***Tuning the Surface Properties of Zeolites:
Organosilane Coatings as Adsorption Modifiers***

by

Irene Ana Maria Zuger, B. Sc.

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfillment of
the requirements for the degree of

Master of Science

Department of Chemistry

Carleton University

Ottawa, Ontario

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Abstract

Modification of the surface of zeolites with organosilane coating materials was performed through the introduction of a dried zeolite with an organosilane-hydrocarbon solution resulting in a covalent linkage between coating and zeolite. Gravimetric techniques (TGA) and spectroscopic techniques (NMR) aided to identify the presence of coating material. This study looks specifically at modifying the surfaces and subsequent characterization of four zeolites: synthetic Linde Type A (LTA): 4Å and 5Å, two natural zeolites that were obtained from sites in the Bay of Fundy, Nova Scotia, with the following coating materials: SurfaSil™ (SS), trimethylchlorosilane (TMCS) and a novel, synthetic pyrene-containing organosilane, pyrene-1-(4-butyl-dimethylchlorosilyl) ether (**Pyrene-Cl**). Through solvent uptake experiments with water, methanol and ethanol, it was found that the coated materials experienced the same degree of solvent uptake as the uncoated material. This was verified through preliminary TGA studies as well as duplicate uptake experiments. Solid state ^{13}C NMR experiments were done to verify the presence of the coating material by looking at the resonance of methyl carbons, specifically adjacent to silicon, shown at 0 ppm. ^{29}Si SS NMR showed that 5 chemical environments were found in both natural zeolite samples, indicating the presence of impurities. Powder X-ray diffraction also provided evidence of impurities within the samples; in addition, correlation of the sample powder patterns to literature values was not successful. ^{27}Al SS NMR showed that only tetrahedrally coordinated aluminum was present in both natural samples.

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Dedication

This thesis is dedicated to

my parents, Davor and Georgie, my brother Christopher,

and my love, Davor Balder.

Without you, I would never have made it this far.

Hvala za sve!

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List of Abbreviations

SBU	Secondary Building Unit
S4R	Single 4-ring
S6R	Single 6-ring
S8R	Single 8-ring
S10R	Single 10-ring
S12R	Single 12-ring
D4R	Double 4-ring
D6R	Double 6-ring
LTA	Linde Type A zeolite
MOR	Mordenite
STI	Stilbite
SS	SurfaSil TM
TMCS	trimethylchlorosilane
TBDMS	<i>t</i> -butyldimethylsilyl chloride
TBAF	tetrabutylammonium fluoride
DCDMS	dichlorodimethylchlorosilane
Neat	non-coated zeolite
PBA	Pyrene-1-butyric acid
Pyrene-TBDMS	Pyrene-1-(4-butyl- <i>t</i> -butyldimethylsilyl)ester
Red-Pyrene-TBDMS	Pyrene-1-(4-butyryl- <i>t</i> -butyldimethylsilyl)ether
Pyrene-But-OH	Pyrene-1-(4-butanol)
Pyrene-Cl	Pyrene-1-(4-butyl-dimethylchlorosilyl)ether
TGA	Thermal Gravimetric Analysis
PXRD	Powder X-ray Diffraction
NMR	Nuclear Magnetic Resonance

SS	Solid-state
CP	Cross-polarization
MAS	Magic angle spinning
JCPDS	Joint Committee on Powder Diffraction Standards
NS1	Natural sample 1, thought to be Mordenite
NS2	Natural sample 2, thought to be Stilbite

Chapter I

General Introduction to Zeolites: Formation, Modification and Implications

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1. Introduction : a brief history

Since the discovery of stilbite in 1756 by Freiherr Axel Fredrik Cronstedt of Sweden, zeolites have become an area of interest for earth scientists, mineralogists and chemists, in discovery, chemical and industrial uses. The word *zeolite* is derived from the Greek words *zein* ($\zeta\epsilon\iota\nu$), which means “to boil” and *lithos* ($\lambda\iota\theta o\varsigma$), “stone”, in allusion to their frothing characteristics when heated. They are very common and well recognized as fine crystals of hydrothermal genesis in geodes and fissures of eruptive rocks, or as microcrystalline masses of sedimentary origin.¹

Zeolites are aluminosilicates with the general formula $(M^{n+})_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot zH_2O$, where n is the charge of the metal cation, M^{n+} , which is usually Na^+ , K^+ or Ca^{2+} , x and y are the total number of tetrahedra per unit cell and z is the number of moles of water of hydration, which can vary. Zeolites possess a framework structure with enclosing cavities occupied by large ions and water molecules, and allow for considerable movement and freedom of included guest species, permitting ion exchange and reversible dehydration, without structural degradation.²

After Cronstedt's initial finding, other researchers followed the path of this discovery. In 1845, Way³ ascertained that certain soils retained ammonium salts. Breck⁴ reported that hydrated silicates in the soil were found to be responsible for this phenomenon and these were probably the first ion-exchange experiments. Weigel and Steinhoff⁵, in 1925, were the first to determine that chabazite selectively absorbed smaller organic molecules and rejected

large molecules. This characteristic behaviour was described by McBain⁶ in 1932 as ‘molecular sieving’. As knowledge of the properties of zeolites gradually increased, it became apparent that they could be utilized for industrial processes; nevertheless, zeolites were considered to be mineralogical curiosities that filled small cavities called vugs, and fractures in igneous rocks.⁷ It was not until the 1940s and 1950s that research on the properties of zeolites increased dramatically.⁷ Large tonnages of natural zeolites were not discovered until the late 1950s when various researchers reported on vast sedimentary deposits in the Western United States. Prior to this time, emphasis was placed on the synthesis of zeolites for commercial use.⁸ There are many natural zeolites, some of which have been synthesized. Of those that have been synthesized, many zeolite structures do not occur in nature.

Zeolites are undoubtedly one of the most important and interesting framework silicates due to the inherent characteristic porous $[(\text{Al},\text{Si})\text{O}_2]_n$ framework. The porosity of zeolites enables them to perform several functions, namely in ion exchange and selective adsorption applications.

1.1 *The structure of a zeolite*

As previously mentioned, zeolites are a well-defined class of crystalline, naturally occurring aluminosilicate minerals. They have infinite, three-dimensional structures arising from a framework of SiO_4 and AlO_4 coordination polyhedra linked through their vertices. The frameworks generally are open and contain channels and cavities in which cations and

water molecules are located.⁹ These channels and cavities form three-dimensional frameworks that have the ability to house guests molecules within their interiors.

1.1.1 Basic building blocks

The basic units of a zeolite are the SiO_4 or AlO_4 tetrahedra, where the Si or Al atom resides in the centre, and the oxygen atoms form the vertices (Fig. 1.1). If an aluminum atom is present rather than a silicon atom, a positive metal ion is required to maintain a charge balance. These tetrahedra are then assembled together to form secondary building units (SBUs). There are eight types of SBU: the single 4-ring (S4R), the single 6-ring (S6R), the single 8-ring (S8R), the double 4-ring (D4R), the double 6-ring (D6R), the natrolite unit (4-1), the mordenite unit (5-1) and the stilbite unit (4-4-1) (Fig. 1.2). When depicted as ball and stick models, only the central atoms are shown for clarity. The D4R and D6R units are obvious combinations of the S4R and S6R units. In some cases, the zeolite framework can be considered in terms of polyhedral units, such as the truncated octahedron (Fig. 1.3 a); these are cage-like units designated by the Greek letters: α , β , γ , etc.¹⁰ The α -cage refers to the largest unit - the truncated cuboctahedron (Fig. 1.3 b), and so on. The SBUs can then subsequently be assembled to form a variety of polyhedra, forming the 133 different zeolite structures that are known today.¹¹

1.1.2 Zeolite Groups

Zeolite classification has evolved with increasing knowledge about their structures, while earlier classification systems were based on morphology and had zeolite species

Fig 1.1 Basic structural units of zeolites: a, tetrahedron with silicon atom at the centre and oxygen atoms at the apices; b, tetrahedron with aluminum atom and attached monovalent cation compensating for the charge imbalance between the two metal centres in a multiple tetrahedron chain.

Fig 1.2 Secondary building units (SBUs) in zeolite structures. The black dots represent the central metal atom in the tetrahedra.

Fig 1.3 Polyhedra of zeolite frameworks: a, the β cage, or truncated octahedron; b, the α cage, or truncated cuboctahedron.

grouped together through commonalities such as texture, colour, and crystal habit. Current classifications of zeolites are based on the framework topology. Breck¹² grouped zeolites by common SBUs into seven categories (Table 1.1). It should be noted that not all zeolites are typical within a group because of slight differences in chemistry and crystallography. Hence, the completed framework structures of the zeolites are composed of the permutations of assemblies of tetrahedra in building units which range from the simple 4-rings to large polyhedra.

1.2 *Geologic formation of zeolites*

Zeolites occur in rocks of many types and in a wide variety of geologic settings. Most of the earlier geological work on zeolites was carried out on typical occurrences in cavities of basalt flows. In the 1950s, however, detailed X-ray diffraction studies of bedded tuffs in the Western United States, Japan and Italy showed large quantities of zeolites in these sedimentary rocks.¹³ According to Hay¹⁴, most naturally occurring zeolites are assignable to six types of geologic environments or hydrological systems: (1) saline/alkaline lakes, (2) saline, alkaline soils and land surfaces, (3) sea-floor sediments, (4) percolating water in an open hydrologic system, (5) hydrothermal alteration and (6) burial diagenesis. Two additional geological occurrences of natural zeolite formation have been added to the list by Iijima¹⁵; magmatic zeolites and zeolites formed in impact craters.

The first, saline/alkaline lakes, where block-faulted terrains and trough valleys associated with continental rifting establish a closed basin system and control the transport

Table 1.1 A listing of the typical classification of the different zeolite groups based on the main component of the zeolite structure.

Group	Secondary Building Unit (SBU)
1	Single 4-ring, S4R
2	Single 6-ring, S6R
3	Double 4-ring, D4R
4	Double 6-ring, D6R
5	Complex 4-1, T_5O_{10} unit
6	Complex 5-1, T_8O_{16} unit
7	Complex 4-4-1, $T_{10}O_{20}$ unit

of clastic material beyond the basin edges; the alkaline zeolites form in these restricted lakes. Alalcime, clinoptilolite and mordenite, among others, commonly form where pH values are around that of 9.5.¹³

The next environment for the formation of zeolites can be found in saline/alkaline soils and land surfaces, where climate is the controlling factor in the formation of zeolites. These deposits form in arid and semi-arid regions where evaporation causes sodium carbonate-bicarbonate to concentrate in the top layers of the soil. Rainwater percolates through, dissolving the formed salts and thereby increasing the pH, allowing it to alter silica glasses and aluminosilicates present in the soil.¹³ Some examples of zeolites that are found are analcime, the most common, followed by smaller amounts of phillipsite, natrolite and chabazite.

The third environment is found in sea-floor sediments, under low temperatures and moderate pH conditions, ranging from pH 7-8. Zeolites in the slow sedimentation regions of the Pacific and Indian Oceans occur in post-Miocene (23-5 million years ago, mya) brown clays, vitric siliceous and calcareous oozes and basaltic volcanic sediments. Here phillipsite is the dominant species. In the Atlantic and Pacific margin can be found calcareous sediments and terrigenous clays of Paleogene (65-24 mya) and Cretaceous ages (144-65 mya), where clinoptilolite is the dominant species. Zeolites in sea-floor sediments form by the reaction of glasses with pore water.¹³

The fourth geologic instance describes the process of percolating water in an open

hydrologic system through porous pyroclastic materials rich in reactive glass. Here the pH and dissolved solid content of the ground water increase as it reacts with the vitric ash, until zeolites are precipitated. Movement of the ground water downward through the system results in a vertical zonation of water composition and minerals, including zeolites.¹⁴ Typical striation that is found: an upper zone of fresh glass, montmorillonite and opal. The next bed can contain up to 90% clinoptilolite and the underlying zone can contain analcime, feldspar and quartz.

Another system is that of hydrothermal alteration, where zeolites precipitate from alkaline to weakly acidic hot water.¹⁵ The assemblies observed are controlled by temperature, host rock composition and permeability, and geothermal fluid composition.¹⁵ Clinoptilolite and mordenite occur in the shallowest and coolest zones, and analcime or heulandite, and other less hydrated forms occur in the deeper and hotter zones.^{13, 14} Submarine hydrothermal activity may be responsible for the formation of some zeolites in deep-sea sediments.

Finally, burial diagenesis, or metamorphism, can occur where zeolites associated with this system of formation are formed in thick volcanoclastic sediments that were metamorphosed at increased temperatures and pressures.¹⁴

1.3 *Synthetic Zeolites*

Hydrothermal zeolite synthesis typically proceeds from a reactive aluminosilicate gel at temperatures exceeding 90°C and autogenous pressures¹⁶⁻¹⁸, according to the scheme

shown (Fig. 1.4). The mechanism of zeolite formation is actually very complicated, where each of the steps outlined in the figure involves a large number of reactive species with varying solubilities that serve as reagents for numerous polymerization-depolymerization and nucleation reactions.¹⁹ The synthesis of zeolites was first documented by St. Clair Deville¹⁰ in 1862, where it was reported that by heating aqueous solutions of potassium silicate and sodium aluminate in a glass tube at 170°C, produced levynite. In 1882, De Schulten¹⁰ reported the synthesis of analcime. However, much of the work by the pioneers of zeolite synthesis cannot be reproduced in the laboratory, due to the unavailability of data from these researchers.²⁰ Often overlooked is the fact that earlier work in turn depended on the first demonstration, by R. H. Milton of Union Carbide, USA in 1949, that zeolites could be synthesized using low temperature hydrothermal methods. At that time, major emphasis was placed on mimicking those conditions under which the zeolites of volcanic origin were presumed to have been formed, i.e. high temperatures and salt concentrations and autogenous pressures.²¹

1.3.1 Laboratory preparation

A typical zeolite synthesis involves mixing together silicate and aluminate solutions (or *sols*) to form an aluminosilicate gel, usually instantaneously, which is then treated hydrothermally to give the crystalline product.²² The composition and structure of the aluminosilicate gel are of considerable interest; therefore, characterization of the aluminosilicate species present would give insight into the crystallization process. Silicate

Fig 1.4 A simple scheme depicting hydrothermal zeolite synthesis from a reactive aluminosilicate gel at temperatures above 90°C.

and aluminate solutions have been well studied so that one can be reasonably sure what species are present in a given solution of known concentration and pH.²² Aluminate solutions have been shown to contain only one type of ion at high pH; the tetrahedral $\text{Al}(\text{OH})_4^-$ ion.²³ At neutral pH, various polymeric ions appear. With the lowering of pH, more ions are formed, of which $\text{Al}(\text{H}_2\text{O})_6^{3+}$ is predominant in these solutions.²² It is the tetrahedral aluminate ion that is the important species for zeolite synthesis, as AlO_4 tetrahedra constitute as a basic building block. Silicate solutions, again at high pH, contain a range of small silicate polymers, formed from corner-sharing tetrahedral SiO_4 units. These polymers depolymerize quickly in response to increasing pH or dilution.²²

1.3.2 Commercial preparation

The preparation of zeolites proceeds by simply loading a gel with components in pre-arranged proportions into sealed glass vials and then into a closed stainless steel ‘bomb’, or into a bomb lined with inert material, at the time of initial investigation of zeolite synthesis, was a dramatic change. Such bombs today are now commercially available (Fig. 1.5), and tuning of the temperature and pressure is routine.²¹

Current processes for manufacturing zeolites fall into one of three categories: (1) the hydrogel process, (2) clay conversion and (3) other processes. Tomlinson²¹ describes the hydrogel process as one that can be based either on homogeneous hydrogels, prepared from solutions of soluble reactants or heterogeneous solutions, which are prepared from reactive alumina or silica in a solid form. Typical gels are prepared from aqueous solutions of

Fig. 1.5 A hydrothermal bomb in a configuration with removable internal attachments and a heating element for preparing giant zeolite crystals through a temperature gradient and nutrient.

reagents such as sodium aluminate, sodium hydroxide and sodium silicate (Fig. 1.6), although other reagents can be used, including alumina trihydrate, colloidal silica and silicic acid. In the clay conversion process, the starting material is usually kaolin, which is first dehydrated three or four times to meta-kaolin by calcination in air (Fig. 1.7). Other processes involve either combinations of the first two processes, or a novel method altogether. One such novel method is called the Mizusawa process, which is unique in utilizing acid clay, a mineral occurring in Japanese deposits of montmorillonite.²¹

A new approach to zeolite synthesis was introduced by R. M. Milton and associates in the Union Carbide Corporation. The process started with very reactive components in closed systems and employed temperatures for crystallization which are more typical of the synthesis of organic compounds than they are of mineral formation.^{24, 25} Many of the synthetic zeolites are formed at temperatures ranging from about room temperature to the boiling point of water.¹⁰

1.4 *Industrial applications of zeolites*

Whether the zeolite species be of natural or synthetic origin, immediate work was done to determine their potential use within industry. While zeolites in the realm of geology were mainly crystallographic marvels, chemists and engineers worked to introduce zeolites as catalysts and indispensable sorbents in industries such as oil-refining and detergent manufacture, and as cation exchangers in water purification plants.

Fig 1.6 A schematic representation of the preparation and crystallization of a $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ system gel.

Fig 1.7 The reactions involved in the clay conversion process starting with kaolin to produce zeolite A.

1.4.1 Catalysis

A catalyst is a substance that increases the rate of a reaction but is not itself consumed. Catalysts are widely used in nature, in industry, and in the laboratory, and it is estimated that they contribute to the majority of all manufactured goods in industrialized countries.²⁶ Zeolites catalyse several types of reactions involving organic molecules. The most important are cracking, isomerization, and hydrocarbon synthesis, but there is an increasing application in the field of synthesis of fine organic chemicals.²⁷ There are two fundamental considerations in zeolite catalysis: the first refers to the basic reaction mechanism; and the second to the way in which the products are controlled by the geometry and topology of the microporous crystal structure.²⁷

The main reaction mechanism within zeolite catalysis is that of the Brønsted acid type, where the bridging hydroxyl groups are the most common type of acid site. They may be considered as protonated oxygens, the protons being present as charge compensators for the negatively charged framework aluminum. The coulombic interaction between the tetrahedral aluminum and the protons means that the Si-OH-Al bridges provide the dominant type of acid species, although acid sites associated with the defects in the zeolite structure are thought to contribute to catalytic processes.²⁷ Depending on the preparation of the zeolite, the surface can consist of either Brønsted or Lewis acid character, or a combination of the two.²⁸ Brønsted acid sites are converted into Lewis acid sites as the temperature is increased above approximately 500°C and water is driven off (Fig. 1.8). The strength of the

Fig. 1.8 Generation of Brønsted and Lewis acid sites in zeolites.

acid sites is related to the framework composition of the zeolite, where those with a high Si:Al ratio have among the strongest acid sites.²⁹

A special feature of zeolites which makes them such superb catalysts in some cases is their shape selectivity, which is manifested in three ways: (1) reactant selectivity, where only certain molecules may be absorbed into the zeolite cavities and thus reach the reactive sites; (2) product selectivity, derived from the fact that only certain products possess the correct dimension to escape the zeolite structure upon formation; and (3) the lesser important manner, transition state selectivity, where certain intermediates, which are formed during the reaction at the active site, will not fit in the cavity, thus limiting which reaction pathway will take place.²⁸

1.4.2 Adsorption

When water is removed from the voids created within the zeolite framework, the zeolite can then take in other molecules. This process is called sorption, and the zeolites are said to 'sorb' molecules into their void volume, that is, they act as sorbents. Frequently clathrate terminology is used, where the sorbing molecules are described as guests within the zeolite host.⁹ Generally, the AlO_4 and SiO_4 tetrahedra are linked together so as to form a ring of oxygen atoms. The oxygen windows having the greatest influence on sieving are those composed of 8, 10 and 12 oxygens, i.e. the S8R, S10R and S12R rings.⁹ It should be appreciated that both synthetic and natural zeolites possess a wide variety of internal channels and cavities accessed by guest molecules through oxygen windows which happen

to be close in size to the dimensions of common organic and inorganic molecules.⁹ Because of this inherent geometry, zeolites are then able to act as molecular sieves, separating mixtures of molecules in both liquid and gas phases on the basis of their effective sizes.

The use of zeolites as selective adsorbants is a recent and rather fascinating development. Unique geometries contained in the zeolitic channels and cavities result in selection sorption properties. These properties arise from the fact that not all oxygen windows are large enough to permit molecular progress through them. It is the smallest window, the S6R, that creates significant separations and is responsible for the selective sorption of water into the β cages of several zeolite structures.

Table 1.2 shows examples that size is paramount in the selective properties of the zeolite. In the centre of the unit cell is a cavity which may be connected to identical cavities in adjacent unit cells by channels or windows. In the hydrated form, all of the cavities contain water molecules. In the anhydrous state, the same cavities may be occupied by other molecules brought into contact with the zeolite, provided those same molecules are able to squeeze through the apertures connecting cavities. The molecules are held by electrostatic and van der Waals forces. Thus, zeolites capture molecules that are just small enough to enter those cavities. They will not absorb molecules that are too large to enter, and will only weakly absorb very small molecules or atoms which can enter but leave easily. For example, zeolites may absorb straight-chain hydrocarbons but will not absorb branched alkanes or aromatic rings.

Table 1.2 Some dimensional properties of common zeolites, where window size dictates whether molecules may be taken up by the zeolite structure.

Zeolite	Restricting windows (number of O atoms)	Effective window size ^a (Å)	Void volume ^b	Other dimensions
Zeolite A	6	2.3	0.47	β cage diameter: 6.6 Å
	8	4.5		α cage diameter: 11.4 Å
Zeolite X	6	2.3	0.53	α cage diameter: 11.8 Å
	12	7.8		
Zeolite L	12	7.1	0.28	
Heulandite	8	4.0 x 5.5	0.35	} Interconnected
	10	4.4 x 7.2		
Phillipsite	8	4.2 x 4.4	0.30	} Interconnected
	8	2.8 x 4.8		
	8	3.3		
Mordenite	12	6.7 x 7.0	0.26	} Interconnected
	8	2.9 x 5.7		

^a May not be the crystallographic measurements.^b Expressed as cm³ liquid H₂O/cm³ crystal.

1.4.3 Ion exchange

The zeolites function as cation exchangers, as observed when placing a zeolite in a solution containing a particular cation. An equilibrium occurs between the cation population outside and inside the zeolite. This equilibrium distribution is achieved rapidly since the porous structure allows rapid passage of ions in and out through the apertures of the zeolite cavities. In general, when there are two types of ions in solution, one sort will have a slightly greater preference for the zeolite environment than the other ion type. This results in a differential concentration between the aqueous phase and the zeolite environment. The naturally occurring zeolites were the first ion exchangers discovered, and industrially they are competing for this purpose with synthetic exchange resins which are designed for the same purpose.

Exchange between cation A^{Z_A} , initially in solution and B^{Z_B} , initially in a zeolite, can be written as follows: $Z_B A^{Z_A} + Z_A \overline{B}^{Z_B} \rightleftharpoons Z_B \overline{A}^{Z_A} + Z_A B^{Z_B}$, where $Z_{A,B}$ are the valencies of the ions and the characters designated with a bar related to a cation inside the zeolite crystal. Some simple exchanges are: $\text{Na}^+ + \overline{\text{K}}^+ \rightleftharpoons \overline{\text{Na}}^+ + \text{K}^+$, for a uni-univalent exchange, and $2 \text{Na}^+ + \overline{\text{Cu}}^{2+} \rightleftharpoons 2\overline{\text{Na}}^+ + \text{Cu}^{2+}$, a uni-divalent exchange. Cation exchange reactions can be characterized by ion exchange isotherms.

Hydrated cations within zeolite pores are loosely bound, and will readily exchange with other cations in surrounding aqueous media.¹⁷ The study of ion exchange is well established and the thermodynamics of ion exchange equilibria are well known. A

traditional application is in water softening, and increasing use of zeolites is found in the detergent industry. Recent applications have concerned the removal of radioactive ions from contaminated water, particularly after the fission reactor incidents at both Three-Mile Island and Chernobyl.²⁷

1.5 Zeolites in Toxicology

Because of their unique selective nature displayed in the fields of catalysis, adsorption and cation exchange, zeolitic molecular sieves have provided, since the very beginning of their commercialization, effective solutions for controlling pollution of the environment.³⁰ The pressing need for environmental protection has given rise to research in the areas of green chemistry, solvent-free synthesis, zero emissions and the like.³¹ The aim is “production or reactor integrated environmental protection”, which implies the use of better catalysts, the determination of thermodynamic and kinetic properties of the chemical reaction as well as the choice of the most suitable type of reactor and the optimal reaction conditions.³¹ In essence, the strategy has now become proactive as opposed to reactive.

As previously mentioned, zeolites find use as catalysts within the petroleum industry. The industrial production is mainly based on catalytic processes, and more than 90% of all chemical products manufactured involve at least one catalytic step, if not more, during a synthetic procedure. To this end, zeolites have the capability to selectively catalyze reactions that may require something either more exotic or harmful to the environment; some heavy metal catalysts come to mind.

Zeolites with framework structures are excellent inorganic ion exchangers, having high stability to radioactivity. Akyil *et. al.*³² report that zeolite exchangers have been widely used in the full-scale separation of ¹³⁷Cs in waste solutions from nuclear power and fuel processing plants. Harjula and Lehto have studied the effect of sodium and potassium ions on cesium adsorption from nuclear power plant waste solutions on synthetic zeolites.³³

It should be appreciated that zeolites in their natural or synthetic form can, with their inherent characteristic catalytic, ion-exchange and adsorbent behaviour be exploited for the benefit of industry and the environment altogether. As replacement catalysts in the catalytic cracking of hydrocarbons, in nuclear and municipal waste management for the exchange and removal of toxic heavy metals from water systems, zeolites that have been geologic mysteries until the present have found well-suited use.

1.6 Zeolites studied

In this study, surface modification and characterization of three zeolite types was done, specifically on the synthetic Linde Type A (LTA), of the 4Å and 5Å variety, and the natural zeolites, mordenite (MOR) and stilbite (STI). Linde zeolites were readily available in large quantities, in both varieties, and MOR and STI were provided from natural sources from The Bay of Fundy, Nova Scotia.

1.6.1 Linde Type A (LTA)

Milton and Breck of the Linde division of Union Carbide, over a period of 5 years, developed and characterized three novel zeolites, Linde A, X and Y, which have become

three of the most profitable synthetic zeolites for industry. In their attempts to readily synthesize chabazite in 1949, they accidentally stumbled across new structures, zeolites A and B, or gismondite, zeolite C, or sodalite, and a crystalline impurity named zeolite X.³⁴ Experimentation came with changing traditional approaches to zeolite synthesis, specifically hydrothermal syntheses, where relatively insoluble forms of silica and alumina were placed in mildly alkaline solutions (pH 8-11), containing calcium, magnesium and sodium cations at temperatures of 200-300°C. Reaction periods varied from a few days to a week; in some experiments there was no reaction, in others analcime or small-pore mordenite was produced. It was then attempted to increase the pressure within the reaction vessel to 2 000 psig, but it was later concluded that this had no effect on zeolite crystallization. Adsorption properties of zeolite A were determined, and followed the discovery that the pore size could be reduced or enlarged by appropriate choice of potassium, calcium or magnesium ions.³⁴ It was also noted that the zeolite was stable at 500°C. Milton and Breck intended for the synthesized zeolites to have some sort of use, so the researchers postulated that zeolites A and X should make good catalysts or catalyst supports, specifically with respect to hydrocarbon cracking, abnormally strong adsorption sites, molecular size selectivity, and the possibility of atomically dispersed metals on the internal surfaces.³⁴

In crystallographic terms, LTA can be characterized by its secondary building units: S4R, and D4R, 8-rings or 6-2. Depending on the cation that was present during synthesis, the aperture size can vary. Those being used in this study are of the 4Å and the 5Å aperture

size, containing sodium and calcium cations within their structure, respectively. The unit cell for LTA can be seen in Fig. 1.9, which shows the view along the [100] plane. LTA has a general formula of $\{\text{Na}_{12}[\text{Al}_{12}\text{Si}_{12}\text{O}_{48}] \cdot 27\text{H}_2\text{O}\}_8$, and crystallizes in the cubic space group $\text{Fm } \bar{3}c$, with unit cell parameter, $a = 24.6\text{\AA}$.¹¹

1.6.2 Mordenite (MOR)

Synthesis of mordenite was first reported by Barrer and then by many successors.³⁵ The structure of mordenite was determined by Meier³⁶ and consists of an orthorhombic structure containing chains of 5-membered rings parallel to the c -axis connected through double 8-membered rings in the a - c -plane. These chains join to give 12-ring channels in the c -direction, with double 8-ring prisms lining the channel in the a - c -plane. As adjacent 8-ring prisms lining are offset about $3.7\text{\AA}$ in the c -direction ($c/2$), the path between the 12-ring channels, with dimensions, $6.5\text{\AA}$ by $7.0\text{\AA}$, is a very distorted 8-ring having a minimum free diameter of about $2.8\text{\AA}$ (Fig. 1.10). Diffusion, in three dimensions, is therefore limited to very small molecules or cations.

Mordenite is one of the best known acid zeolites, with a well understood pore chemistry. It acts as a catalyst in protonation reactions of alkanes, alkenes and aromatic ring compounds, which require Brønsted acid sites. A typical example is the protonation of adsorbed terpenes, where electron paramagnetic resonance techniques have demonstrated that stable carbocations are formed.³⁷ The thermal stability of MOR due to the high Si/Al ratio makes it applicable in thermal swing adsorption processes where high temperature is

Fig. 1.9 Framework of LTA viewed along [100]. Blue spheres indicate cation positions within the framework structure.

Fig. 1.10 Framework of MOR viewed along [001].

required for desorption.³⁸ Not only the peculiar skeleton and pore structures of MOR, but also the arrangement of cationic species and positions have an important role in its application to adsorption and separation.³⁸ Mordenite is one of the more siliceous zeolites, with an idealized composition: $\text{Na}_8\text{Al}_8\text{Si}_{40}\text{O}_{96} \cdot 24\text{H}_2\text{O}$.

1.6.3 Stilbite (STI)

Stilbite, which is commonly found as a vein mineral in volcanogenic rock, is associated with minerals of the heulandite group. Stilbite has been investigated in different countries by several workers. The crystal structure of STI has been reported by Gottardi, Slaughter and later refined by Galli.³⁹ They report the crystal structure of stilbite is characterized by large, intersecting, relatively open channels of 10- and 8-membered tetrahedral rings (Fig. 1.11). The 10-membered rings have dimensions of $4.9\text{\AA} \times 6.1\text{\AA}$ in the [100] plane that are interconnected to the channels formed by the 8-membered rings in the [101] plane that have dimensions $2.7\text{\AA} \times 5.6\text{\AA}$.¹¹ STI belongs to the monoclinic space group, with C2/m, with unit cell parameters, $a = 13.6$, $b = 18.2$ and $c = 17.8\text{\AA}$, and $\beta = 91^\circ$. STI is a silica-rich zeolite, and could be potentially used as an adsorbent and catalyst, with idealized composition $\text{Na}_4\text{Ca}_8[\text{Al}_{20}\text{Si}_{52}\text{O}_{144}] \cdot 56\text{H}_2\text{O}$. However, due to easy collapse of the framework during dehydration at elevated temperature, makes use of this zeolite difficult. The collapse is caused by cell contraction of the stilbite structure.⁴⁰

1.7 Limitations of current zeolite knowledge

Everything said thus far concerned the structures of zeolites, their uses, properties,

Fig. 1.11 Framework of STI viewed along $[100]$.

synthetic and natural origins; this knowledge is accessible in all classic textbooks. A relatively unexplored area of zeolite literature is the study of the chemically modified surfaces of zeolites, and the effect on the adsorptive nature of the zeolite subsequent to surface modification. It is intended through the studies shown in this thesis, to increase the current knowledge of the effect of the modification of zeolite surfaces, and to study the change in one of the intrinsic characteristics of zeolites: their capability to adsorb water from the atmosphere.

1.8 Thesis overview

Based on previous work done with coating of glass surfaces⁴¹, and knowing the chemistry involved in the attachment of covalently-bound organosilanes to those surfaces, it was demonstrated that this could be generalized to the modification of zeolite surfaces. By exploiting the available surface hydroxyls that exist on zeolite surfaces, covalent linkages result in the formation of Si-O-Si covalent bonds via the introduction of organosilane materials that contain a chlorine functionality.

The zeolites that are studied here are the synthetic Linde 4Å and 5Å varieties and the natural zeolites stilbite (STI) and mordenite (MOR). Because it is known that most zeolites are hydrophilic materials, it is thought that this hydrophilicity could be controlled in some manner, i.e. inhibited by a hydrophobic coating agent such as an organosilane. The organosilane chosen possesses a chlorine functionality that is expected to react with the surface hydroxyls of the zeolite, where the organic moiety varies in chain length and degree

of branching. This coating capability has been observed and exploited in the coating of glass, where the surface hydroxyls of the glass are available for bonding with the chlorine of the organosilane. Once the coating material is introduced to the zeolite, the interaction results in a covalent linkage between the coating agent and the zeolite, providing the zeolite with a layer of intrinsically hydrophobic material above the zeolite, inhibiting the sorption of water by the zeolite. This protective layer then allows the zeolite to adsorb organic molecules into its structure that it would not normally take up as a result of the water molecules that would rush into the cavities taking up all available space.

Of all the organosilane agents that could be used, the ones chosen for this study are the commercially available SurfaSil™ (SS), trimethylchlorosilane (TMCS) and a newly synthesized pyrene derivative, pyrene-1-(4-butyl-dimethylchlorosilyl) ether (**Pyrene-Cl**).

In addition to the manipulation of this hydrophilic/hydrophobic behaviour, the addition of the organic layer also allows the zeolite to behave as a molecular sieve in another way than just the traditional manner where the cavity size controls the sieving behaviour, as in the instance of cation exchange. To this end, it was proposed that the organic layer on the surface of the zeolite could not only behave as a “protector” from atmospheric water entering the zeolite structure, but also as a filter for organic materials that might also be present. By controlling the branching nature of polarity of the zeolite coating, one can tailor the sieving behaviour to a desired compound to be filtered out from a mixture of compounds.

The synthesis of the pyrene derivative shows the potential for a “trap door”

mechanism, where the pyrene moiety is able to behave as a door that could possess the ability to trap substances within the zeolite pore structure by increasing or decreasing the temperature, giving rise to a novel mechanism for gas storage and transport, perhaps eventually eliminating the need for pressurized gas cylinders altogether.

Overall, this project entails the modification and characterization of both synthetic and natural zeolites. Using various analytical and spectroscopic techniques allows for the determination of degree of coating, amount of water loss and gain, surface area, rate of water adsorption and structure analysis. Through the introduction of readily available and newly synthesized organosilane coatings, a new use for zeolites has been introduced, and a novel method of molecular sieving and potential solvent purification and gas storage/transport is envisioned.

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Chapter II

Experimental Techniques

1. Introduction	II-2
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1. Introduction

This chapter outlines the physical techniques to be employed for the characterization of the neat and modified zeolite samples in this study. Specifically, thermal gravimetric analysis (TGA) was employed for the observation of weight loss or gain by the zeolite due to the effects of the coating material covalently bound to the zeolite surface. Powder X-ray diffraction (PXRD) chiefly was used for the confirmation of crystal structure of both the first natural sample (NS1), thought to be mordenite and the second natural sample (NS2), thought to be stilbite. ^{13}C solid-state magic angle spinning nuclear magnetic spectroscopy (SS MAS NMR) determined the existence of methyl carbons from the coating material; ^{29}Si and ^{27}Al SS MAS NMR were used to look at the local nuclear environments within NS1 and NS2 crystal structures, again, to determine sample identity.

1.1 Thermal Gravimetric Analysis (TGA)

The technique of thermal gravimetric analysis is used to measure the amount and rate of weight change in a material, either as a function of increasing temperature, or isothermally as a function of time, in a controlled atmosphere. It can be used to characterize any material that exhibits a weight change and to detect phase changes due to decomposition, oxidation, or dehydration. The derived percent weight change helps to identify and correlate chemical structure, processing, and end-use performance.¹

1.2 Porosimetry

The study of the determination of sample pore size, surface area and isothermal

adsorption of gas by a zeolite will be, in this work, referred to as the technique of porosimetry. The growing importance of adsorption has resulted in the appearance of an ever increasing volume of scientific and technical literature on novel adsorbents and catalysts. Also, various new procedures have been introduced over the past few years for the interpretation of adsorption data - particularly surface area determination, micropore and mesopore analysis.²

1.3 Powder X-ray Diffraction (PXRD)

An X-ray powder diffraction pattern is a set of lines or peaks, each of different intensity and position that can be calculated using Bragg's Law: $n\lambda = 2d \sin\theta$, where d -spacing or Bragg angle, θ , for a given substance describe the line positions that are essentially fixed and are characteristic of that substance. The line intensities may vary somewhat from sample to sample, depending on the method of sample preparation and the instrumental conditions. For identification purposes, principal note is taken of line positions together with a semi-quantitative consideration of intensities.³ Powder diffraction techniques are used to identify a sample of a solid substance by comparison of the positions of the diffraction peaks and their intensities with a large data bank, The Powder Diffraction File, which is maintained by the Joint Committee on Powder Diffraction Standards (JCPDS), and contains information on over 30 000 substances. The technique is also used for the initial determination of the dimensions and symmetries of unit cells.⁴

1.4 *Solid-state Nuclear Magnetic Resonance Spectroscopy (SS NMR)*

Most NMR spectroscopy is performed on fluid samples, specifically solutions. Where solid materials are to be analysed using this non-destructive evaluation technique, a different method is required. NMR is a spectroscopic technique based on the phenomenon that some atomic nuclei possess a spin which interacts with an applied magnetic field, B_0 . For a nucleus with spin quantum number I , this Zeeman interaction gives rise to $2I + 1$ separate energy levels between which transitions can be induced by radiofrequency irradiation. The Zeeman interaction usually is the greatest interaction, but not the only one.⁵ Other interactions which contribute to the appearance of the NMR spectrum are (1) the dipolar interaction, H_d , defined as the interaction of the spin with other spins; (2) the chemical shift interaction, H_{cs} , the interaction of the spin with the electrons in the electron cloud around the nucleus; (3) the quadrupole interaction, H_q , which is the interaction of the quadrupole moment of the nucleus with the electric field gradient at the nuclear site (where $I > \frac{1}{2}$).

An essential difference between NMR of fluids and solids is the anisotropic spin interactions that occur in a solid sample, whereas these interactions are averaged out in a fluid by rapid tumbling of the molecules. For a solid sample, this random tumbling does not occur and the anisotropic spin interactions yield NMR frequencies which depend on the orientation of the magnetic field with respect to the molecular or crystal axes.⁵

For powders, such as zeolites, all possible orientations of crystallites are present,

which may lead to broad and featureless resonances in the NMR spectrum. The anisotropy of the chemical shift is removed by a technique called magic angle spinning (MAS). In this technique, the sample is spun around an axis which is inclined at an angle of 54.74° to the main static magnetic field, so that all tensor interactions within the sample are scaled down to zero to yield clean spectra with sharp lines.⁶

While MAS leads to line-narrowing and thus increases the sensitivity as well as resolution, cross-polarization (CP) can be used to further enhance the sensitivity of a nucleus with a low gyromagnetic ratio.⁷ The process begins with the generation of transverse magnetization from the more sensitive spin species. This magnetization can then be “spin-locked” along an rf-field, B_1 , that precesses in phase with it in the transverse plane. Because the B_1 field is much smaller than the external field, B_0 , which was the original field for establishing magnetization, the spin-locked magnetization is in a non-equilibrium state.⁷ If an rf-field of the appropriate amplitude, is simultaneously applied to the other spin species, energy-conserving magnetization transfer can occur between the two types of spins, leading to the enhancement of the signal of the less-sensitive spins.⁷ CP has been widely applied to many inorganic materials and is frequently combined with MAS to yield well-resolved spectra with a good signal-to-noise ratio. It is particularly useful for enhancing the spectra of nuclei with a low natural abundance, which otherwise would be difficult to observe. Although CP MAS has most commonly been used with spin-1/2 nuclei, it has been applied to quadrupolar nuclei as well.⁷

It is the technique of CP MAS that is used in this study, specifically ^{13}C SS NMR to show the presence of coating materials used to modify the zeolite surfaces, and ^{29}Si and ^{27}Al nuclei for the characterization of NS1 and NS2. The details of ^{29}Si and ^{27}Al SS NMR techniques are described below.

1.4.1 ^{29}Si NMR

Silicon has only one naturally-occurring isotope with non-zero spin, namely ^{29}Si , which has spin $I = \frac{1}{2}$ and a natural abundance of 4.70%. This places it among the category of “rare” spins, and implies that all the modern techniques can be applied in a similar fashion to their use for ^{13}C , for example. A number of review papers have been published⁸ summarizing the structural information and relationships available through the ^{29}Si NMR on zeolites. One of the most important results of Lippmaa, Engelhardt and coworkers^{9, 10} was to establish the relationship between the ^{29}Si chemical shift sensitivity and its surrounding environment: the number and type of tetrahedrally coordinated atoms (T-atoms, with $\text{T}=\text{Si}$, Al or other lattice atoms) connected to a given SiO_4 unit. The degree of connectivity is symbolized by $\text{Si}(n\text{Al})$ where $n = 0, 1, 2, 3$ or 4 , where n indicates the number of Al atoms sharing oxygens with the SiO_4 tetrahedron under consideration. Furthermore, the ^{29}Si chemical shift is influenced by the Si-O-T bond angle, and Si-O bond length, which means that chemically equivalent but crystallographically inequivalent Si nuclei may have different chemical shifts.¹¹ Chemical shift ranges are given in Fig. 2.1. Generally, the ^{29}Si chemical resonance shifts to lower field by approximately 5 ppm per additional aluminum. Therefore,

up to five lines per crystallographically inequivalent Si site may be observed in the ^{29}Si NMR spectrum. Hence, useful information about the local environment of the SiO_4 tetrahedra forming the zeolite lattice can be ascertained from the ^{29}Si chemical shift data.¹²

1.4.2 ^{27}Al NMR

The main applications of ^{27}Al NMR spectroscopy in connection with zeolites has been in the monitoring of dealumination processes and the detection of extra-framework aluminum, since extra-lattice aluminum is octahedrally coordinated and gives rise to resonance lines at about 0 ppm, whereas framework aluminum is tetrahedrally coordinated and resonates between approximately 50 and 65 ppm.⁸ ^{27}Al has a nuclear quadrupole moment, with spin $I = 5/2$, which interacts with the electric field gradient caused by the non-spherically symmetric charge distribution around the ^{27}Al nucleus. Both line broadening/distortion and chemical shift changes may arise from those quadrupolar interactions resulting in more difficult interpretations of the ^{27}Al NMR spectra. Conversely, the high sensitivity of the ^{27}Al isotope, in 100% abundance with generally short relaxation times, allows the determination of very small amounts of aluminum in the samples. Spin-lattice relaxation times (T_1) of ^{27}Al in zeolitic frameworks have been measured by Haase *et al.*¹³ in the range of 0.3 to 70 ms. Obeying Loewenstein's rule, where Al-O-Al linkages are forbidden, zeolites give rise to quite simple ^{27}Al NMR spectra, consisting of signals due only to one type of tetrahedral aluminum environment, $\text{Al}(\text{OSi})_4$, in addition to the eventual octahedrally coordinated aluminum. The quantitative use of ^{27}Al MAS NMR is a valuable

tool in probing the coordination, location and quantity of Al in zeolites, but less useful than ^{29}Si MAS NMR for the detailed study of lattice structure.¹⁴

Fig 2.1 Ranges of ^{29}Si chemical shifts of $\text{Q}^4(n\text{Al})$ units in aluminosilicates.

2. *Experimental*

2.1 *TGA experiments*

TGA measurements were performed using a 2050 Thermogravimetric Analyzer (TA Instruments) with nitrogen, helium or oxygen as the purge gas, where indicated, at a flow rate of 40 cc/min. Where temperatures were to exceed 500°C, open, platinum pans were utilized; otherwise, experiments were carried out in open, aluminum pans. Sample masses ranged between 5-20 mg. Before analysis, samples were dried to 300°C, allowed to cool in a dessicator, then placed in an atmosphere of water (97% humidity, maintained with a saturated K₂SO₄ solution), methanol or ethanol for several days. Samples were quickly placed into the TGA sample pan once removed from the solvent atmosphere.

2.1.1 *Sample weight loss measurements*

Experiments were run at a ramping rate of 5°C/min to 300°C, and subsequently kept isothermal for 60 minutes, with nitrogen flow. Weight loss experiments, where oxygen was utilized as the purge gas, were run at a ramping rate of 5°C/min to 1000°C, and subsequently kept isothermal for 60 minutes.

2.1.2 *Temperature cycle experiments*

Experiments were run with a temperature increase ramping rate of 5°C/min to 350°C, kept isothermal for 30 minutes, then a temperature decrease ramping rate of 2°C/min to 25°C, and also kept isothermal for 30 minutes. This cycle was repeated five times, with either nitrogen or helium as the purge gas.

2.2 Porosimetry measurements

Nitrogen adsorption measurements at 77K were carried out on samples NS1 and NS2 and were done using an ASAP Micrometrics 2010 porosimeter. Outgassing of the samples prior analysis was done for several days at 250°C.

2.3 PXRD measurements

Powder diffraction patterns for NS1 and NS2 were collected on a Scintag X2 powder diffractometer ($\text{CuK}\alpha 1 = 1.54056 \text{ nm}$, $5^\circ \leq 2\theta \leq 65^\circ$, 0.02° step interval, 0.5 second count time per data point). Powder pattern search and match was done through the JCPDS database.

2.4 SS MAS NMR spectroscopy methods

2.4.1 ^{13}C SS MAS NMR experiments

^{13}C SS MAS NMR experiments were performed on a Tecmag Apollo 200 MHz spectrometer using 7mm, double-bearing magic-angle spinning zirconia rotors. All ^{13}C spectra were spun at approximately 4000 Hz. Experiments were performed at a resonance frequency of 50.33 MHz. Chemical shifts were referenced to adamantane. Proton decoupling was applied, and at least 4096 scans were acquired for each spectrum with sweep width of 20 000 Hz, a pulse length of $10\mu\text{s}$, and a repetition time of 10s. Analysis and curve fitting of spectra was done using Microcal Origin 6.0.

2.4.2 ^{29}Si SS MAS NMR experiments

^{29}Si SS MAS NMR experiments were performed on a Tecmag Apollo 200 MHz

spectrometer using 7mm, double-bearing magic-angle spinning zirconia rotors. All ^{29}Si spectra were spun at approximately 4000 Hz. Experiments were performed at a resonance frequency of 39.76 MHz. Chemical shifts were referenced to tetramethylsilane. Proton decoupling was applied, and at least 1024 scans were acquired for each spectrum with sweep width of 10 000 Hz, a pulse length of $11\mu\text{s}$, and a repetition time of 100s. Analysis and curve fitting of spectra was done using Microcal Origin 6.0.

2.4.3 ^{27}Al SS MAS NMR experiments

^{27}Al SS MAS NMR experiments were performed on a Tecmag Apollo 200 MHz spectrometer using 7mm, double-bearing magic-angle spinning zirconia rotors. All ^{27}Al spectra were spun at approximately 4000 Hz. Experiments were performed at a resonance frequency of 52.15 MHz. Chemical shifts were referenced to a dilute aqueous solution of $\text{Al}(\text{NO})_3$. Proton decoupling was applied, and at least 2048 scans were acquired for each spectrum with sweep width of 20 000 Hz, a pulse length of $2\mu\text{s}$, and a repetition time of 0.2s. Analysis and curve fitting of spectra was done using Microcal Origin 6.0.

2.5 General procedure for the coating of zeolites

Approximately 2-3g of zeolite¹⁵ was placed in a 2-necked round bottomed flask. The zeolite was heated to 150-200°C under vacuum on a Schlenk line for 2 days to ensure complete removal of water from the zeolite structure. After heating, the flask with the contents was allowed to cool. A solution of the coating agent was prepared by diluting the organosilane: **SS** (Pierce), **TMCS** (Aldrich), or **Pyrene-Cl** in *n*-pentane (Fisher Scientific)

(1:10 m/v). Maintaining vacuum in the flask, and using a syringe, the coating solution was introduced to the zeolite, enough to wet it completely. The system was then purged with N₂ gas, and opened to atmosphere. To the flask was added excess of the same solution (50 mL). Stirring was then initiated and maintained overnight. After stirring was stopped, the excess solution was decanted, and the zeolite was then rinsed with pure *n*-pentane (x3). After rinsing, the supernatant liquid was decanted again. The remaining zeolite was dried under vacuum to remove excess solvent. The coated zeolite was then stored in a vial, ready for analysis.

2.5.1 *Pre-coating of Glass Vessels*

This procedure is followed if a silation reaction is to be done. Because the surface of glass possesses hydroxyl groups, it is necessary to protect the vessel from reacting with the silating reagent needed.

A vessel, dried in an oven at 150°C, and cooled to room temperature, was filled with a solution containing a 1:10 (m/v) ratio of organosilane (SS, TMCS, etc.) and *n*-pentane. This solution was allowed to stand in the vessel for at least 30 minutes. After the time had elapsed, the contents of the vessel were decanted. The vessel was then inverted and allowed to air dry for at least one half hour. The vessel was then rinsed three times with pure *n*-pentane and air-dried.

2.6 *General Pyrene-derivative Synthetic Procedure*

All reagents were obtained from Aldrich and used as received unless otherwise

indicated. All solvents were used directly from the bottle. Glassware and magnetic stir bars were dried in the oven at 150°C prior to use.

2.6.1 Synthesis of Pyrene-TBDMS

To a 2-necked, 500mL round-bottomed (r.b.) flask equipped with a magnetic stir bar and a reflux condenser, was added 1.5g (0.0052 mol) of **PBA (1)** (purified by sublimation) and a molar equivalent of **TBDMS**. The reaction was conducted in ethyl acetate (EtOAc, Fisher) (~250 mL), under reflux overnight, resulting in a clear, yellow supernatant liquid with a light brown precipitate.

The resulting product was then extracted with EtOAc. After drying over MgSO₄ (Fisher), the solution was filtered and evaporated under vacuum to produce a yellow, pungent-smelling solid. The yield was 60% . The product, **Pyrene-TBDMS (2)**, was dried under a stream of N₂ gas, and was purified by sublimation to give a pale, yellow powder. ¹H NMR, 400 MHz, dmso-d₆, (**Pyrene-TBDMS**: δ 0.06, s, 9H; 2.01, m, 2H; 2.39, t, 2H; 3.34, s, 6H; 7.93-8.41, aromatic, 9H), (EtOAc: δ 1.2, t, 3H; 2.01, s, 3H,; 4.06, q, 2H), (dmso: 2.50, p, 6H), m.p. 184-186°C.

2.6.2 Synthesis of Red-Pyrene-TBDMS

To a 2-necked, 250mL r.b. flask equipped with a magnetic stir bar and a reflux condenser, was added 1g (0.0025 mol) of **Pyrene-TBDMS (2)** and two molar equivalents of NaBH₄. The reaction was conducted in EtOAc (~250 mL), under reflux overnight, yielding a yellow precipitate. The resulting product was then extracted with EtOAc. After

drying over MgSO_4 , the solution was filtered and evaporated under vacuum to produce a yellow solid. The yield was 80%. The product, **Red-Pyrene-TBDMS (3)**, was dried under a stream of N_2 gas, and purified by sublimation to give a yellow powder. ^1H NMR, 400 MHz, dmso-d_6 , (**Red-Pyrene-TBDMS**: δ 0.48, d, 6H; 2.88, t, 2H; 2.99, s, 2H; 3.84, t, 4H; 7.94-8.49, aromatic, 9H), (EtOAc: δ 1.33, s, 3H; 1.66, t, 3H; 4.52, q, 2H), (dmso: 2.50, p, 6H), m.p. 179-183°C.

2.6.3 Synthesis of Pyrene-But-OH

To a 2-necked, 250mL r.b. flask equipped with a magnetic stir bar and a reflux condenser, was added 0.52g (0.0013 mol) of **Red-Pyrene-TBDMS (3)** and four molar equivalents of **TBAF**. The reaction was conducted in EtOAc (~250 mL), under reflux overnight, resulting in a clear, yellow liquid.

The resulting product was then extracted with EtOAc. After drying over MgSO_4 , the solution was filtered and evaporated under vacuum to produce a yellow solid, with 75% yield. The product, **Pyrene-But-OH (4)**, was dried under a stream of N_2 gas, and purified by sublimation to give a pale-yellow powder. ^1H NMR, 400 MHz, dmso-d_6 , (**Pyrene-But-OH**: δ 0.85, t, 1H; 0.90, t, 0.5H; 2.01, p, 2H; 2.39, t, 4H; 3.34, m, 4H; 7.93-8.41, aromatic, 9H; 12.12, bs, 1H), (EtOAc: δ 1.33, t, 3H; 2.01, s, 3H; 4.06, q, 2H), (dmso: 2.50, p, 6H), m.p. 167-175°C.

2.6.4 Synthesis of Pyrene-Cl

To a pre-coated, 2-necked, 500mL r.b. flask, closed to atmosphere, equipped with a

magnetic stir bar and flushed with nitrogen, was added 0.52g (0.0013 mol) of **Pyrene-But-OH (4)** and slight molar excess of **DCDMS** (0.2 mL). The reaction was conducted under nitrogen, in anhydrous EtOAc (~250 mL), resulting in a clear, yellow liquid.

The solvent was isolated by evaporating the solvent under a stream of nitrogen gas to produce a yellow-brown solid, with moderate yield. The product, **Pyrene-Cl (5)** was dried further under a stream of N₂ gas, and stored in a drybox, away from moisture. ¹H NMR, 400 MHz, dmso-d₆, (**Pyrene-Cl**: δ -0.11 to -0.02, bs, d, 6H; 1.2, t, 2H, 2.02, m, 2H; 2.39, t, 2H; 3.34, t, 2H; 7.63-8.41, aromatic, 9H), (**DCDMS**: δ 0-0.13, d, t, s, 6H), (EtOAc: δ 1.33, t, 3H; 2.01, s, 3H; 4.03, q, 2H), (dmso: 2.50, p, 6H), m.p. 181-183°C.

2.7 Adsorption experiment setup

All zeolite samples were dried in an oven at 150°C for several days, then heated at 300°C for 24 hours, then placed in a dessicator to cool before use. Duplicates of each zeolite sample were weighed out (0.06-0.08g) and were then placed in pre-weighed glass weighing bottles. The samples were then placed in a closed environment of either saturated water (humidity kept at 97% with a saturated K₂SO₄-H₂O solution), methanol or ethanol, and allowed to equilibrate over several days, in a cool, dark place. Weight readings were taken at prescribed intervals, taking care to place the lids on the vials as quickly as possible once the storage container was opened. After observing the mass of the samples equilibrate after 15 hours, the samples were placed again in the oven for several days to drive off all solvent, allowed to cool in a dessicator and re-weighed.

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Chapter III
Modification of Surfaces
and the Synthesis of a Novel Coating Material

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1. *Modification of Surfaces*

Material science is typically driven by a desire to produce novel compounds or to modify known compounds for various applications. In this study, modification of external zeolite surfaces is examined and the effects of such modification is determined. Surface modifications can be carried out most conveniently with the use of organosilanes. A hydrolyzable chlorine substituent allows covalent grafting of hydrophobic organic functional groups to otherwise hydrophilic zeolites.

The strategy of adding a coating to zeolite structures is currently the subject of intensive study due to the potential applications such as protective coatings, optoelectronic devices, catalysts and modified electrodes, as well as for fundamental studies of wetting, adhesion, and general behaviour.¹ In particular, organosilanes have rapidly gained popularity, and are widely used. For instance, alkylsilane films have been one of the most widely used classes of coatings due to the fact that they can be deposited on a variety of substrates and are both thermally and chemically stable.²

Arkles³ describes in his review on tailoring surfaces with silanes, that encounters between dissimilar materials involve at least one member that is siliceous, or that has surface chemistry with siliceous properties such as silicates, aluminates, borates and so on. Interfaces involving such materials have become a dynamic area of chemistry where surfaces have been modified in order to generate desired heterogeneous environments or to incorporate the bulk properties of different phases into a uniform composite structure. In

general, a coating and substrate conglomerate is produced when a material is exposed to a modifying agent. The modifying agent of interest is that of an organosilane, with the general formula $R_nSiX_{(4-n)}$ where X is a hydrolyzable group, usually an alkoxy, acyloxy, amine, or as in this study, a halogen. The R group is a non-hydrolyzable organic group in possession of a functionality imparting desired characteristics that can be rationally designed.

1.1 Silane coating chemistry

Silane coatings are chosen for reactivity and functionality that is compatible with the substrate to be coated. This means that the hydrolyzable (X) group has predictable chemical behaviour, and the nonhydrolyzable (R) group has the desired characteristics that will give the coating layer the properties being sought. The performance of a coating agent is independent of the nature of the X groups if adequate moisture is available for hydrolysis, either from the solvent in which the reaction is taking place, or at the site of reaction.⁴

Additionally, either extremity of the silane molecule can undergo chemical modification, either separately, or simultaneously. The X groups can be exchanged or hydrolyzed without altering the R group. Chemical modification of the R group may precede application to a surface or may take place at a surface after silylation.⁴ In particular, this overall chemistry of coating surfaces is known to work, because the X group reacts readily with hydroxyl groups on substrate surfaces, specifically in the case in modifying the surfaces of zeolites (Fig. 3.1).⁵

Fig. 3.1 A schematic representation of the reaction of a coating material with a substrate.

1.2 The coating of glass surfaces

The surface treatment of materials, such as metal oxide surfaces, clay minerals, glass and zeolites with organochlorosilanes has widespread use in diverse areas such as the production of self-assembled monolayers, chromatography and xerography.⁶ The successful application of the treatment of materials with organochlorosilanes has been limited by the variability in the quality of the films produced. Much of the day-to-day variance can be traced to a critical dependence on reaction temperature and on the level of surface water.⁶ Most silation reactions are performed near room temperature in non-aqueous solutions.⁶ Under these conditions, surface hydroxyls are needed to hydrolyze the chlorosilane moiety, to form an intermediate silanol species, which reacts with surface hydroxyl groups to form the final chemical species.

It is well known that chlorosilanes react readily with all hydroxyl groups to generate hydrochloric acid.⁷ Utilizing this reaction, many different organic functional groups can be introduced onto glass surfaces through covalent bonds.⁷ Surface modification specifically of porous glass membranes by a covalently bonded molecular monolayer is thus a special way of altering membrane performance to introduce various organic functionalities.⁷ The voids within porous glass are rigid in shape and are modified by the organic monolayer. These surface-modified membranes can then exhibit high thermal stabilities and high permeance as well as organic functionality, or high selectivity to organic compounds that come into contact with the modified glass.

1.3 *Modification of zeolite and zeolite-type materials*

Many studies have investigated methods to control the surface properties of zeolites and related materials by exposing them to silicon compounds.^{5, 8-10} It is the presence of the hydroxyl groups on the surface that can be used to anchor -SiR groups via a silanation process, which can be tailored to function as pore-blockers, or selectively change the surface properties and adsorption capacity. The modification can be carried out using organosilicon compounds containing one or several functional groups, which makes further reactions on the surface of the modified adsorbents possible; in this way, selective adsorbents can be prepared.¹¹ It has been observed that modifying zeolites and related materials causes a change in adsorption properties, where the adsorption capacity of such adsorbents is higher than that of the chemically unmodified ones.¹¹ It is the modification of zeolite surfaces that is of interest in this study, specifically with the coating materials: SurfaSil™ (SS), trimethylchlorosilane (TMCS) and newly synthesized pyrene-containing molecule, pyrene-1-(4-butyl-dimethylchlorosilyl) ether (**Pyrene-Cl**) (Fig. 3.2).

2. *Synthesis towards a new coating material: Pyrene-Cl*

Commercially available, straight-chained organosilane molecules have been the most popular type of coating material in the surface modification of substrate surfaces. Some slightly branched materials have also been utilized, but what has not been extensively studied in the literature is the use of larger organic functional groups, such as pyrene, that are part of the organosilane coating used to coat a surface. This is what is intended in this study: the

synthesis of a new coating material and the introduction via a covalent bond to the surfaces of zeolite LTA of the 4Å and 5Å types.

2.1 Synthetic Strategy

Pyrene butyric acid was the starting point of the synthetic sequence as shown in Fig. 3.3. The carboxylic acid functionality is the reactive group used in the modification of this compound, that will be useful for the modification of a zeolite surface. Specifically, it is the protection of the carboxyl -OH group that will first be accomplished, the carbonyl will be removed by a double reduction reaction, followed by the removal of the protecting group to yield a terminal alcohol that will then be available for the attachment of a chloro-silyl group.

The strategy of protection of a hydroxyl functionality and its subsequent deprotection at a later stage is frequently used in multi-step synthesis.^{12, 13} Of all the hydroxyl protecting groups, *t*-butyldimethylchlorosilyl (**TBDMS**) ether has become the most popular and widely used means of protecting groups because of its ease of preparation, and its stability to a wide range of reaction conditions.¹⁴ The reduction of the carbonyl group, that results from the attachment of the **TBDMS** protecting group, is performed using two molar equivalents of NaBH₄, which works well in reducing carbonyls in good yield.¹⁵ Numerous methods are now available in the literature¹⁴ for the deprotection of **TBDMS** ethers under a variety of conditions. The transformation of an alcohol to its corresponding **TBDMS** ether has been a common and useful method for protecting the hydroxyl group since its introduction by Corey¹⁶ in 1972.

Fig. 3.2 Ball-and-stick model, with van der Waal's radii, representation of the organosilane coating materials: a, trimethylchlorosilane; b, SurfaSil™; c, pyrene-1-(4-butyl-dimethylchlorosilyl) ether.

Fig. 3.3 Sequence of steps for the synthesis of pyrene-1-(4-butyl-dimethylchlorosilyl) ether; the last step shows the introduction of the material to a zeolite surface.

One of the most effective ways for the cleavage of silyl ethers is based on the exploitation of the high affinity of silicon towards fluoride ions.¹⁴ Thus, a number of reagents involving one form of the fluoride ion or another, such as tetrabutylammonium fluoride (**TBAF**), the reagent of choice in this study, boron trifluoride etherate, hydrofluoric acid, have been developed for the deprotection of **TBDMS** ethers. Among these, **TBAF** is the most frequently used. Concerns have arisen to the use of **TBAF** as a deprotection reagent due to the basicity of the bare fluoride ion in tetrahydrofuran, which directly affects cleavage of **TBDMS** ethers of the β -ketol system of phenolic compounds and may promote β -elimination reactions, transacylations and other base-catalyzed undesired side reactions. However, **TBAF** is used only in one aspect of the workup in the reaction sequence described in this study; these difficulties are not expected. Only one hydroxyl group is to be protected, and any complications that have been described^{14, 17}, involve either several protected sites, or complex systems. Once the protecting group is removed, the resulting terminal hydroxyl functionality is then available for the covalent linkage of an organochlorosilane, by exploiting the same chemistry that has been used in the coating of glass surfaces and other materials that possess surface hydroxyl groups. In this case, a dichloro-organosilane where one chlorine is to react with the hydroxyl of this pyrene-containing organic coating material, and the remaining Cl is available for reaction with surface hydroxyls of the substrate to be coated, is introduced.

3. *Synthesis of a novel pyrene coating*

The modification and substitution of sites of pyrene have been studied previously¹⁸; however, the use of a pyrene-substituted molecule as a surface modification agent is not understood. The chemistry at each individual synthetic step has been well documented; hence, the surface chemistry of the pyrene-substituted coating agent should also be predictable. Observation of the changes to the molecule were monitored via ¹H NMR spectroscopy. Evidently, the aromatic moiety, in all steps, remained unmodified; therefore, what was being searched for was evidence of the appearance of proton signals of the groups being added, namely the **TBDMS** protecting group after the first synthetic step. Using the ¹H NMR spectrum of **PBA**, which was purified via sublimation, as a reference, the subsequent spectra from each following steps were compared. There was an appearance of several new peaks after the introduction of **TBDMS** resulting in the formation of **2**. Methyl protons in the 0-1 ppm range are observed. After the double reduction step in the synthesis of **3**, it would be expected to see the appearance of more alkyl proton resonances, as was indeed the case, at 1.25 ppm. In the next step of the sequence, in producing **4**, the ¹H NMR spectrum revealed the appearance of a new peak at δ 0.83, indicating that there was the production of a terminal hydroxyl, and the absence of the methyl and *t*-butyl signals from **TBDMS** confirmed the success of this step. The final step, where the introduction of **DCDMS** to **4** to produce **5** (Fig 3.4), methyl proton signals appeared, from lowfield to highfield, as a cluster of a singlet, triplet, doublet, doublet and singlet in the region around

0 ppm. The last two peaks at -0.08 and -0.04 ppm give an integral of 6H. This appearance confirms the successful addition of **DCDMS** to **4**. The remainder are attributed to **DCDMS** that was not successfully removed from the product. The other sets of peaks in the spectrum are assigned the following: the pyrene-H resonances for nine hydrogens appear in the aromatic region of 7.94-8.42 ppm; hydrogen resonances for the alkyl chain appear: a triplet at 3.34 (2H), a triplet at 2.34 (2H) and a pentuplet at 2.01 ppm (2H), and a triplet at 1.21 ppm (2H). A peak at 4 ppm is attributed to traces of the reaction solvent, EtOAc, that had not been removed. All ^1H NMR spectra for the preliminary steps of the reaction sequence products are given in the Appendix. Figure 3.5, displaying the mass spectrum (ES^+), does not seem to show the M^{+1} peak for the compound proper; however, the larger peaks that do show prominence are 242.3 and 186.3, which correspond to the Pyrene-1-butyl moiety and the O-**DCDMS** moiety, respectively. Evidently, it is the C-O bond connecting these two moieties that is one of the weakest points in the molecule.

Fig. 3.4 ^1H NMR spectrum of Pyrene-Cl (5). The annotations is defined as: 'p'= product.

Fig. 3.5 Mass spectrum of Pyrene-Cl (5).

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Chapter IV
Results and Discussion

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1. *Thermal Gravimetric Analysis (TGA)*

All samples were held in a closed atmosphere for at least several days to allow for equilibration of the atmosphere within the container, and for optimum uptake of solvent by the zeolite samples. The samples were placed out of direct sunlight to ensure ambient temperature conditions. After the waiting period, TGA experiments were carried out to determine the maximum loss of solvent. In the case of the temperature cycle experiments, gains and losses in sample mass were observed in a repeated manner. Those TGA plots not shown in this chapter and are presented in the Appendix. It should be noted that to determine whether the materials were going to undergo solvent uptake in the solvent atmosphere, preliminary experiments were conducted in order to determine whether any observable effect could be noted. Hence, TGA experiments were performed to provide some background as to the behaviour of the zeolite exposed to various solvent atmospheres.

1.1 *Initial survey of weight loss of coated vs. non-coated zeolites*

In general, upon heating the samples to 1000°C under oxygen flow to determine total weight loss of both neat and coated zeolite samples, it can be stated that no pattern can be discerned as to the overall weight loss of the coated samples versus the neat samples. However, this does not indicate that no weight loss due to the burning off of the coating material occurred. This loss of coating material is observed in the temperature regions of 250-550°C, as shown in the TGA plots. Table 4.1 summarizes the total weight loss of all zeolite samples to 1000°C.

**Table 4.1 Total weight loss as a % where the final temperature was 1000 °C.
Values are based on original weight.**

Zeolite sample	Coating	Total weight loss (%) [*]
LTA 4Å	Neat (uncoated)	20.62
	SS	21.13
	TMCS	20.87
	Pyrene-Cl	14.09
LTA 5Å	Neat	19.28
	SS	20.45
	TMCS	20.11
	Pyrene-Cl	22.06
NS1	Neat	13.24
	Neat (H ₂ O ₂ - leached)	14.26
	SS	17.32
	TMCS	11.96
NS2	Neat	14.03
	Neat (H ₂ O ₂ - leached)	13.36
	SS	13.86
	TMCS	15.84

^{*} Values shown here are within 1% error.

Table 4.2 Total weight loss of zeolite samples after exposure to solvent atmosphere. Values are based on original weight. For the NS1 and NS2 values, the reported literature value is given in parentheses.

Zeolite sample	Coating	Solvent atmosphere	Total weight loss (%)	Final T (°C) isothermal for 60 min
LTA 4Å	Neat (uncoated)	H ₂ O	19.98 ± 0.8	300
	SS		19.25 ± 0.3	
	TMCS		20.16 ± 0.9	
	Pyrene-Cl		20.57 ± 1.0	
LTA 4Å	Neat	Methanol	18.86 ± 0.7	300
	SS		18.11 ± 1.1	
	TMCS		18.64 ± 0.8	
	Pyrene-Cl		18.30 ± 1.4	
LTA 4Å	Neat	Ethanol	19.95 ± 0.6	300
	SS		18.90 ± 0.1	
	TMCS		19.36 ± 0.04	
	Pyrene-Cl		19.06 ± 0.1	
NS1	Neat	H ₂ O	12.57 * (16)	450
NS2	Neat	H ₂ O	9.99 * (17)	450

* Values shown here are within 1% error.

Table 4.2 shows the weight loss of LTA 4Å that was exposed to three solvents: water, methanol and ethanol. It could be stated that, in general, the coated materials in all three solvent atmospheres exhibited a tendency to take up less of the solvent molecules than in the neat zeolite case. This would suggest that the coating material inhibits the uptake of solvent, acting as a pore-blocker, where the neat sample has no such protection. Methanol and ethanol in comparison to water show only slightly less of an affinity for the zeolite, whether the sample is coated or not. Water is easily taken up by the zeolite structure, as water molecules are small enough to pass through the apertures and diffuse through the channels and cages of the zeolite and tend to surround cations that reside in the zeolite structure due to electrostatic attraction. Methanol and ethanol do not share the same properties as water does, being less polar. In addition to polarity differences among the three solvents, there is also a difference in size (Fig. 4.1, 4.2). Water is not hindered by its size to enter the LTA 4Å zeolite structure and can enter the zeolite structure regardless of orientation, as is the case with methanol. Conversely, ethanol must be properly oriented, such that the molecule should face the apertures of the zeolite structure in an “end-on” orientation to guarantee diffusion into the zeolite. A “face-on” entrance is not possible, as the length of ethanol from tip to tail is greater than 4Å. The calculation of the length of the ethanol molecule, as well as for water and methanol was based on the addition of standard bond lengths of: C-H, C-C, C-O and O-H as are provided in classical texts. In the case of the LTA 5Å, all three solvents can enter

Fig. 4.1 **Ball and stick models of : a, water (~ 1.5 Å length; b, methanol (~ 3.5 Å length); c, ethanol (~ 4.5 Å length). Molecules shown are to illustrate how slight difference in size can alter diffusion into a zeolite.**

Fig. 4.2 Space filling models of water, methanol and ethanol molecules. The top diagram illustrates the difference in length; from left to right: water, methanol, ethanol. The bottom diagram shows a side view, where the cross-sectional diameter of all three molecules is similar.

the zeolite structure, as the apertures are large enough to accommodate the molecules, again, regardless of orientation. The versatility of the zeolite samples with respect to the solvent molecules is evident in that the weight percent uptake does not greatly differ from water to methanol and finally to ethanol.

The NS1 and NS2 samples were heated to 450°C to determine total water loss of these natural samples. Literature values¹ show an increased weight loss due to the evolution of water from the zeolite structure in comparison to the experimental values shown in Table 4.2. Given that these are natural samples, and not purified to remove mineral impurities, it would be expected that those impurities such as quartz, mica or feldspar do not have water uptake capabilities, due to their mineral structure devoid of pores and channels. This would, therefore, give the sample less water uptake overall.

1.2 Cycle experiments

These experiments were carried out to document some unusual observations, the fact that weight was regained on cooling the samples. Table 4.3 summarizes the initial weight loss due to water and the subsequent uptake of flow gas for all zeolite samples. Table 4.4 summarizes the average gain and loss of flow gas for all zeolite samples. All the samples were placed in a sealed container, exposed to an atmosphere of water vapour. During analysis, nitrogen was employed as the flow gas. In general, all materials exhibited repeatable weight loss with the increase of temperature, and a weight gain with the decrease of temperature. In the initial weight loss, water is driven off. When the temperature is

decreased, weight is gained, indicating the uptake of nitrogen. The cycle is repeated, where weight loss occurs with temperature increase, and conversely, weight gain with temperature decrease. A sample TGA plot is shown in Fig. 4.3. It is not thought that water is being re-adsorbed into the zeolite structure, as a constant flow of nitrogen, from a cylinder containing nitrogen at 99.998% purity, is maintained throughout the cycle. The most N₂ uptake is observed in the 4Å and 5Å samples coated with the **Pyrene-Cl** coating. Since this is a relatively large molecule in comparison to **SS** and **TMCS**, it is thought that when the sample is being cooled, N₂ that is adsorbed into the zeolite structure might also be trapped under the coating material as it bends towards the surface of the zeolite at lower temperatures. In the cases of NS1 and NS2, this idea does not hold true, as the **TMCS** coated versions lost more initial water and gained more N₂. This allows for postulation of whether the smaller, less flexible coatings have the ability to trap sorbent molecules just underneath the methyl groups that are substituents of the silicon moiety bound to the zeolite surfaces (Fig. 4.4).

In addition to cycle experiments with nitrogen, it was of interest to take a look at the uptake of LTA 4Å and 5Å, neat, in a cycle experiment with helium as the flow gas (Fig. 4.5). It was observed that a substantial initial uptake of 14.99% for 4Å and 13.94% for 5Å for the case of helium in contrast to the 6% uptake for nitrogen. Helium atoms are much smaller and can diffuse much more easily into the into the β cages of the zeolite structure; conversely, nitrogen is only able to diffuse into the α cages.

Table 4.3 **Initial water loss and initial gain of gas during the first cycle of temperature cycle experiments, where the maximum temperature was 350 °C, and the minimum 25 °C. Values are based on original weight.**

Zeolite sample	Coating	Initial H ₂ O loss (%) [*]		Initial N ₂ gain (%) [*]	Initial He gain (%)
		N ₂ flow	He flow		
LTA 4Å	Neat (uncoated)	19.27	19.78	6.22	14.22 ± 1.10
	SS	20.09		5.73	
	TMCS	19.93		4.84	
	Pyrene-Cl	19.02		9.80	
LTA 5Å	Neat	20.15	19.26	5.66	13.44 ± 0.71
	SS	19.51		5.21	
	TMCS	19.10		6.08	
	Pyrene-Cl	20.71		6.66	
NS1	Neat	11.30		4.32	
	SS	11.90		4.35	
	TMCS	12.89		4.72	
NS2	Neat	9.31		2.32	
	SS	9.62		2.56	
	TMCS	10.29		2.74	

^{*} Values shown here are within 1% error.

Table 4.4 **Average water loss and average gain of gas during temperature cycle experiments, where the maximum temperature was 350 °C, and the minimum 25 °C. Values are based on original weight.**

Zeolite sample	Coating	Average N ₂ gain (%)	Average N ₂ loss (%)
LTA 4Å	Neat (uncoated)	5.83 ± 0.55	5.85 ± 0.56
	SS	5.39 ± 0.48	5.43 ± 0.49
	TMCS	4.56 ± 0.39	4.59 ± 0.42
	Pyrene-Cl	9.01 ± 1.12	9.04 ± 1.14
LTA 5Å	Neat	4.72 ± 1.31	4.72 ± 1.32
	SS	4.83 ± 0.64	4.91 ± 0.69
	TMCS	5.01 ± 0.57	5.08 ± 0.62
	Pyrene-Cl	5.85 ± 1.04	5.93 ± 1.06
NS1	Neat	4.05 ± 0.25	4.07 ± 0.29
NS2	Neat	2.28 ± 0.22	2.30 ± 0.23

Fig. 4.3 Cycle experiment for zeolite LTA 4Å. The green curve is the neat sample, the blue is SS-coated sample, and the red is the TMCS-coated sample. Where the curves show a decrease in mass, the temperature is being increased to 350 °C; conversely, where the curve shows an increase, the temperature is being decreased to 25 °C.

Fig. 4.4 **Cartoon representation of the possible behaviour of the coating material, and the suspected ability to trap water or other solvent molecules (small blue spheres).**

Fig. 4.5 TGA plot of a cycle experiment with LTA 4Å (blue curve) and 5Å (red curve) with helium as the flow gas. The temperature range was from 25°C to 350°C. Weight loss denotes temperature increase; conversely, weight gain denotes temperature decrease.

2. Porosimetry

The natural, neat samples of NS1 and NS2 were subjected to porosimeter analysis to determine the available surface area and pore size and volume. The data for these samples is summarized in Table 4.5. MOR has reported² pore sizes of 6.5 x 7.0 Å and 2.6 x 5.7 Å, and it would be expected to see a value around these figures in the porosimeter analysis. The values calculated for the average adsorption and desorption pore diameters for NS1 are given as 213 and 68 Å respectively. Were this a sample of pure mordenite, it would be expected to see a value around that of the literature values, and even were there organic matter trapped in the zeolite structure, blocking pores and channels, one would expect a decrease in pore size. The pore volume of NS1 has been reported³ to be 0.26 cm³/g, whereas the experimental data reports a value of about 0.015 cm³/g. This decrease in pore volume would support the presence of organic impurities that might be present in the zeolite. Surface area calculations have given values of less than 20 m²/g, which is quite low, as molecular sieves with the same pore diameter have surface areas around and above 100 m²/g.⁴ The same argument can be made for the natural NS2 sample, where the calculated pore diameter is larger than the pore dimensions reported in the literature² (6.1 x 4.9 Å). Calculated pore volumes are also low, around 0.007 cm³/g. Surface area calculations give values less than 10 m²/g. These discrepancies could be attributed to mineral impurities, again, such as quartz, feldspar and mica, with the absence of internal porosity. These additional minerals might have undergone erosion to having “pits” form on the surfaces, perhaps giving inflated pore diameter readings.

Table 4.5 Porosimeter data for NS1 and NS2, showing calculated surface area, pore diameter and pore volume.

Measured Parameter	NS1	NS2
Single point surface area at P/P_0 (m^2/g) (± 0.05)	12.53	4.92
BET surface area (m^2/g) (± 0.05)	12.19	5.02
Langmuir surface area (m^2/g) (± 0.05)	18.02	7.20
BJH Adsorption Cumulative Surface Area of Pores (m^2/g) (± 0.05)	2.96	2.02
BJH Desorption Cumulative Surface Area of Pores (m^2/g) (± 0.05)	8.63	3.22
BJH Adsorption Cumulative Volume of Pores (cm^3/g) (± 0.05)	0.016	0.008
BJH Desorption Cumulative Volume of Pores (cm^3/g) (± 0.005)	0.015	0.007
BJH Adsorption Average Pore Diameter ($\text{\AA}$) (± 0.05)	212.99	156.81
BJH Desorption Average Pore Diameter ($\text{\AA}$) (± 0.05)	68.26	80.81
Horvath-Kawazoe Maximum Pore Volume (cm^3/g) (± 0.005)	0.006	0.002
Horvath-Kawazoe Median Pore Diameter ($\text{\AA}$) (± 0.05)	6.54	8.03
Time outgassed (days)	3	2.5
Temperature outgassed ($^{\circ}\text{C}$)	300	300

These minerals may also contribute to low surface areas, as only external surface does not provide much area for adsorption as would a zeolite that possesses both internal and external available surface. In addition to this, the pore sizes determined have no relation to the internal micropores of the minerals and are most likely related to the sample morphology.

3. *Powder X-Ray diffraction (PXRD) of the natural zeolite samples*

The use of PXRD allowed for powder patterns to be obtained for the natural zeolite samples. Direct comparison using the JCPDS database did not aid in the verification of the NS1 and NS2 samples. Fig. 4.6 shows the NS1 powder pattern compared to the JCPDS file, indicated by red, narrow lines superimposed on the raw data file. Comparing the ray pattern for NS1 to the JCPDS pattern for MOR, there seems to be no direct correlation of the peaks to be able to make a definite statement as to the identity of the natural sample as being MOR. Many impurities are present in the sample; however, sample purity was not assessed. A few peaks at low angle match up between the two patterns; however, this hardly constitutes a match. NS1 contains impurities, either of organic or inorganic nature. A search and match sequence was done to determine to which zeolite powder pattern NS1 most closely correlates; unfortunately, no match was found. The sample can be said to possess crystal character, as the peaks are sharp; hence, glassy, amorphous materials are not major constituents of the sample matrix.

Similarly, in the case of NS2, on being compared to the JCPDS pattern (Fig. 4.7), the same statements can be made as to the gross mis-matching between the raw and the database

patterns. In the case of NS2, there seems to be a closer overlapping of the peaks than in the former example, but again, no definite conclusion can be made as to the identity of the sample, as no JCPDS database patterns were able to match exactly.

Fig 4.6 PXRD pattern of NS1; JCPDS peaks are shown in red.

Fig 4.7 XRD pattern of NS2; JCPDS peaks are shown in red.

4. *Solid State Nuclear Magnetic Resonance (SS NMR) Spectroscopy*

This technique allowed observation of chemical environments of three distinct nuclei: ^{13}C , in coating material present on the zeolite surface; ^{29}Si , to attempt to determine sample purity and identity of NS1 and NS2; and ^{27}Al , to verify the coordination of Al nuclei in the NS1 and NS2 zeolite samples.

4.1 *^{13}C SS NMR spectroscopy of coated LTA 4Å*

Fig. 4.8 shows the ^{13}C SS MAS spectrum for LTA 4Å, surface modified with SS. Methyl carbons that are adjacent to silicon are characteristically shown to have a chemical shift at around 0 ppm; this spectrum confirms their presence. SS has only methyl carbons, so additional peaks should not be present in the spectrum. The large, broad peak that is observed is attributed to carbon signals in the polyethylene spinner assembly surrounding the sample. What is of interest here is the peak at the 0 ppm region, which confirms the presence of the coating material.

4.2 *^{29}Si SS NMR spectroscopy of the natural zeolite samples*

Solid-state NMR spectroscopy, specifically that of the ^{29}Si nucleus, was performed to determine the chemical environment of the Si in the NS1 and NS2 natural samples. ^{29}Si SS NMR can also be used as a zeolite identification tool. MOR and STI are shown, in the literature⁵, to possess three and four chemically inequivalent Si species with resonances at -100.1, -105.7 and -112.1 ppm (MOR); -98, -101.5 + -103.6 and -108 ppm (STI). These peaks correspond to the Si(2Al), Si(1Al) and Si(0Al) chemical environments, respectively.

Fig 4.8 ¹³C SS NMR spectrum of SS-coated zeolite LTA 4Å.

Fig 4.9 ²⁹Si SS NMR spectrum of NS1. Asterisks denote the peaks that closely match the literature values.

Fig 4.10 ²⁹Si SS NMR spectrum of NS2. Asterisks denote the peaks that closely match the literature values.

The spectra for NS1 (Fig. 4.9) and NS2 (Fig. 4.10) show that there exist, within the sample, all 5 chemical environments, represented by 6 peaks in both NS1 and NS2. The extra peaks suggest mineral impurities, and correlate with the same inference derived from the appearance of extra peaks that appear in the PXRD patterns. The evolution of a sixth peak in these cases does not imply a sixth chemical environment, but probably indicates a crystallographic inequivalence between chemically equivalent Si nuclei. This sixth peak can be assigned to a mineral impurity, as the Si-O-Al angle or bond length must be different from that which is present in the zeolite structure.

Employing the equation:

$$Si / Al = \sum_{n=0}^4 I_{Si(nAl)} / \sum_{n=0}^4 \frac{n}{4} I_{Si(nAl)}$$

the Si:Al ratio can be determined, which is characteristic of a particular zeolite structure. Using the peaks in the spectra that match most closely to those in the literature, the Si:Al ratios for NS1 and NS2 were calculated to be 1.94 and 2.26 respectively, compared to 4.4-5.5 (MOR) and 2.6 (STI). It is evident that the ^{29}Si NMR results of NS1 show even more disparity from those of the known values for MOR, and than those from PXRD. NS2 results show more similarity towards those of the STI values given; however, again, no significant match is found. Table 4.6 shows the peak values obtained for these minerals with the literature values, and the corresponding chemical environment for ^{29}Si .

Table 4.6 **²⁹Si experimental chemical shifts of NS1 and NS2 in comparison to the literature values. Chemical shifts are correct to within 10% error.**

Chemical Environment	<i>Experimental^a</i>	<i>Literature^b</i>	<i>Experimental^c</i>	<i>Literature^d</i>
Si(4Al)	-86.8		-85.2	
Si(3Al)	-92.3		-92.3	
Si(2Al)	-101.6	-100.1	-100.4	-98
Si(1Al)	-106.6	-105.7	-106	-101.5
	-107.6		-108.1	-103.6
Si(0Al)	-112.3	-112.1	-112.3	-108

^a Mordenite^b NS1^c Stilbite^d NS2

Fig 4.11 ^{27}Al SS NMR spectra of NS1 (top) and NS2 (bottom). Spinning sidebands are shown with asterisks.

4.3 *²⁷Al SS NMR spectroscopy of the natural zeolite samples*

²⁷Al SS NMR spectroscopy of NS1 and NS2 were performed to determine the chemical coordination of the Al nucleus in the zeolite structures. Both NS1 and NS2 give clean, simple spectra with one peak at approximately 50 ppm, the value that corresponds to tetrahedrally coordinated Al. NS1 is reported⁵ to have a ²⁷Al chemical shift at 55.8 ppm. No other environments for Al are present in the samples; that is, no octahedrally coordinated, or free aluminum is in the zeolite structure. Fig 4.11 shows the ²⁷Al spectra for NS1 and NS2; spinning sidebands are denoted with asterisks.

5. *Uptake experiments*

Duplicates of Linde 4Å and Linde 5Å of both the neat and coated samples were placed in sealed containers with one of three solvents: water (97% humidity maintained with a K₂SO₄ brine solution), methanol or ethanol. It was intended to observe the rate of uptake of these samples as well as to compare maximum uptake of solvent, by allowing the sample to become saturated by the solvent in its vapour phase. Figures 4.12 to 4.14 illustrate how the rate of uptake is similar for all samples in each solvent atmosphere, show overlapping regions of error, and all reach a plateau of uptake at 15 hours of exposure time. Again, this overlap, suggests that all the zeolites, coated and uncoated, exhibit the same amount of uptake capability in each of the solvent atmospheres. No real trend can be established as to pattern of uptake among the coated materials and the neat samples; however, it is observed that there is a larger uptake of water in comparison to that of methanol and ethanol

Fig. 4.12 Uptake experiments for LTA 4Å and LTA 5Å exposed to water at 97% humidity.

Fig. 4.13 Uptake experiments for LTA 4Å and LTA 5Å exposed to methanol.

Fig. 4.14 Uptake experiments for LTA 4Å and LTA 5Å exposed to ethanol.

respectively. Table 4.7 shows the average ratio of moles of solvent per unit cell of zeolite.

The unit cell for LTA is given as $\{\text{Na}_{12}[\text{Al}_{12}\text{Si}_{12}\text{O}_{48}] \cdot 27\text{H}_2\text{O}\}_8$, which gives a total of 216 water molecules per unit cell of zeolite. In the case of the water uptake experiments, the amount of water:zeolite ratio was below this number, in the area of 120-160 moles of water to zeolite, which indicates that there is the potential for more uptake if the samples were exposed to the solvent for a greater amount of time. Again, the trend of uptake from water to methanol to ethanol shows a decreasing ratio of solvent to zeolite. This observation can be explained by the simple fact that more water molecules are able to fit in the zeolite structure in contrast to methanol and even less so, ethanol.

The rate of uptake of water is faster than that of methanol and ethanol. Maxima in the water uptake cases are observed within a an hour, whereas the two latter solvents take longer times to reach the same. It could be reasoned that if given sufficient exposure times, all samples would reach the maximum of 20-25% gained mass.

Table 4.7 Ratio of moles of solvent per mole of zeolite LTA.

Zeolite Sample	Coating material	Solvent Atmosphere		
		H ₂ O	MeOH	EtOH
LTA 4Å	Neat	125.11 ± 10.03	36.56 ± 15.12	29.57 ± 5.25
	SS	157.70 ± 19.98	49.47 ± 15.09	29.12 ± 0.48
	TMCS	135.92 ± 0.75	53.05 ± 2.85	42.56 ± 2.46
	Pyrene-Cl	160.20 ± 0.40	37.52 ± 16.7	42.25 ± 5.53
LTA 5Å	Neat	119.87 ± 17.53	37.28 ± 2.53	27.38 ± 6.69
	SS	133.83 ± 8.61	57.56 ± 1.09	7.36 ± 8.10
	TMCS	127.63 ± 4.18	58.01 ± 5.65	11.49 ± 0.37
	Pyrene-Cl	108.47 ± 1.32	45.98 ± 0.01	11.93 ± 8.65

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Chapter V

Conclusions

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- 1. Concluding remarks V-2*
 - 2. Future work V-4*
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1. *Concluding remarks*

In general, the modification of the surfaces of LTA, NS1 and NS2 was successful. Preliminary tests of immersing the coated zeolite material into water, showed that the material floated and formed an aggregated mass on the surface of the water. Zeolite LTA has been known to uptake water, methanol and ethanol into its structure, and it was intended by modifying the zeolite surface to enhance its hydrophobicity. TGA analysis first showed that the modified as well as the neat zeolite samples showed the ability to uptake gaseous guests. Cycling experiments have shown that zeolites are robust to a cycling of temperatures, and show repeated uptake of flow gas without degradation to structure or loss of coating. Conclusions from these experiments are that no appreciable difference is noted between the coated and neat samples with respect to gas uptake. Subsequent uptake experiments with water, methanol and ethanol as solvents also did not show any appreciable difference in uptake in all samples, though it could be stated that within the time frame of the experiment, the samples showed preference in the following relationship: water > methanol > ethanol. The same relationship is also observed for the rate of uptake.

¹³C SS NMR of the SS-coated LTA 4Å sample, verified the presence of coating material in that a peak was observed at 0 ppm. TGA experiments were done to observe the burning off of the organic coating material by exposing the coated samples to temperatures up to 1000°C. Loss of mass was observed for the coated materials at temperatures ranging from 250-550°C.

There was quite the substantial uptake of helium by both the LTA 4Å and 5Å neat samples. Helium, a small atom, has unhindered access to the zeolite pores and channels. This allows for the continuation along that line of thought to perhaps attempt the same uptake experiment, but with hydrogen as the flow gas, to determine whether the uptake is even more substantial. This could prove to be very lucrative for hydrogen storage or fuel cell capabilities. Heating of the zeolite to release the gas does not have to exceed that of the boiling point of water to extract all gas from the sample, if this method of gas storage were to become commercialized.

The natural samples, NS1 and NS2 showed ease in instrumental analysis, but proved elusive when identification was attempted. ^{29}Si NMR showed that 5 different Si species were present in both cases. In comparison of the spectra to those in the literature, it was determined that impurities were present in the sample. Conversely, ^{27}Al NMR spectra for these samples were simple to analyze: all aluminum was tetrahedrally coordinated. PXRD patterns also showed evidence of impurities in the zeolite samples, and patterns obtained for this thesis could not be matched to any known zeolite powder pattern available in the JCPDS database.

The development of a very efficient and straightforward method to prepare a pyrene-1-(4-butyl-dimethylchlorosilyl) ether compound has been realized via simple protection using **TBDMS**, reduction with NaBH_4 , deprotection through the use of **TBAF**, and finally, the reaction with **DCDMS**. Purification and characterization is simple, and reaction conditions

are mild, while experimental yields are good.

2. *Future Work*

Future work in this area could entail studying the effect on a series of organosilane coating materials with varying length, or degree of branching of the organic moiety on the coating material. With varying the coating, a study of various sorbent molecules could also be completed, to determine whether there is a relation between coating chain length and size of sorbent molecule. In addition to covalently bonded coating materials, the area of cation-exchanged coating materials could be explored. Some ammonium-substituted compounds such as trimethyl- or triethylammonium come to mind.

Kinetic experiments would also prove interesting to observe the bending and flexing behaviour of the coating materials at various temperatures. This could easily be observed with hyperpolarized ^{129}Xe NMR spectroscopy.

***Appendix:
Additional Data***

Fig. A.1 ^1H NMR spectrum of PBA (1).

Fig. A.2 ^1H NMR spectrum of Pyrene-TBDMS (2).

Fig. A.3 ^1H NMR spectrum of Red-Pyrene-TBDMS (3).

Fig. A.4 ^1H NMR spectrum of Pyrene-But-OH (4).

Table A.1 PXRD data for MOR.

2 Theta	Intensity	h	k	l
6.446	50	1	1	0
9.711	90	2	0	0
13.384	90	1	1	1
13.869	40	1	3	0
14.509	50	0	2	1
15.290	50	3	1	0
17.618	10	2	2	1
18.201	20	1	3	1
19.580	80	3	3	0
21.446	30	4	2	0
22.206	90	1	5	0
23.143	60	2	4	1
23.643	20	0	0	2
24.571	10	1	1	2
24.992	10	5	1	0
25.576	100	2	0	2
26.267	90	3	5	0
26.914	10	2	2	2
27.681	100	5	1	1
28.775	20	4	4	1
30.314	20	5	3	1
30.850	60	3	3	2
32.618	10	1	5	2
33.152	30	1	7	1
33.941	10	3	7	0
35.022	40	4	6	1
35.567	50	4	4	2
36.418	20	6	4	1
36.852	20	7	1	1
38.387	20	2	8	1
39.151	10	6	2	2
39.581	10	5	7	0
40.452	20	4	8	0
41.744	20	1	9	1
42.548	10	7	1	2
44.209	40	3	9	1
44.855	40	3	5	3
45.353	40	8	4	1
46.458	40	6	8	0
46.890	10	1	9	2

47.383	20	4	8	2
48.293	40	0	0	4
48.789	10	4	10	0
49.211	10	1	11	0
50.284	30	4	10	1
50.824	30	1	11	1
51.751	10	2	10	2
52.616	10	10	2	1
53.210	20	9	3	2
53.955	10	8	8	0
54.370	20	5	7	3
55.114	20	4	8	3
55.768	10	3	5	4
56.705	20	9	7	1
57.675	30	4	12	0
59.767	20	6	10	2
60.588	30	6	4	4
61.434	10	11	1	2
62.165	5	0	2	5
62.821	10	9	9	1
64.426	30	1	9	4
65.390	20	12	4	1

Table A.2 PXRD data for STL.

2 Theta	Intensity	h	k	l
9.691	999	0	2	0
9.911	326	0	0	2
12.993	4	2	0	0
13.878	7	0	2	2
16.234	51	2	2	0
16.367	123	2	0	2
16.712	63	1	2	1
16.970	10	1		3
19.055	596	2	2	2
19.452	15	0	4	0
19.896	22	0	0	4
20.756	273	3	1	1
21.888	922	0	4	2
21.888		1	3	3
22.174	96	0	2	4
23.463	11	2	4	0
23.836	130	2	0	4
24.966	2	3	3	1
25.143	4	3	1	3
25.526	52	2	4	2
25.784	19	1	5	1
25.784		2	2	4
26.157	139	4	0	0
26.264	151	1	1	5
27.955	181	4	2	0
27.955		0	4	4
28.034	244	4	0	2
28.752	67	3	3	3
29.444	292	1	5	3
29.747	217	4	2	2
29.747		1	3	5
30.038	34	0	0	6
31.058	16	0	6	2
31.633	22	0	2	6
31.846	10	3	5	1
32.225	127	2	6	0
32.225		3	1	5
33.081	94	4	0	4
33.625	3	5	1	1

34.328	56	2	2	6
34.328		4	4	2
34.550	15	4	2	4
34.952	105	3	5	3
35.212	32	3	3	5
35.407	12	1	7	1
35.720	19	0	6	4
35.792	14	1	5	5
36.039	277	0	4	6
36.174	21	1	1	7
36.598	59	5	1	3
38.161	25	2	6	4
38.260	35	1	7	3
38.463	6	2	4	6
38.665	13	4	4	4
38.859	10	1	3	7
39.259	1	5	3	9
39.684	24	6	0	0
39.684		4	6	0
40.245	11	3	7	1
40.245		4	0	6
40.426	15	0	0	8
40.541	22	3	5	5
40.885	18	5	1	7
40.948	15	6	2	0
40.948		6	0	2
41.495	2	4	2	6
41.671	10	5	5	1
41.671		0	2	8
42.000	7	5	1	5
42.236	2	6	2	2
42.501	20	0	6	6
42.639	15	2	0	8
42.777	4	3	7	9
43.017	14	2	8	2
43.324	8	3	3	7
43.488	11	1	7	5
43.813	47	1	5	7
43.813		2	2	8
44.175	16	5	5	3

44.389	68	5	3	5
44.562	42	6	4	0
45.073	8	4	4	6
45.238	5	0	4	6
45.768	5	6	4	2
45.924	8	6	2	4
46.540	9	1	1	9
46.655	9	2	8	4
47.229	2	7	1	1
47.229		2	4	8
47.852	15	1	9	3
47.852		3	5	7
47.990	25	4	8	0
48.590	11	5	7	1
48.753	7	1	3	9
48.888	19	5	5	5
49.185	16	4	9	2
49.185		5	1	7
49.419	6	7	3	1
49.482	6	3	9	1
49.482		7	1	3
49.966	36	0	0	0
50.123	20	6	6	0
50.404	27	0	8	6
50.404		3	1	9
50.560	22	6	0	6
50.560	22	4	6	6
50.742	7	0	6	8
50.832	4	5	7	3
51.175	34	0	0	10
51.175		6	6	2
51.312	29	5	3	7
51.634	11	7	3	3
51.634	11	3	9	3
52.217	1	0	2	0
52.441	4	4	8	4
52.612	11	3	3	9
52.612		2	6	8
52.935	15	2	0	2
52.935		1	5	9

53.034	8	2	0	10
53.876	28	8	0	0
53.876		7	1	5
54.051	16	2	2	10
54.212	15	3	7	7
54.824	18	8	2	0
54.824		8	0	2
55.117	32	5	7	5
55.260	20	0	4	10
55.390	6	5	5	7
55.864	21	8	2	2
55.864		7	3	5
56.069	14	1	1	1
56.563	5	3	5	9
57.026	6	2	4	10
57.260	11	6	8	0
57.260		4	0	0
57.410	7	1	1	11
57.659	8	4	8	6
57.659		5	1	9
57.797	25	8	4	0
57.797		0	8	8
57.968	64	8	0	4
57.968	64	4	6	8
58.106	35	1	1	3
58.243	17	6	8	2
58.243		4	0	2
58.364	9	4	0	0
58.545	5	1	9	7
58.899	21	1	7	9
58.899	21	6	2	8
59.319	30	4	2	0
59.319		1	3	1
59.515	31	2	8	8
59.515	31	3	11	1
59.741	11	7	5	5
60.000	2	7	1	7
60.099	2	0	6	10
60.629	2	3	1	11
61.097	8	2	10	6

61.097		5	7	7
61.240	6	6	8	4
61.240		4	10	4
61.446	5	7	7	3
61.446		3	11	3
61.723	5	6	4	8
61.723	5	8	4	4
61.925	3	0	12	2
61.925	3	3	9	7
62.053	5	1	11	5
62.264	5	3	7	9
62.489	6	0	0	12
62.489		8	6	0
62.685	5	3	3	11
62.758	5	5	9	5
62.867	6	8	0	6
63.063	11	1	5	11
63.345	6	5	5	9
63.345		0	2	12
63.448	6	8	6	2
63.615	4	9	1	3
64.075	4	2	0	12
64.5	27	4	8	8
64.749	16	0	12	4
64.981	5	2	2	12
65.427	15	9	3	3
65.52	15	7	5	7
65.618	11	6	10	0
66.141	8	5	11	1
66.141		0	10	8
66.309	10	3	5	11
66.309	10	2	12	4
66.553	8	0	8	10
66.553	8	6	10	2
66.64	5	6	0	10
66.64		4	6	10
66.818	3	7	9	1
67.235	6	1	13	1
67.427	10	4	12	0
67.427	10	9	1	5

Fig. A.6 Weight loss experiment TGA plot for LTA 4Å exposed to water vapour.

Fig. A.7 Weight loss experiment TGA plot for LTA 4Å exposed to methanol.

Fig. A.8 Weight loss experiment TGA plot for LTA 4Å exposed to ethanol.

Fig. A.9 **Temperature cycle experiment TGA plot for LTA 5Å.**

Fig. A.10 Temperature cycle experiment TGA plot for LTA 4Å and 5Å, coated with Pyrene-Cl.

Fig. A.11 Temperature cycle experiment TGA plot for MOR.

Fig. A.12 Temperature cycle experiment TGA plot for STL.

Fig. A.13 Weight loss experiment TGA plot for 4Å, where the final temperature was 1000°C, under oxygen flow.

Fig. A.14 Weight loss experiment TGA plot for 5Å, where the final temperature was 1000°C, under oxygen flow.

Fig. A.15 Weight loss experiment TGA plot for MOR, where the final temperature was 1000°C, under oxygen flow.

Fig. A.16 Weight loss experiment TGA plot for STI, where the final temperature was 1000°C, under oxygen flow.