with too much noise to make any conclusions as to the identity of that particular structure.

6.7 References

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7 Conclusions And Future Work

7.1 Conclusions

The aims of this project was to synthesise and characterise silsesquioxane based polymers and their subsequent functionalisation and further characterisation with the addition of a variety of transition metals.

The characterisation of a copolymer prepared from octavinylsilsesquioxane and octahydridosilsesquioxane in equal molar quantities results in a material that is known to be porous[1], with a structure that shows a large degree of randomness. An assumption that was made directly from this was that postsynthetic changes to the composition of these copolymers could be made without having too much effect upon the structure and porosity of the materials. In this way functional materials were prepared.

Slight alterations to the relative quantities of the two reactants so they were used in an unequal molar ratio still resulted in the formation of a highly porous polymeric species with the same ease as the initial preparation. As the ratio between the two starting materials increased, the tendency to polymerise was noticed to lessen, but porous polymers were still produced. However thermal gravimetric analysis of these indicates that the relative quantities of the two starting silsesquioxanes within the final copolymer product differed slightly from what might have been expected, implying that the excess silsesquioxane was not incorporated into the polymers.

Similarly the use of decahydridosilsesquioxane as a partial substitute for octahydridosilsesquioxane has been observed to result in a copolymer without any major differences in comparison to the initially prepared copolymers.

Attempts to insert four different transition metals (titanium, zirconium, molybdenum and cobalt) into the structure have met with various degrees of success. Whilst titanium, zirconium and cobalt have been seen to insert reasonably well into ring opened silsesquioxanes, the method used failed to produce any such results for molybdenum, despite the use of a similar metal complex which was successful with zirconium.

The use of EXAFS to achieve characterisation of these materials has proved partially successful, but unfortunately several of the samples used possessed too much noise in the data obtained to enable a valid fit of a reasonable quality. However, for many of the samples, in particular the copolymers, resulted in a feasible structure surrounding the central atom.

When inserting the transition metals into the ring opened copolymers titanium, zirconium and cobalt all resulted in tetrahedral species as determined by EXAFS. Although the zirconium differed from the others as it only formed two rather than three metal to oxygen bonds to the silsesquioxane. Where data was collected for the equivalent materials prepared with incompletely condensed silsesquioxanes, the determined structure was almost identical, all possessing the same types of bonds and co-ordination numbers.

The use of incompletely condensed silsesquioxanes to model the bonding around the transition metals has not been shown to be a success, with EXAFS data obtained from these samples being no more use than those from the copolymers. Although they did, however, tend to be close enough to agree to the structure determined. As these materials did not result in crystals, other techniques that might have proved useful, such as single crystal diffraction, were unable to be employed.

As an alternative to inserting transition metals into ring opened copolymers, efforts to add the metal to a silsesquioxane prior to copolymerisation have failed to result in a structure. Attempts to prepare a monomeric species of an incompletely condensed vinylsilsesquioxane proved futile, and the addition of cobalt to octahydridosilsesquioxane did not enable a product to be readily isolated that could be used. However, results from the addition of zirconium to octavinylsilsesquioxane proved more successful. From this species a copolymer was prepared which was observed to be highly porous from nitrogen adsorption, and the presence of the zirconium could be detected by x-ray fluorescence analysis. Unfortunately the EXAFS collects for samples of this material proved to possess too much noise to enable a possible structure to be determined.

A final method for the preparation of metal containing species deriving from silsesquioxanes was the calcination of a dispersed metal species within a copolymer. Whilst the copolymer on its own was seen to retain a reduced porosity as it was slightly calcined, when heating the metal containing species to a point where the copolymer breaks down the resulting product is observed to be non-porous. EXAFS of these material produced a variety of structures, which differed depending upon the metal used.

7.2 Suggestions For Future Work

7.2.1 Polymeric Structure

Laine and co-workers observed during their preparation of various silsesquioxane copolymers that the physical properties of these materials does depend greatly on the monomeric species involved[1]. Whilst longer chain groups enable quicker polymerisation, the materials are seen to be quite porous. Although none of these other materials used are either as convenient to prepare nor result in as porous copolymers in comparison with those based upon octavinylsilsesquioxane with hydridosilsesquioxanes, they could offer other methods by which transition metals can be found within the structure.

The copolymerisation method used has been the hydrosilation reaction between a vinyl group with a silicon to hydrogen bond. Using a silsesquioxane which consists of a metal containing chain with an attached vinyl group would therefore offer this possibility. However, as yet no such group has been attached to a silsesquioxane core, although silicon containing species have been successfully achieved by Hasegawa and Motojima[2].

The material they created possesses a $-OSi(CH_3)_2C_2H_3$ group (***figure*** *7.1*) deriving from the reaction of dimethylvinylchlorosilane with the silicate anion $Si_8O_{12}^{8-}$. A suggestion to introduce additionally functionality in this instance would be to attempt these reactions with similar compounds containing elements other than silicon.

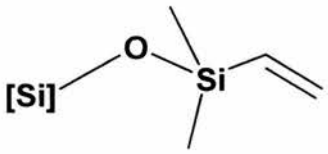

Figure 7.1: Vinyl containing group attached to a silsesquioxane

The equivalent dimethylvinylchloro- species is known with the silicon substituted for the carbon, germanium and tin[3], although the addition reaction to the silsesquioxane core has not been recorded. If this were to prove successful, in particular with reference to tin, a bridging group would be formed containing a metal.

However, the formation of metal containing polymers is not the only potential variation that could be considered for the bridging group. These materials have been seen to be amorphous, but to enable the production of such materials with a crystalline structure (***figure*** *7.2*) would in all likelihood require the use of inflexible bridging groups.

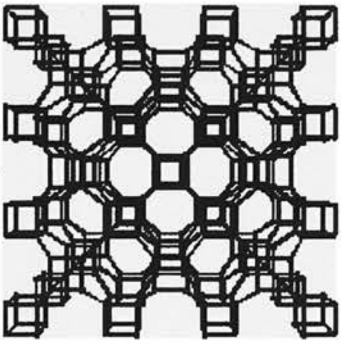

Figure 7.2: Highly ordered material

Without the consideration of major alterations to the reaction, one option to try would be the use of a silsesquioxane possessing alkyne groups[4]. This is known to exist as a functional group on a trichlorosilane and to be capable of undergoing hydrosilation reactions[5]. The cubic silsesquioxane species has not yet been prepared, although if this proved to be possible, the organic groups prior to a copolymerisation reaction would be straight. An unsaturated bridging group would not be straight, but is inflexible, which could possibly result in a lower degree of unreacted groups.

7.2.2 Functionalising Polymers

After preparing copolymers it has been shown that a sizeable proportion of groups remain uninvolved with the reaction taking place, in the instance of the octavinylsilsesquioxane based copolymer that vinyl groups will be found within the pores of the material.

With these vinyl groups it would be worth reacting them so that either they are further functionalised or removed from the copolymer. The former is undoubtedly the simpler, with many methods outlined in the literature for reactions involving such groups[6,7].

Attempting to remove the group and replace it with a spatially smaller atom or group would be expected to result in larger pores throughout the structure of the copolymer. Ideally this would result in the replacement of the vinyl group with a hydrogen atom, but as yet no synthetic method has been reported for this transformation.

A relatively simple example of a reaction that could possible be carried out upon the vinyl groups is bromination[6], with syntheses dating back over fifty years. Although relatively hindered in comparison to materials in solution, with a pore size distribution starting at 10Å reactions such as this should be possible to proceed.

During this work the addition of cobalt and zirconium to monomeric silsesquioxanes was attempted, with the intention of then using them in the formation of copolymers. The zirconium species proved more successful, but in the case of cobalt, the difficulty in the preparation was the isolation of a mono-substituted species. If the pore sizes prove large enough to enable this reaction to take place upon the copolymer, it will offer another route to the preparation of a cobalt containing species.

7.2.3 Catalysis

Various different transition metals have successfully been inserted within the basic structure provided by silsesquioxane copolymers. One possible use for such materials is to act as catalytic materials[8-10]. Transition metals are known to be catalysts in a large number of processes.

Titanium has been shown to be an effective catalyst for several reactions, such as the oxidation of hydrocarbons described by Corma and co-workers[11,12] together with the oxidation of peroxides reported by Pinnavaia and co-workers[13] when used within titanosilicate molecular sieves. Catalytic reactions could be conducted, with silsesquioxane following these two methods and their behaviour compared.

In addition to comparisons with already observed solid state catalysts[14], silsesquioxane copolymers could be investigated to see the potential to act as supports for transition metal catalytic species normally used homogeneously[15-17]. Although this may alter the properties of a material, the important advantage of such a compound would be the ease of recovering the catalyst.

7.2.4 Incompletely Condensed Silsesquioxanes

The formation of two incompletely condensed silsesquioxanes has been used with the intention of providing further understanding of the polymeric silsesquioxanes after the insertion of various transition metals. Unfortunately EXAFS data for such materials proved of no higher quality than those obtained from the larger polymers. Unfortunately, however, all incompletely condensed silsesquioxanes prepared to date are found with unreactive organic functional groups.

An attempt was made to synthesise this type of compound with vinyl groups, which would be ideal for polymerisation, enabling the insertion of metals without the possible hindrance around some potential sites in a polymer. However, this was unsuccessful, but further attempts to prepare this could investigate the conditions under which such a reaction is conducted. Alternatively a modification of the condensation reaction to form the cubic species itself could be used, perhaps using a smaller time scale for the reaction and isolating a product prior to precipitation.

The vinyl group is however only one functional group which could prove useful in this respect, when referring to the copolymer it would be a suggestion to attempt a synthesis of a similar species based upon octahydridosilsesquioxane.

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