

Zeolite Frameworks With β -cages



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Doctor of Philosophy

Michaelmas 2015

This thesis is dedicated to my family, especially
my father, Leung Lem Chung, and my mother, Tong Oi Yin.
Although they are 9692 kilometers away, I will never forget their
words of encouragement. More importantly, as a self-funded student,
without their financial support, I will not be able to finish my degree.
I am also thankful that my auntie, Tong Hau Yin, and my brother,
Leung Ka Man, have never left my side and are very helpful.

Acknowledgements

Firstly, I would like to express my sincere gratitude to my supervisor, Dr. Asel Sartbaeva, for the continuous support of my DPhil study, for her patience, encouragement, and inspirations. Her guidance helped me in all the time of research and writing of this thesis. I will always remember those days when we work together in the laboratory, and it is my honour to be her first Ph.D student.

I would also like to thank Prof. Peter P. Edwards for all his helpful advices and support, especially in the last two years of my study.

Beside my supervisors, my sincere thanks goes to: Dr. Stephen A. Wells, who taught me the geometric simulation in my research, and is a magician who made everything so easy to understand for a non-physicist; Dr. Matt Tucker, who works in ISIS and helped with the set up, data collection and analysis of the high pressure experiments in my research; Dr. David C. Apperley and his colleagues of the EPSRC National Solid-state NMR Service who collect all the NMR data in this research and his professional comments on the NMR spectra.

Abstract

This study focuses on five zeolites: sodalite, zeolite A, linde type N, zeolite Y, and EMC-2, with SOD, LTA, LTN, FAU, and EMT framework topologies respectively. All of these zeolites have β -cages as the framework building units. The aims are to understand the conditions which control the formation of different zeolite phases and some of the physical properties of zeolite frameworks, mainly the framework flexibility, and the capacity of β -cage to accommodate guest molecules such as water and methanol.

The hydrothermal and microwave syntheses of zeolite with no organic structure directing agents require precise control of synthesis conditions and form the fundamental part of this study. Reaction temperature and synthesis time control the phase purity in zeolite A synthesis. A transformation from zeolite A to sodalite is observed and is related to framework density and reaction temperatures. Microwave syntheses of sodalite show that the batch compositions and methods of preparation also affect the as-synthesised zeolite phases and a new sodalite morphology is found. By using microwaves instead of traditional hydrothermal methods, one of the most complex zeolites, linde type N zeolite, was synthesised. This is the

first study to report this new method.

The newly defined extrinsic flexibility window is studied on more depth in this work. While the intrinsic flexibility is defined by the ability of an empty framework to flex with no distortions in the primary tetrahedral building units; the extrinsic flexibility window is limited by the host–guest steric interactions between the framework and the extra framework contents. In zeolite Y, the extrinsic flexibility window can be limited not only under compression, but also in expansion, as the β -cage in a maximally expanded framework lack the flexibility to adapt to bulky contents such as a combination of methanol and water molecules. It is also found that the β -cage in zeolite Y can only accommodate a maximum number of two water molecules and one methanol molecule.

The same phenomenon is observed in sodalite under compression. In the sodium form, the framework remains within its intrinsic flexibility window when fluorinert is used as pressure transmitting media, as fluorinert does not enter the zeolite pores. However, an extrinsic flexibility window is observed in both the sodium and sodium bromide forms with methanol/ethanol/water mixture as pressure transmitting media.

An exception is seen in EMC-2. The intrinsic and extrinsic flexibility windows are identical to each other. The presence of 18-crown-6 ether molecules in the pores does not affect the flexibility window. The crown ether, despite its steric bulk, does not limit the geometric flexibility of

the framework since the cage of the EMT framework has enough space to accommodate the crown ether molecule and can adapt to the contraction. This shows that the extrinsic flexibility window of zeolite frameworks is controlled not only by the extra framework contents, but also by the framework building units.

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Chapter 1

Introduction

1.1 What is a zeolite

The term “Zeolite” was coined in 1756 by the Swedish mineralogist, Axel Fredrik Cronstedt [1]. When he heated a material (later known as Stilbite) with a blowpipe frame, it produced a large amount of steam. He therefore called this mineral “Zeolite” which means “boiling stone”. Since then, more naturally occurring zeolites have been discovered and put to different uses. However, since naturally occurring zeolites are rarely phase-pure and are contaminated by other minerals, scientists have been spending decades trying to synthesise and tailor them for specific applications [2].

Zeolites are crystalline aluminosilicates with meso- or micropores inside their framework structures [3–5]. They have highly crystalline three dimensional frameworks formed by the corner-sharing of the oxygen atoms of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra, which are the primary building units of most zeolites [5–8]. The difference in valence between Si and Al atoms is charge balanced by alkali metal cations such as sodium. The general formula of a zeolite is shown in 1.1 on the following page, where n is the valency of the metal ion M which balance the negative charges in the

aluminosilicate framework. The numbers x and y depend on the framework being described, for example, the sodium form of zeolite A has $x = y = 12$ in 1 : 1 ratio. The combination of intricate cages, pores and channels of various sizes produces open frameworks with complex structures. Although the arrangement of tetrahedra can produce numerous possible frameworks (there are millions of hypothetical frameworks in theory), only a very small number of these possible frameworks exist [9]. At the time of writing this thesis, 229 zeolites can be synthesised in the laboratory, out of which about 40 are naturally occurring [5].

$$M_{x/n} \left((AlO_2)_x (SiO_2)_y \right) \cdot mH_2O \quad (1.1)$$

Zeolite formation involves several steps from a solution, to a gel, and finally, the crystalline product [10]. In a typical sol-gel synthesis, a silica source and an alumina source are mixed with the source of cation and sodium hydroxide. The hydroxide provides the necessary alkaline condition, at $pH > 10$, for the hydrolysis of starting materials. At the point when these materials are mixed together, a primary amorphous phase is formed. It can either be a visible gel or a transparent colloidal solution. This primary amorphous phase is in a non-equilibrium state, and contains unreacted materials as well as amorphous aluminosilicates. When such a mixture is treated to a certain temperature, the reaction reaches equilibrium. Reactants continuously go through hydrolysis and condensation and are converted into a secondary amorphous phase. A characteristic distribution of silicate and aluminosilicate anions is established and maintained. Although the secondary amorphous phase does not contain any periodic lattice which is essential to the formation of a crystalline zeo-

lite phase, there is an increase of structural ordering by continuous dissolution and reconstruction. The oxygen linkage of the framework is also formed at this point. Given sufficient time, nucleation occurs, and once the nuclei grow to a critical size, crystal growth can begin by propagation of periodical building units. Over time, a crystalline zeolite structure is formed.

Zeolite synthesis requires precise control of various parameters [11, 12]. The preparation can be sometimes very delicate. The choice of starting materials can affect the as-synthesised zeolite phase due to the solubility and the specific surface area of the particles [13, 14]. The use of different cations and anions, the so-called ‘mineralizer’, also plays an important role. Majority of zeolite syntheses use sodium hydroxide to create the necessary alkaline condition, but solutions containing fluoride ions or phosphate ions can also be used [15, 16], and for some zeolite frameworks, the use of cations other than sodium can achieve a better result [17, 18]. Organic structure directing agents can be added to the reaction to achieve a pure zeolite phase, but the removal of the organic template after synthesis is a time consuming process, and may release other toxic chemicals. For example, the removal of tetramethylammonium ions for zeolite A synthesis would produce toxic ammonia gas. Aging, seeding, stirring or static conditions during gel preparations are known to affect zeolite synthesis [19, 20]. The reaction temperature and synthesis time are considered to be the most important factors. For zeolite frameworks with a higher density, a higher reaction temperature and longer synthesis time is usually required [21]. Different crystallisation methods may also affect the final zeolite phase. The hydrothermal method is common for zeolite synthesis, and it has been used for several decades. However, the

microwave method has become more and more popular in the last 20 years.

One of the most significant improvements of synthesising zeolite materials using microwave energy is the reduction of reaction times by up to over an order of magnitude [22–24]. From an industrial and commercial points of view, less energy is involved in the production, thus reduces cost and the amount of fuel being used. Continuous production would be possible instead of batch synthesis, and improves the efficiency of mass production. More uniform crystals with less defects can also be synthesized using microwave energy which increase the performance of zeolite as catalyst. Although many experiments have been done to show that using microwave energy can result in dramatic decrease in reaction time, the mechanism and engineering for the enhanced rate of syntheses are still unknown. Several hypotheses suggested that microwave energy may affect the dissolution of precursors, and increase the heating rate of the synthesis mixture with a more uniform heating [25]. It is shown in the study by Conner et al. [26] and Panzarella et al. [27] that microwave irradiation causes rapid nucleation in the precursor gel, therefore reduces the induction period during zeolite formation. The microwave energy distribution is suggested to affect the nucleation rate and depends on various factors such as vessel size, precursor volume, and irradiation method of microwave energy. Vessel with wider diameter cause uneven distribution of electric field with local hot spots being observed which enhanced dissolution, and bigger crystals were synthesised. Increase in precursor volume led to slower synthesis. Microwave reactor with multi-mode irradiation reduced the induction time compared to mono-mode irradiation. However, the enhance in rate of synthesis cannot be merely explain by one factor such as the

variation in microwave electric field, since different reactants, intermediate species, and solid response differently to microwave [27]. The effect of silica precursor, reaction temperature distribution, and other factors should also be considered [28, 29].

Zeolites are widely used in industry due to their porous framework structure, diverse and highly selective catalytic and ion exchange properties [30–32]. They are particularly valuable materials in the petroleum industry. For example, millions of tonnes of zeolite Y is used in petroleum refinery catalytic cracking to increase the yield of gasoline and diesel fuel from crude oil. The different shapes and sizes of cavities, pores, and channels of zeolite frameworks only allow molecules of a certain size to access their interior, and thus provide size and shape selectivity for catalytic reactions, as well as industrial gas separations [33, 34]. The high internal surface area of zeolite allows them to accommodate a large number of active sites including the Brønsted acid sites and Lewis acid sites [35, 36]. The Brønsted acid sites are bridged hydroxyl groups, SiO(H)Al , with protons directly bonded to framework oxygen ions, and act as a proton donor. One of the applications of Brønsted acidity is the methanol–olefin conversion using zeolites with CHA framework typology, such as chabazite [37, 38]. The Lewis acid sites are electron-pair acceptors, which are three-coordinated aluminium ion in zeolite framework [39]. They can form bonds with lone pair electrons of oxygen or nitrogen atoms of guest molecules. The high internal surface area of zeolite also means that a large amount of substance can be adsorbed. Different zeolites have affinities for different types of molecule. Zeolites with a very high Si:Al ratio favour the absorption of non-polar molecules such as hydrocarbons which can make catalytic cracking processes more efficient.

The cations associated with the hydrated zeolite framework can be exchanged with other cations in the surrounding solution. The major applications of zeolites as ion-exchangers are the removal of heavy metal ions or radioactive elements in contaminated water [40]. Other common applications using the ion-exchange property of zeolites include detergent builders in washing powder, and water softener [41, 42]. Zeolites are also good drying agents. They can be heated under vacuum to remove water inside the framework and once exposed to ambient condition, absorb water and return to their hydrated form. The potential applications of zeolites are unlimited. Most recently, they are being investigated for drug delivery in medicine [43].

One of the main focuses in this study is the behavior of zeolite frameworks under pressure. Since the framework oxygen bridges between tetrahedral units are not rigid, majority of zeolite frameworks show some degree of flexibility [6]. The range of densities over which the tetrahedral units in the framework can in principle be made geometrically ideal is defined as the flexibility window. In theory, the arrangement of tetrahedral units can produce numerous possible frameworks, but yet only 229 frameworks can be synthesised. There are several criteria to determine whether a hypothetical zeolite can be selected as synthetic targets. It is suggested that the flexibility window is one of the necessary structural features for such selection [6, 44]. It is also important to understand the structural change of zeolite framework under pressure, since zeolite applications are not limited to ambient conditions. Zeolite under pressure has already shown several interesting properties such as change in ionic conductivity, pressure-induced over-hydration, and volume expansion [45]. However, zeolite frameworks eventually become amorphous if excess pressure is applied [46].

Such amorphization reduces the size and volume of the pores and channels of the zeolite framework, thus affects the catalytic, ion exchange, and separation properties of zeolite in industrial applications.

1.2 β -cage as a building unit

Among all the different types of zeolite frameworks, I focused my research on those which are made of sodalite cages, also known as β -cages. They are built by two secondary building units (SBUs) - every cage is formed by connecting eight 6-membered rings (6T atoms) and six 4-membered rings (4T atoms), assembled as a truncated octahedron. The zeolites in this study are zeolite A, sodalite, Linde Type N, zeolite Y, and EMC-2, which have the LTA, SOD, LTN, FAU, and EMT framework topology respectively. The three letter code is assigned by the Structure Commission of the International Zeolite Association. It refers to the way in which the tetrahedral units are interconnected, irrespective to its composition, symmetry or physiochemical properties. Each framework topology can include several framework materials, and it is not limited to aluminosilicates. For example, the topology FAU, which is found in natural occurring faujasite, includes the synthetic zeolite X and Y, as well as the silicoaluminophosphate material SAPO-37.

Figure 1.1 on the next page shows the zeolite framework topologies being studied, and their respective building units. Table 1.1 on the following page gives more information about each of the topologies including the corresponding zeolite, the unit cell geometry, the building unit(s) involved, and the density. The frameworks in figure 1.1 can be divided into three categories: (1) SOD and LTA frameworks (figure 1.1(a))

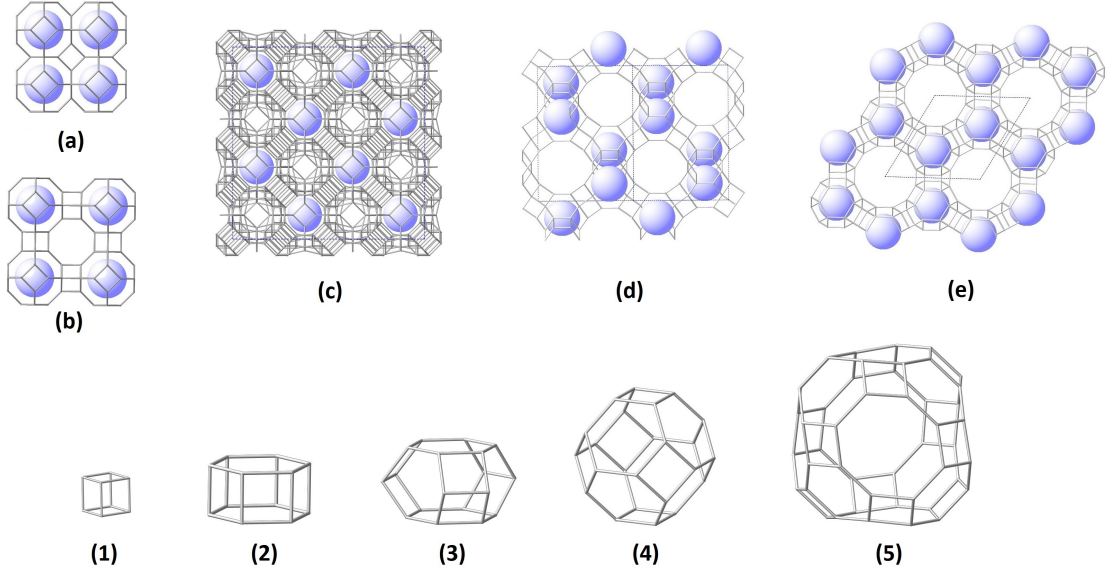


Figure 1.1: Framework topologies and building units. Framework topology: a) SOD, b) LTA, c) LTN, d) FAU, and e) EMT. Building unit: (1) Double 4-ring (D4R), (2) Double 6-ring (D6R), (3) *can*-cage, (4) β -cage, and (5) distorted α -cage. Blue transparent spheres are included to show where β -cages are located in the frameworks.

Table 1.1: Frameworks and the corresponding zeolites in this study.

Framework topology	Zeolite	Unit cell	Building unit(s)	Density (T/nm ³) ¹
SOD	Sodalite	Cubic	(4)	16.7
LTA	Zeolite A	Cubic	(1), (4)	14.2
LTN	Linde Type N	Cubic	(2), (3), (4), (5)	17.0
FAU	Zeolite Y	Cubic	(2), (4)	13.3
EMT	EMC-2	Hexagonal	(2), (4)	13.3

¹ Number of tetrahedral units per nm³

and (b)), (2) LTN framework (figure 1.1(c)), (3) FAU and EMT framework (figure 1.1(d) and (e)).

SOD and LTA frameworks both have a cubic unit cell. The SOD framework is the least complex among the five being shown in figure 1.1. It is formed by stacking the β -cage on top of each other through the 4-rings with no space in between. It has a 0-dimensional channel system, meaning that the framework is relatively dense. The

LTA framework is also formed by stacking the β -cages, however cages are connected by an extra building unit, the D4R unit. This creates the α -cavity, also known as LTA-cage, with an 8-ring opening, which is similar to the one shown in figure 1.1(5), but not distorted. A 3-dimensional channel system is formed when the α -cavities are connected to each other. This makes the LTA framework useful in term of ion-exchange properties since ions can easily access the relatively big α -cages from all three directions [47].

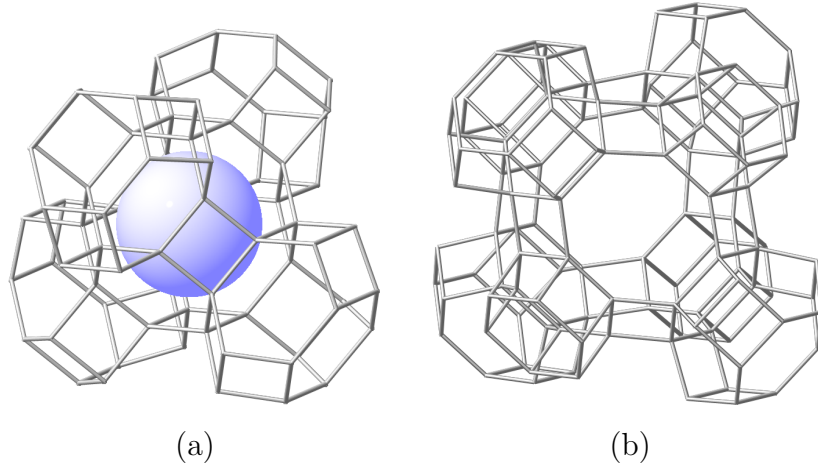


Figure 1.2: Periodic building units of LTN framework. (a) BU1 consists of a β -cage and four *can*-cages, and (b) BU2 has a distorted α -cavity connected to four *can*-cages and four D6R units. The blue sphere in BU1 shows the position of the β -cage.

The LTN framework, compared to the SOD and LTA frameworks, has a more complex structure. Its unit cell is about four times bigger than the SOD framework and three times to the LTA framework. It is also the densest framework among the five in this study. Two periodic building units (PerBUs) are present in the structure, as shown in figure 1.2. BU1 is formed by connecting a β -cage to four *can*-cages through the 6-ring, as shown in figure 1.2(a). The second building unit, BU2, consists of a distorted α -cavity connected to four *can*-cages and four D6R units. These two

building units are then arranged in a repeated pattern to form the complicated LTN framework. Although the framework does not form any channel system, the zeolite can be used as a desiccant for oxygen and nitrogen streams due to the fact that it only absorbs water.

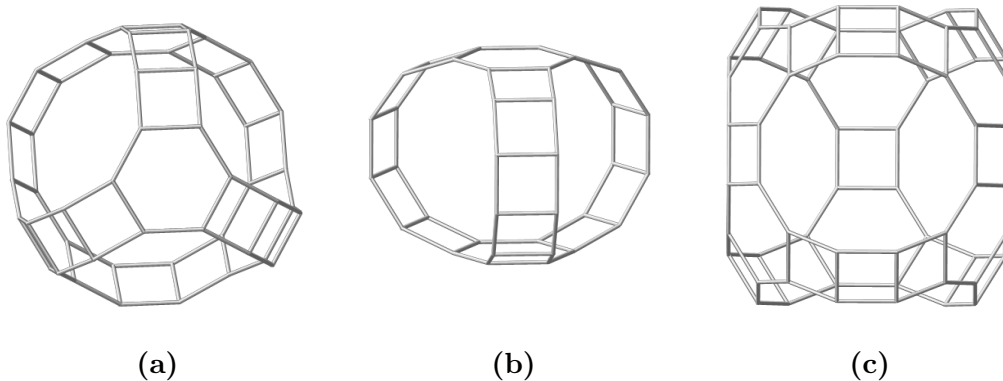


Figure 1.3: Supercages present in FAU and EMT frameworks form by 12-ring windows of the faujasite layer. (a) 12^4 supercage of FAU framework, (b) 12^3 supercage of EMT framework, and (c) 12^5 supercage of EMT framework. The superscript represents the number of 12-ring which forms the supercage. For example, 12^4 supercage has four 12-rings as building unit.

Both FAU and EMT frameworks are formed by stacking the β -cages and D6R units which come together in a hexagonal array to form a two-dimensional PerBU, the faujasite layer. Within the layer PerBU, β -cages are connected to each other through D6R units. It is the variation in stacking of these faujasite layers that affords two distinct framework types with different symmetry [48, 49]. The cubic FAU framework arises from an ABC stacking sequence, each faujasite layer is rotated by 60° and each β -cage related to its partner by an inversion centre. The ABA stacking of faujasite sheets affords the hexagonal EMT type framework, with pairs of β -cages related to each other through a mirror plane. One characteristic feature of the faujasite layer is the presence of 12-ring windows. The relative orientations of 12-ring windows give rise to the formation of supercages with different geometry.

The cubic FAU framework contains four 12^4 supercages within its unit cell, referred to as the *t-fau* cavity, whereas EMT contains two different supercages; one smaller 12^3 supercage termed the *t-wof* cavity, and one larger 12^5 , known as the *t-wou* cavity [48]. The geometry of the corresponding supercages is shown in figure 1.3.

1.3 Literature review

1.3.1 Sodalite

Sodalite is a naturally occurring zeolite which can also be synthesised in the laboratory, either with no organic template or with inorganic anion template. The first reported sodalite synthesis without using organic template was reported by Robert Milton [50] in 1949 when he was working in the Linde's research facilities aiming to synthesise chabazite. It was regarded as a hydroxy form of sodalite since only sodium hydroxide was used in the synthesis. The absence of the 3D channel system in sodalite means that it has no known catalytic properties. It is useful in the ceramic industry as a glaze, or is used as a silica/alumina source [51]. In the early 90s, Stein et al. [52, 53] reported that sodalite can be synthesised using different halogen anions. Although the sodium bromide (NaBr) form of sodalite can be easily synthesised, the huge bromide anions occupy majority of the space inside the β -cages making it not suitable for any gas adsorption or ion exchange application.

Some more applications were found during the 90s which includes the patent registered by Tadafumi Koyama [54]. It involves the use of a sodium intermediate to immobilize waste chloride salt containing radioactive nuclei. The sodium intermediate will then be converted to sodalite and the radioactive nuclei trapped within the β -

cage.

Millimeter-sized sodalite single crystal has been synthesised by Shiraki et al. [55] in 2001. In the 20th century, scientists are still trying to make sodalite using different precursors and find new applications [56]. A hydrothermal synthesis and a microwave synthesis are given below as examples.

Fan et al. [57] synthesised sodalite nanocrystals hydrothermally without organic structure directing agent (OSDA). By carefully controlling the ratio of SiO_2 : Al_2O_3 : Na_2O : H_2O , as well as the reaction time and temperature, Fan et al. successfully synthesised hydroxy-sodalite crystals of 20 - 40 nm. During the synthesis of hydroxy-sodalite, they reported from the observed powder pattern that a zeolite A phase is formed before the sodalite phase, which indicated a transformation of zeolite A into sodalite. They also reported that the final product was affected by the order of mixing of the Al and Si source during gel preparation.

In another study, Julbe et al. [58] used a microwave method to synthesise sodalite on an alpha Al_2O_3 membrane without SDAs. They used gel composition 5SiO_2 : $1\text{Al}_2\text{O}_3$: $38\text{Na}_2\text{O}$: $1000\text{H}_2\text{O}$. By changing the reaction temperature and time, sodalite with different size and morphology was successfully synthesised. They concluded that by carefully controlling the synthesis parameters, microwave synthesis can be used to synthesis sodalite with desired size.

1.3.2 Zeolite A

There is no naturally occurring zeolite A. Like sodalite, zeolite A was also first synthesized in 1949 by Robert Milton [50]. No template reagent was used and a mixture

with zeolite X impurity was obtained. 10 years later, in 1959, the synthesis of zeolite A was patented [59]. In 1961, Barrer et al. [60] and Kerr et al. [61, 62] proposed the use of quaternary ammonium cations (tetramethylammonium cations) to synthesise zeolite A. Kerr et al. in addition synthesised the silica-rich version of zeolite A, which was named ZK-4. Since then, studies on zeolite A are mainly about the effect of synthesis conditions towards the final zeolite phase, and some examples are given below.

Bayati et al. [63] synthesised zeolite A hydrothermally using different $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios and different reaction time and temperatures. They characterised the as-synthesised zeolite A using X-ray powder diffraction (XRPD) and scanning electron microscopy (SEM). Their results show that by increasing reaction temperature, both particle size and crystallinity of zeolite A increase dramatically. They proposed the optimum temperature range to synthesise cubic zeolite A crystals with particle size of $2\mu\text{m}$ is between 60°C and 90°C , with a maximum reaction time of 24 hours, and a gel composition of $10\text{SiO}_2:1\text{Al}_2\text{O}_3:50\text{Na}_2\text{O}:1000\text{H}_2\text{O}$. They observed that sodalite was formed instead of zeolite A when a gel with low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio was used. Therefore, they concluded that $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is also an important factor to control the phase behaviour and morphology of zeolite A.

Proverbio et al. [64] synthesised zeolite A using a household type microwave without OSDAs. They fixed the molar ratio of the gel to $2\text{Na}_2\text{O}:1\text{Al}_2\text{O}_3:1.9\text{SiO}_2:65\text{H}_2\text{O}$, and used a multiple-step microwave synthesis method. They found that not only the power of the microwave, but also gel quantity affected the synthesis of zeolite A, and demonstrated that they can synthesise zeolite A in a total processing

time of 1 hour, thus concluding that microwave methodology was faster compared to hydrothermal synthesis. However, most of their zeolite A phase was contaminated by hydroxy-sodalite. They further commented on the microwave method that during the short heating time, a lack of nuclei formation occurred in the gel, therefore, a low crystal yield and formation of impurities was observed. Long aging time and adequate stirring are required for microwave methods, so the increase in speed of zeolite crystallization using microwave methods may not be that advantageous.

1.3.3 Linde Type N

Linde Type N is another synthetic zeolite. There are not many reports about this zeolite in the literature. The first Linde Type N hydrothermal synthesis was reported by Acara et al. [65] in a patent in 1968 using tetramethyl ammonium cations as an OSDA. They mentioned in this patent several conditions which favored the formation of Linde Type N. It tends to form with no aging of the resulting gel, under dynamic conditions (stirring/shaking) during an agitation step, and at optimum temperature for crystallisation between 90 °C and 100 °C. Static conditions produce zeolite A. Since activated Linde Type N does not adsorb oxygen or nitrogen but only water, it is suggested that the zeolite can act as a desiccant for oxygen and nitrogen streams. In 1971, Duecker et al. [66] in a patent mentioned an OSDA free synthesis of a zeolite named “Z-21”, which has the same framework structure as Linde Type N. Zeolite Z-21 is a large pore zeolite with a pore diameter of about 17 Å, and it is suggested it can function as a carrier for a wide variety of chemical compounds. It was not until 1982 that the crystal structure of Linde Type N was solved by Färlth et al. [67].

Recently I described a new microwave method to synthesise Linde Type N zeolite [68].

1.3.4 Zeolite Y

Zeolite Y, and its counterpart, zeolite X, are both synthetic forms of the naturally occurring faujasite. Zeolite X was first synthesised as an impurity by Robert Milton when he attempted to synthesise zeolite A in 1949. The pure form was isolated a year after, in 1950. The main difference between zeolite Y and zeolite X is the Si/Al ratio; it is above 3 for zeolite Y, and between 2 and 3 for zeolite X [69, 70]. Although zeolite X has higher Al content and thus more exchangeable cationic sites than zeolite Y, it is mainly used for CO₂ adsorption and gas separation [71]. The stability of zeolite Y is due to its relatively high Si content and the appropriate pore diameter makes it extremely useful in petroleum industry for catalytic cracking - breaking the long chain carbons in crude oil to smaller chains used in gasoline, diesel, etc. [72]. Zeolite Y can also be exchanged with various rare-earth metals after dealumination to increase the catalytic properties [73–75].

The earliest publications regarding zeolite Y structure were in the 1970s. Gallezot *et al.* [76, 77] reported three partially decationised, and two protonated, cerium exchanged zeolite Y structures using XRPD in 1971. In 1974, two more zeolite Y structures were reported by Gallezot *et al.*, the dealuminated form and the CO₂ exchanged form [78, 79]. In the following decades, the structure of zeolite Y has been thoroughly studied. One of the more remarkable structural characterizations was done and published by Su *et al.* in 2012 [80]. They synthesised single sodium zeolite

Y crystals, and saturated the framework with sodium ions by stirring with a sodium chloride solution. The crystals were dehydrated and characterised by X-ray single crystal diffraction. Su et al. were able to identify the framework silicon, aluminium and oxygen sites, as well as the five other extra-framework sites partially occupied by sodium ions.

Siliceous zeolite Y under pressure was studied by Colligan et al. in 2004 [81]. They collected high pressure data using two different pressure transmitting media – methanol/ethanol/water mixture (penetrating pressure transmitting medium) and silicon oil (non penetrating pressure transmitting medium). Rietveld refinement of synchrotron powder patterns was performed using the siliceous zeolite Y data with methanol/ethanol/water mixture from ambient pressure to 7.9 GPa. Although the zeolite had no extra-framework content, pore filling was observed as a function of pressure up to 4 GPa. Above 4 GPa, the framework became distorted with more extra-framework sites being refined. Although Colligan et al. was able to refine the atom coordinates of framework sites, the shape and size of molecules which entered the zeolite and occupied the extra framework sites were not identified. The pore filling was not observed when silicone oil was used as pressure transmitting medium.

1.3.5 EMC-2

EMC-2 is the only zeolite with EMT framework topology, which is a hexagonal polymorph of FAU framework, and can only be synthesised in the laboratory. It was first observed in 1970s as an intergrowth phase with FAU framework. The pure form of this zeolite was synthesised in 1990 by Delprato et al. [82] using the OSDA 18-crown-

6 ether. Since then, more successful syntheses using crown ether were reported in the literature [83–86]. In 2012, Ng et al. [87] synthesised EMC-2 nano-crystals using an organic-template-free system at low temperature. In 2015, Mou et al. [88] reported a seed-directing method from an organic-template-free system to synthesise EMC-2 crystal with size of several μm .

The first structural study of EMC-2 was done by Baerlocher et al. in 1994 [48]. In this study, X-ray powder patterns were collected on both partially dehydrated and calcined EMC-2 samples. Structural refinement was performed on the two sets of data to compare the positions of framework atoms. The Rietveld refinement result showed there was no crown ether molecule inside the β -cage, but there was evidence that the 18-crown-6 occupied the larger cages of the framework.

1.4 The flexibility window in zeolites

According to Sartbaeva et al. [6], the flexibility window is defined as the range of densities over which the tetrahedral units in the framework can in principle be made geometrically ideal. In their 2006 publication, a full study of the flexibility window of faujasite using geometric simulation was given as an example. A set of cubic zeolite frameworks was then modelled as the pure silica form, and they showed that all these frameworks possess a flexibility window. Moreover, the majority of zeolite frameworks under ambient conditions would prefer to be maximumly extended, which sat close to the low density end of the flexibility window. This can be explained by the Coulomb repulsion between co-dimeric oxygen atoms - the most extended form minimizes such repulsion and avoids steric clashes.

Another study reported by Sartbaeva et al. [7] applied the theory of flexibility windows to explain the pressure-induced phase transition of analcime. Such transitions happened under pressure at around 1 GPa from a high-symmetry cubic form to a low-symmetry triclinic form, without going through any intermediate-symmetry form. Geometric simulation was done using a pure-silica cubic ANA framework to compare with the experimental data. It was found that the experimental cell parameters were within the simulated flexibility window, and the ambient framework lay slightly inside the low-density edge of the window. However, at the high-density edge, the framework was no longer ideal with even a small change of the cell parameter. Two more distortions were then introduced to the ANA framework - the orthorhombic and trigonal distortion. These intermediate-symmetry forms showed limited flexibility, and there was no space at the edge of the window for the cell to compress. This would explain the fact that no intermediate forms were observed between the cubic and triclinic phase transition. At the higher-density end, the cubic framework attempted to remain within its flexibility window and a triclinic distortion was the only option. Similar behaviour is seen in leucite, pollucite and wairakite [89, 90].

Geometric simulation can also be used to study the response of framework structure to different types of pressure media. In another study reported by Sartbaeva et al. [44], a high silica zeolite, Silicalite-1, was being studied. Silicalite-1 has MFI framework topology and exists in a monoclinic form under ambient condition, but became orthorhombic, then metrically tetragonal under pressure. High pressure structural experiments were done on synthetic silicalite-1 using two different pressure mediums. Silicone oil was used as a non-penetrating pressure transmitting media while carbon

dioxide and argon were used as penetrating pressure media. Geometric simulation was then performed to see if the experimental results can be explained using the flexibility window theory. It was found that with a non-penetrating pressure transmitting medium, the structure was relaxable and remained in the flexibility window through the monoclinic to orthorhombic phase transition, as well as the pressure induced amorphisation. Further compression would lead to the structure being forced out of the flexibility window. However, with a penetrating pressure medium, the framework remains crystalline through a wide pressure range, and eventually cannot stay within the flexibility window as it is stressed.

Chapter 2

Characterization techniques

2.1 X ray powder diffraction

Zeolites are polycrystalline framework materials. For such materials usually synthesised in a powder form, X-ray powder diffraction (XRPD) is a powerful technique to identify the as-synthesised zeolite phase. The powder pattern of an as-synthesised zeolite once obtained can be compared to the simulated models from the “Database of Zeolite Structures” to confirm its identity, if the desired zeolite phase is known from the synthesis. For high resolution powder patterns, Rietveld refinement can be done to get more information such as the position of extra-framework contents, and the location of template molecules. However, XRPD only gives an average structure for the sample being characterized; the presence of defects or the ordering of Si and Al tetrahedra cannot be identified using XRPD.

Diffraction occurs when X-rays are scattered by a periodic array with long-range order. Crystals are built up from regularly repeating structural building units, which can be atoms, molecules or groups of atoms and molecules. To simplify a crystal structure, the locations of identical repeating environments are specified by lattice

points. These lattice points are joined together in three dimensions to form a “unit cell”, which is the the smallest volume portion of the highest symmetry in a crystal. In 3-dimensions, the unit cell in a crystal array has three sides and three angles. An axial system is used to name the three sides, denoted a , b , and c , which are the unit cell parameters of the cell; the three angles are denoted with symbols α (between side b and c), β (between side a and c), and γ (between side a and b). When atoms/molecules arrange themselves in periodic and specific configurations, they can be described using a set of symmetry operation known as crystallographic point groups. The combination of these 32 crystallographic point groups creates 219 distinct types of space groups in three dimensions, and based on the restrictions placed on the unit cell parameters and the angles of the lattice by these space groups, 7 crystal systems are formed which includes triclinic, monoclinic, orthorhombic, rhombohedral, tetragonal, hexagonal, and cubic. The number of lattice points and their positions in the unit cell dictate the lattice type, which can be Primitive (P), Body-centred (I), Face-centred (F), or Base-centred (C). These lattice types, combined with the seven crystal systems give 14 unique “Bravais lattices” which can be used to describe all crystal structures [91].

The axial system, which is used to name the three sides of a unit cell, is called the Weiss index in the order of a , b , and c . Lattice planes are joined by linking different lattice points, and they intersect with the three sides of the unit cell. Each Weiss index refers to one plane, and therefore, parallel planes have indices which are multiples of each other. Miller indices are the reciprocals of the Weiss indices with the fractions removed. Each Miller index (h , k , l) corresponds to a family of parallel

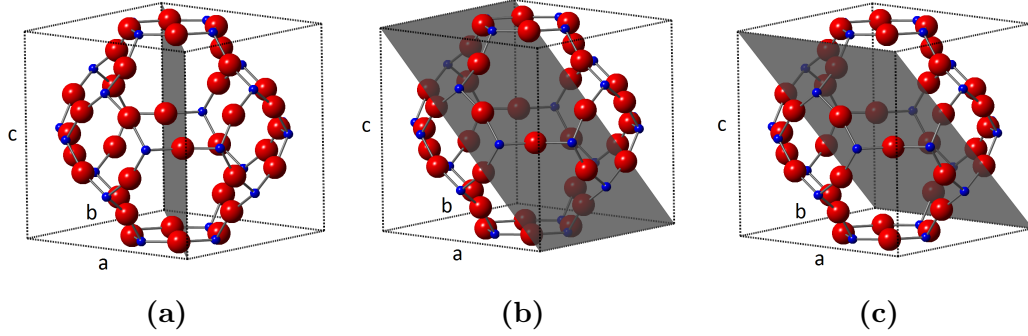


Figure 2.1: Lattice planes of a cubic unit cell contains a single β -cage with Miller indices (a) 110, (b) 101, and (c) 011. Lattice planes are shown in grey, with blue and red spheres represent the Si and O atoms respectively.

lattice planes with a characteristic inter-planar spacing (d). Some lattice planes of the cubic crystal system are given as an example in figure 2.1, with their corresponding Miller indices. The unit cell parameters and inter-planar spacings of cubic symmetry, as well as the orthorhombic symmetry, are related by equation 2.1.

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (2.1)$$

For cubic symmetry, such as the LTA framework, where $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$, equation 2.1 is then simplified to equation 2.2.

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (2.2)$$

Some planes are equivalent because of the symmetry of the unit cell. For example, in the cubic unit cell of zeolite A, the (200), (020) and (002) lattice planes are the same. A multiplicity factor also arises due to the fact that different lattice planes,

with different orientations, can have the same d-spacings, for example the (644) and (820) lattice plane for zeolite A. The diffraction peaks are then overlapped, and this makes it difficult to determine intensity of individual peaks.

$$n\lambda = 2d\sin\theta \quad (2.3)$$

X-rays interact with electron clouds of atoms in a crystal. The principle of X-ray powder diffraction can be explained by the Bragg's Law [92], and is illustrated by equation 2.3, where λ is the wavelength of the X-ray, θ is the angle between the incident rays and the crystal lattice planes, d is the distance between lattice planes, and n is an integer number of wavelengths (1, 2, 3 etc.).

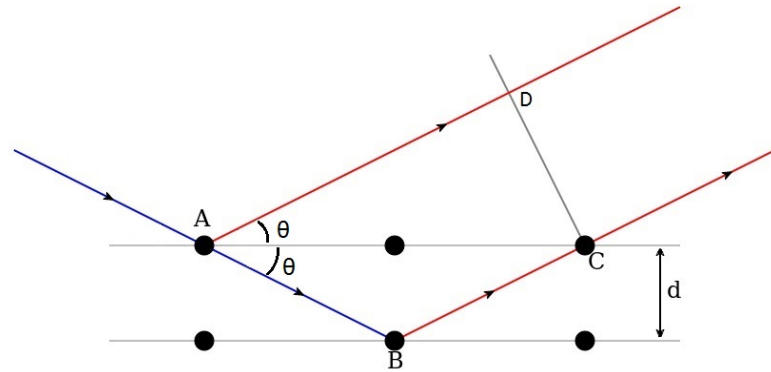


Figure 2.2: Graphical representation of Bragg's Law

A graphic representation is shown in figure 2.2. Imagine a single X-ray (blue line) with a certain wavelength hits lattice planes separated by the interplanar distance d , it is reflected by two of the atoms, A and B. The path difference between the reflected X-ray AD and BC (red lines) is $2d\sin\theta$. A peak is shown in the powder pattern when the reflected X-rays, AD and BC, interact with each other by constructive interference.

For this to happen, the path difference must equal to a whole number of wavelength, $n\lambda$. Appendix A gives more detail about Bragg's equation.

It can be seen from Bragg's equation that the angle of reflection, θ , is inversely proportional to the d-spacing. Peaks with bigger number of Miller indices have a larger reflected angle, and thus a smaller d-spacing between lattice planes. For certain Bravais lattice, destructive interference from some lattice planes occurs leading to general absences - the peak has zero intensity although X-rays have been reflected. Bragg's law does not give any information about the intensities of the diffraction peaks. The intensity relates to the electron density at any point in the unit cell. All atoms have electron clouds different in size, and are able to scatter X-rays in different ways. Each atom, therefore, has an atomic scattering factor which is proportional to the number of electrons (atomic number) at low Bragg angles. As θ increases, the interaction with X-rays decreases. Thus in a powder pattern, peaks with stronger intensities are being observed at lower 2θ , and *vice versa*. Elements with high electron density, so called "heavy atoms", give a greater intensity, compared to those with low electron density, e.g. hydrogen.

All powder patterns acquired in this thesis were obtained using either a Philips X'pert X-ray diffractometer or a Philips PW1792 X-ray diffractometer, both operating with Cu $K\alpha$ radiation, unless otherwise stated.

2.2 Solid-state magic angle spinning nuclear magnetic resonance

Solid-state magic angle spinning nuclear magnetic resonance (SS MAS NMR) is an analytical tool to study the local environment (ordering) of crystalline solids. Most of the zeolite frameworks contain isotopes which possess nuclear spin (I) and are NMR active, for example, ^{29}Si ($I = 1/2$), ^{27}Al ($I = 3/2$), and ^{23}Na ($I = 5/2$) are all common zeolite isotopes with natural abundance of 4.7%, 100% and 100% respectively [93]. NMR works by applying a magnetic field to a nuclei with spin; since different isotopes interact differently to the applied magnetic field, signals are obtained as chemical shifts. Chemical shift is defined as the resonant frequency of a nucleus relative to a standard in a magnetic field, and depends on the structure of the compound being studied. The applied magnetic field does not only interact with the nuclei, but also with the surrounding electron shell. The interacting electrons produce an induced field which is opposed to the applied magnetic field. Nuclei that have higher electron density are therefore being shielded, and those have relatively low electron density, are deshielded. For systems with abnormally high electron density, e.g. the π system of benzene, such anisotropic interactions can lead to signal broadening and thus reduce the resolution of the NMR spectra. In solutions, since molecules have freedom of movement, anisotropic interactions can be averaged. However, as a solid, the freedom of movement is extremely limited, and the anisotropic interactions have to be overcome by magic angle spinning (MAS). This technique involves spinning the solid sample at a magic angle, θ_m , at 54.74° with respect to the direction of

the magnetic field. Since the dipolar interactions and anisotropic chemical shielding equations contain the term $(3\cos 2\theta^{-1})$, this becomes zero when θ_m is approximately 54.74° [94]. The anisotropic interaction is thus minimized, and the broadened signal becomes narrower which increases the resolution of the NMR spectrum.

Almost all zeolites obey the “Loewenstein rule” [95]. It was suggested by Walter Loewenstein in 1954 and the rule states that when two tetrahedra are linked by an oxygen bridge, only one of the tetrahedral centers can be occupied by an Al atom. It means that Al–O–Al linkages are forbidden since the Al ion is four-fold coordinated to oxygen and carries a negative charge. This rule explains why the maximum substitution of Al to a zeolite framework cannot exceed 50%. In a zeolite framework, Si tetrahedra can coordinate with a maximum of four Si or Al tetrahedra. This creates five different Q^4 Si local environments in the ^{29}Si NMR spectrum with 0, 1, 2, 3, and 4 O–Al linkage, notated as Si(0Al), Si(1Al), Si(2Al), Si(3Al), Si(4Al) respectively. Figure 2.3 on the following page gives an example of an NMR spectrum of an as-synthesised zeolite A sample using tetramethylammonium hydroxide as an organic structural directing agent, which consists of the five mentioned Si local environments. The chemical shifts occupy a range from -84 ppm to -114 ppm, with small overlap between individual environments [4, 96], and is summarized in figure 2.4 on the next page. If Si tetrahedron shares only three corner oxygen atoms, a Q^3 silanol species is formed, with an OH group attached – $\text{Si}(\text{OSi})_3\text{OH}$. ^{29}Si cross polarization (CP) MAS NMR can be used to confirm the presence of silanol species. The chemical shifts of these silanol species, mainly Q^3 or Q^2 species in zeolite framework, occupy a wide range from -60 ppm to -100 ppm, and overlap with the Q^4 species [94].

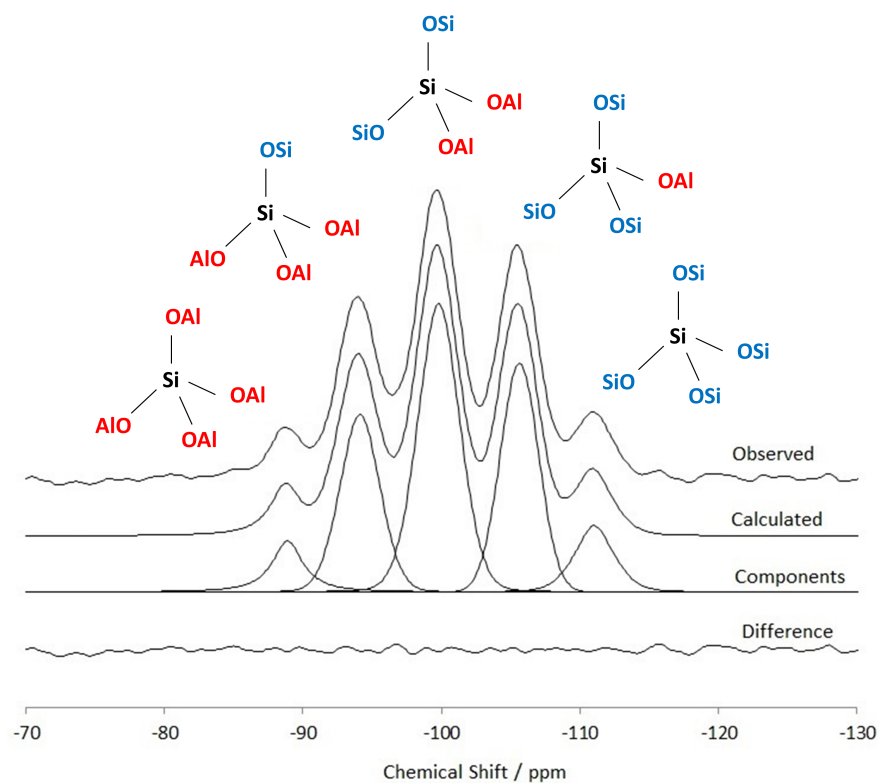


Figure 2.3: SS MAS NMR spectrum of an as-synthesised zeolite A sample using tetramethylammonium hydroxide as organic structural directing agent. The spectrum contains five typical Si local environments: Si(4Al), Si(3Al), Si(2Al), Si(1Al), and Si(0Al).

Notation	Si(4Al)	Si(3Al)	Si(2Al)	Si(1Al)	Si(0Al)
Coordination					
Chemical shift (ppm)	-80.0 to -90.5	-88 to -97	-93 to -102	-97.5 to -107.0	-102.0 to -116.5

Figure 2.4: Chemical shifts of the five local Si environments.

$$\left(\frac{Si}{Al}\right)_{framework} = \frac{(\sum_{n=0}^4 I_{Si(nAl)})}{(\sum_{n=0}^4 0.25nI_{Si(nAl)})} \quad (2.4)$$

Another useful piece of information from solid state NMR is to use the ^{29}Si NMR spectrum to calculate the Si/Al ratio of the as-synthesised zeolite sample [96–99]. For a zeolite framework that obeys the Loewenstein rule, an aluminum atom will always be surrounded by four silicon atoms. Therefore, the total number of aluminum atoms in the framework will be one-fourth of the total number of Si–O–Al bonds. Since the intensity of a silicon resonance is proportional to the number of associated silicon atoms, the Si/Al ratio can be given by equation 2.4, where I is the intensity of a particular silicon resonance and n is the number of coordinated Al atoms for that resonance. It is common that the silicon resonances of a zeolite sample are partially overlapped or broadened, thus a deconvolution step is needed to determine the intensity of a particular Si local environment before the Si/Al ratio can be calculated. Deconvolution of the spectra involves fitting of individual peaks. This consists of modelling the experimental NMR spectra with analytical peak functions: Gaussian, Lorentzian or a mixture of both. Peak intensities, widths and positions are adjusted in an iterative process in order to fit the calculated curve to the experimental NMR peaks by minimising the sum of the squared residuals. However, if more than one zeolite phase of similar framework structures are found in an as-synthesised zeolite sample, for example, a mixture of zeolite A and sodalite, the Si/Al ratio cannot be accurately determined as the Si resonance will be strongly overlapped. The error in

the Si/Al ratio calculated using equation 2.4 depends on how the local Si environments being assigned in the ^{29}Si NMR spectrum. This affects the intensity – the $I_{\text{Si}(n\text{Al})}$ term in the equation, and a range of Si/Al ratio is observed.

Since Al–O–Al linkage is forbidden in zeolite frameworks according to the Loewenstein rule, there is only one Al local environment that exists for ^{27}Al SS MAS NMR if all Al are tetrahedral coordinated. The chemical shift for $[\text{Al}(\text{OSi})_4]$ units consist of a single signal in the chemical shift range of 50 - 70 ppm. However, there are two more Al environments, the penta and octahedrally coordinated species. The octahedral coordinated Al usually occupy the extra framework sites as a result of calcination, steaming or acid leaching [100], and has a chemical shift around 0 ppm, while pentagonal species have chemical shifts around 30 ppm.

All the NMR spectra in this study were collected at the EPSRC UK National Solid-state NMR Service at Durham.

2.3 Scanning electron microscopy

Scanning electron microscopy (SEM) can be used to study the morphology of the zeolite samples. Zeolite crystals have their own unique morphology, for example, zeolite A is cubic while faujasite is tetrahedral in shape, though some zeolites have multiple morphologies depending on the synthetic conditions. SEM can also be used to study the different stages of zeolite crystallisation [101].

SEM works by emitting a narrow and high energy electron beam to the surface of the sample under vacuum. The incident electron beam causes backscattered electrons to be emitted from the sample’s surface and the difference in energy is detected and

shown as a difference in brightness, thus an image is obtained. For backscattered electron imaging, the sample can either be conductive or non-conductive. However, the image quality can be improved by coating the sample with a thin layer of conductive material, such as carbon, gold, platinum, etc. The sample is loaded on a carbon substrate to improve conductivity. The advantages of using SEM to study zeolite morphology are the high resolution (down to nanometer scale) and the depth of field, so crystals can be seen clearly in 3-dimension. However, SEM only works on the surface of material which means the framework structure cannot be observed.

2.4 Geometric simulation of flexibility window

The geometric simulation in this study is done by using the software “Geometric Analysis of Structural Polyhedra” (GASP) which was written by Stephen A. Wells. There are several structural analyses can be performed using this piece of software such as protein simulation, phase transition, and framework disorder, etc. [102], however, the flexibility window is the main subject of interest. Although the details of the calculation and theory behind the GASP program is out of the scope in this study, a full explanation is given in the publications by Wells et al. [103, 104].

From [102], the geometry simulation is a template-based method, and the process is illustrated in figure 2.5 as a simplified 2D version. The input is a list of atomic positions. GASP then links the corresponding atoms by geometry and forms vertex-sharing clusters. Templates resembling the shape of the vertex-sharing clusters are then constructed. The mismatch is minimized by rotating the template to get the initial fit. The residual mismatch from the previous fitting step is finally overcome by

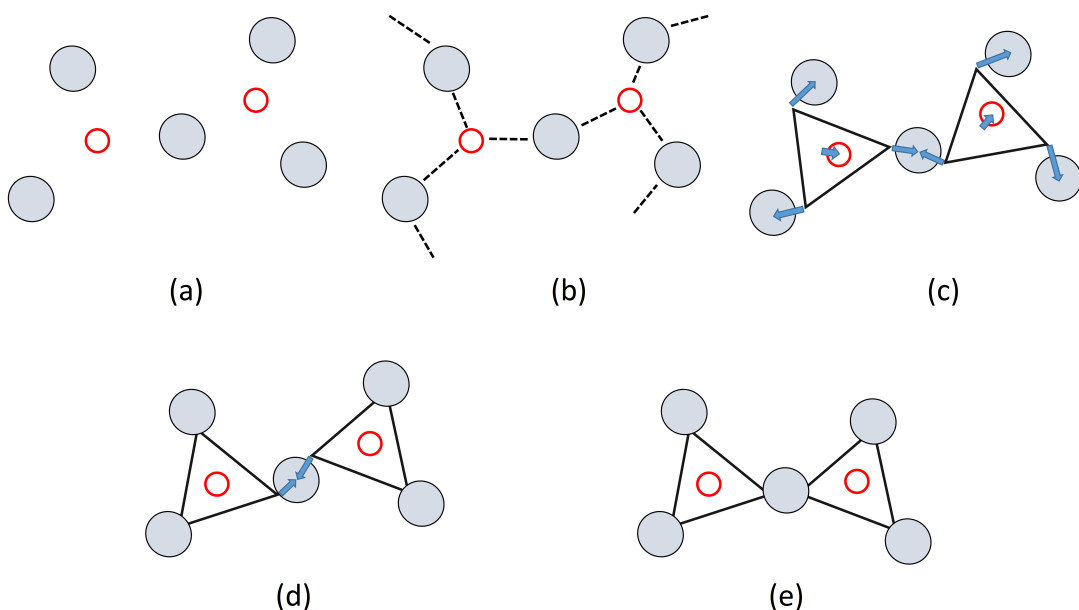


Figure 2.5: Schematic illustration of the geometric simulation process in a simplified 2D version. (a) The input structure consists of a list of atomic positions; (b) Atoms are linked and vertex-sharing clusters are formed; (c) Templates are constructed to resemble the shape of vertex-sharing clusters, mismatches are identified; (d) Mismatches are minimised by rotating the templates, with some residual mismatches; (e) The residual mismatches are further minimized by relaxing the atomic position.

relaxing of the atomic position. The fitting steps are repeated until all the mismatches are minimized.

In the case of zeolite flexibility window simulation, a rigid model is applied. The model takes the tetrahedral unit of a zeolite framework as a rigid unit, and the only flexible component is the T–O–T bonding linking the two tetrahedral units. The Si–O bond length is set to be 1.61 Å, while the Al–O bond length is 1.75 Å for the tetrahedral units. The atomic radii of an aluminosilicate zeolite framework that consists of Si, Al, and O are 0.26 Å, 0.39 Å, and 1.35 Å respectively. The input structure depends on the zeolite framework being studied, but is in the P1 space group to create the minimum symmetry equivalent position within the unit cell. The

extra framework species, such as sodium ions, can be customised and included in the geometric simulation. GASP uses full periodic boundary conditions during geometry simulations; atoms at one edge of the unit cell “see” a periodic image of the atoms near the opposite edge. Bonds go out of one wall of the unit cell come back in through the opposite wall, so atoms in the unit cells are always bonded to each other. There are no dangling bonds at the edge of the unit cell.

Chapter 3

Synthesis of LTA, SOD, and LTN framework zeolites with no organic structure directing agent

In this chapter, I will describe synthesis and characterization of zeolite A, sodalite and Linde Type N with no organic structure directing agent (OSDA) and the transformations between these zeolites during the crystallisation process. The chapter will begin with the synthesis of zeolite A using both hydrothermal and microwave methods with no OSDA, followed by the microwave synthesis of sodalite. The transformation between zeolite A and sodalite will then be discussed. Finally, this chapter will end with a new method of synthesising Linde Type N using a microwave method, and a hydrothermal synthesis of this zeolite will also be present for comparison. Part of the study in this chapter has been published in [68].

3.1 Synthesis of zeolite A with no OSDA using microwave and hydrothermal methods

For the microwave synthesis, a modified method reported by Smaïhi et al.[105] is used. 6.78 g of sodium hydroxide (Fisher) was dissolved in 40 cm³ of deionized water

and divided into two 20 cm³ portions. 0.988 g of sodium aluminate was added to one portion while 2.42 g of colloidal silica (Ludox HS-30, 30 wt% SiO₂, Aldrich) was added to the other. Both the Al₂O₃/Na₂O/H₂O solution and the silica solution were stirred for 90 minutes at room temperature. The silica solution was then added to the Al₂O₃/Na₂O/H₂O solution in a 60 ml polypropylene bottle, and stirred for 15 minutes. The homogeneous gel with batch composition 2SiO₂:Al₂O₃:14Na₂O:400H₂O was sealed and treated using a specialised microwave oven (CEM Mars 6) at 40 °C (600 W) for 1 hour (LTA40M). The sample was then washed with distilled water until pH 7 was attained, and dried in an oven at 110 °C overnight. For comparison, the synthesis was repeated using a conventional oven at 40 °C for 24 hours (LTA40D24) and 1 hour (LTA40D1). All as-synthesised zeolites were characterized by XRPD, as shown in figure 3.1 on the following page.

The powder pattern of LTA40M is almost identical to LTA40D24. It is interesting to see that the sodalite 110 peak is present in the LTA40M sample. This indicated that the formation of zeolite A and sodalite depends on the synthesis condition. No zeolite phase is observed in the powder pattern of LTA40D1 when the gel was treated hydrothermally at 40 °C for an hour. The experiment proves that the microwave method can reduce reaction time dramatically compared to hydrothermal synthesis, from 24 hours to 1 hour, and zeolite A can be synthesised without OSDA using a microwave method.

Figure 3.2 on page 36 shows the morphology of the two as-synthesised zeolite samples acquired by SEM. Zeolite A synthesised hydrothermally (LTA40D24) gives aggregates of small crystals with uneven size distribution (figure 3.2(a), 3.2(b)). The

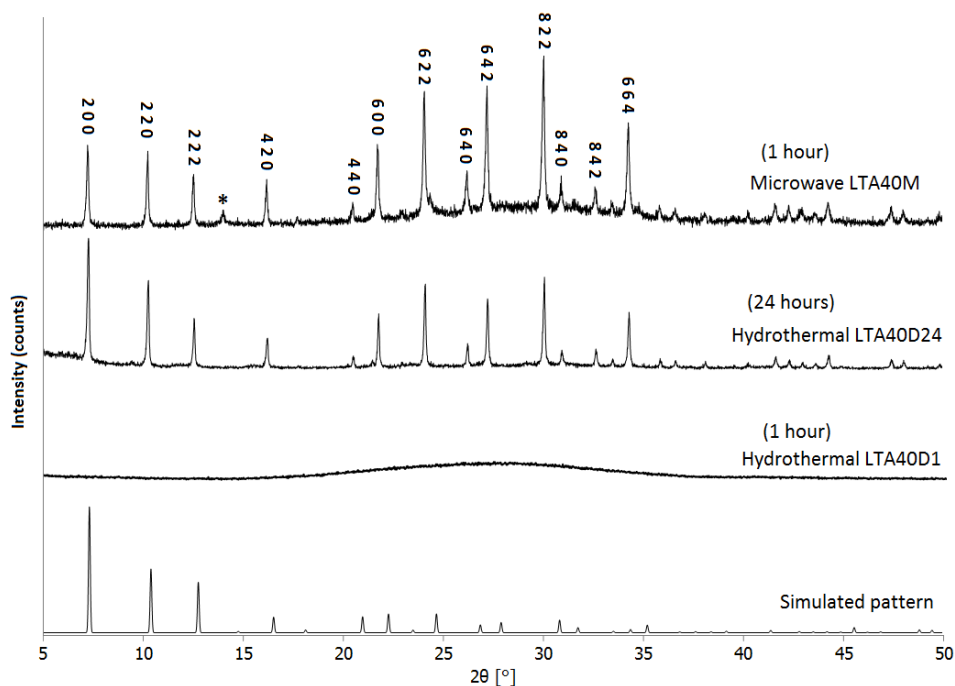


Figure 3.1: Powder pattern of as-synthesised zeolites - microwave synthesised LTA40M, and hydrothermal synthesised LTA40D24 and LTA40D1, with corresponding Miller indices. The SOD 110 peak is marked with an asterisk.

biggest cubic crystals were around $0.5\ \mu\text{m}$ in size. Crystallites of zeolite A synthesised using a microwave method (LTA40M) are bigger and more uniform in size to about $1\ \mu\text{m}$. Inter-growth of cubic crystals are common (figure 3.2(d)), and impurities (amorphous materials) are observed around the cubic crystals (figure 3.2(c), 3.2(d)). An attempt to characterise the particle size distribution using the Scherrer equation were not successful due to the low resolution of the PXRD pattern and asymmetric nature of the peaks.

In a study reported by Sathupunya et al.[106], they synthesised zeolite A using sol-gel microwave techniques with organic precursors (silatrane and alumatrane) and OSDAs. Cubic zeolite A crystals with uniform size of $4.5\ \mu\text{m}$ formed only at $110\ ^\circ\text{C}$ with a minimum reaction time of 4 hours. When zeolite A was synthesized at the

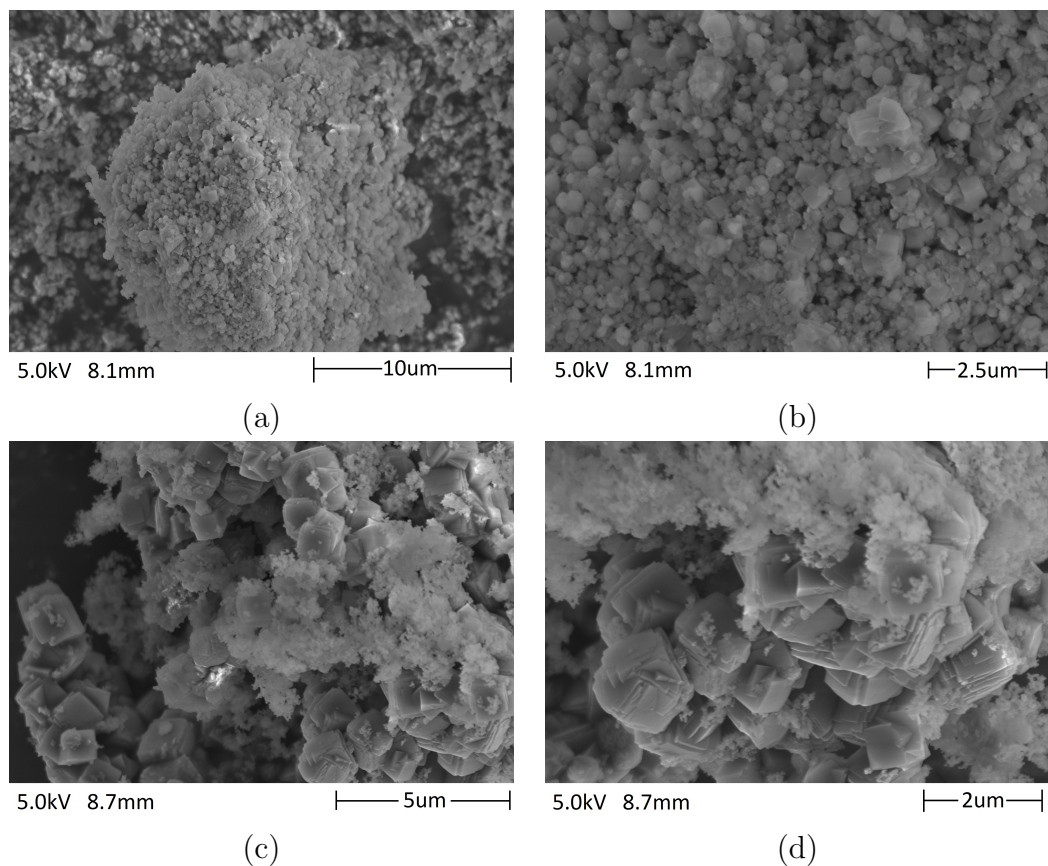


Figure 3.2: SEM images of (a), (b) LTA40D24 synthesised at 40 °C hydrothermally, and (c), (d) LTA40M synthesised at 40 °C using a microwave method.

same temperature for less than 4 hours, impurities were always present. No crystal was formed in 1 hour syntheses. In this study, the morphology of LTA40M is similar to what was reported by Sathupunya et al., but without using OSDA, at a lower temperature, and a shorter reaction time. It is expected that by increasing the reaction time of the LTA40M synthesis, cubic crystals with no impurity will form. However, this may also increase the amount of the sodalite phase.

Sathupunya et al. also reported the concentration of NaOH in the starting gel strongly affects the particle size. A high $\text{Na}_2\text{O}:\text{SiO}_2$ ratio (10:1) produced small zeolite A crystals less than 1 μm , while a low $\text{Na}_2\text{O}:\text{SiO}_2$ ratio (3:1) gave bigger crystals with

size of 4.5 μm . In this study, the $\text{Na}_2\text{O}:\text{SiO}_2$ ratio was 7.5:1 for both microwave and hydrothermal synthesis, which is closer to the higher end of the suggested $\text{Na}_2\text{O}:\text{SiO}_2$ ratio, and therefore small zeolite A crystals were obtained.

3.2 Synthesis of sodalite with no OSDA using microwave methods

N.B. - See appendix B on page 105 for further information about this section.

To see if sodalite can also be synthesised using microwave methods, different synthetic conditions were used. Figure 3.3 on the next page summarized the three different recipes of making sodalite with the corresponding starting materials, batch compositions and methods of preparation. Each sample was synthesised under four different conditions. Two methods were used to prepare the gel. In both preparations, a large amount of sodium hydroxide was dissolved in water, and the solution was then halved and mixed with the Al and Si source separately, or the Al and Si sources were added stepwise, and stirred for 2 hours. The powder patterns of the corresponding as-synthesised zeolite are shown in figure 3.4 on the following page, and table 3.1 summarized the zeolite phase of all reactions.

Table 3.1: Summary of the as-synthesised zeolite samples prepared as mentioned in figure 3.3.

Samples	Recipe		
Condition	1	2	3
1	SOD	SOD	SOD+LTA
2	SOD+LTA(T ¹)	SOD+LTA(T)	SOD+LTA(T)
3	SOD	SOD	SOD
4	SOD	SOD	SOD

¹ T=in trace amount

Conditions	Preparation		
	Recipe 1 & 2	Recipe 3	
1. Microwave, 20 mins, 150 °C 2. Microwave, 60 mins, 80 °C 3. Microwave, 120 mins, 140 °C 4. Oven, 24 hours, 100 °C			
Recipe 1	Recipe 2	Recipe 3	
Sodium aluminate Fumed silica Sodium hydroxide Deionized water	Sodium aluminate 98% ppt. Silica Sodium hydroxide Deionized water	Sodium aluminate 98% ppt. Silica Sodium hydroxide Deionized water	
Recipe 1 & 2 composition - $7.52\text{SiO}_2 : 1\text{Al}_2\text{O}_3 : 22.77\text{Na}_2\text{O} : 200\text{H}_2\text{O}$			
Recipe 3 composition - $4.91\text{SiO}_2 : 1\text{Al}_2\text{O}_3 : 38\text{Na}_2\text{O} : 1038\text{H}_2\text{O}$			
	Water + NaOH ↓ Half + Si source 25 °C ↓ Half + Al source 25 °C ↓ Stir for two hours	Water + NaOH ↓ 25 °C Mix with Al Source ↓ 25 °C Mix with Si Source ↓ Stir for two hours	

Figure 3.3: Synthesis conditions, starting materials, batch compositions and preparation methods for sodalite.

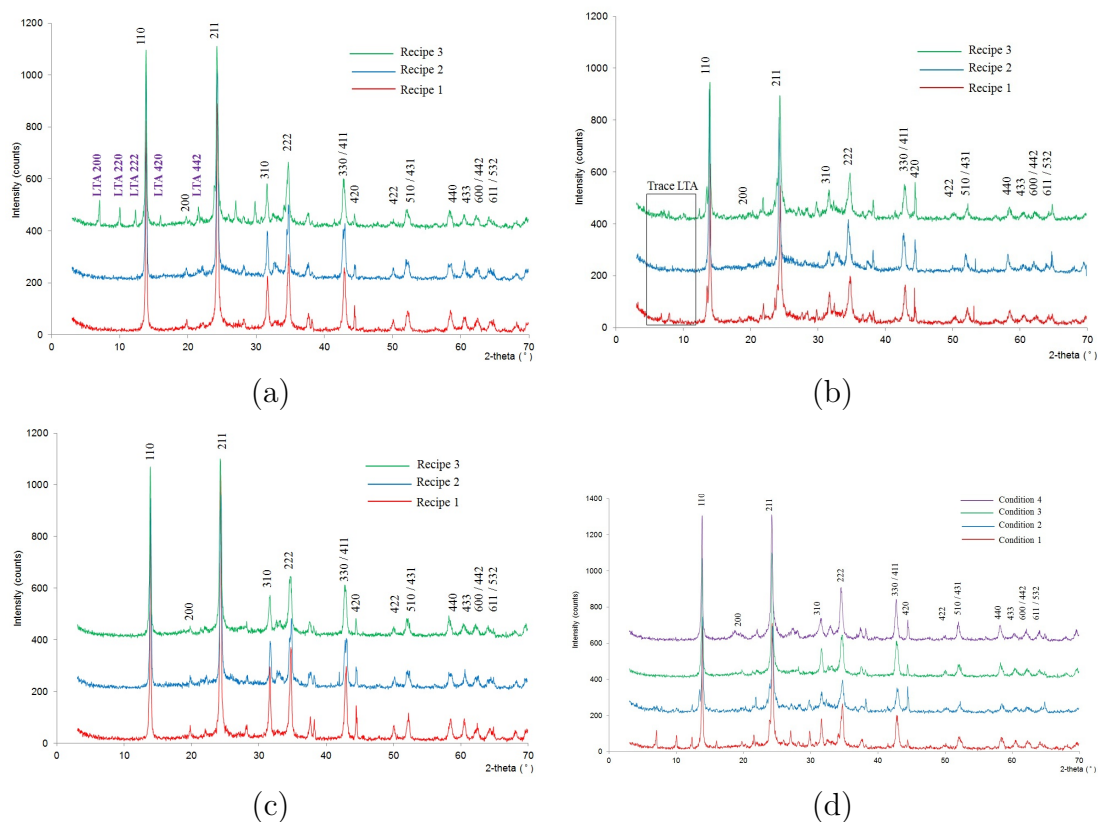


Figure 3.4: Powder patterns of as-synthesised zeolite under (a) condition 1, (b) condition 2, (c) condition 3, (d) using recipe 3 in four conditions.

Figure 3.4(a) shows the powder pattern of the as-synthesised zeolite under condition 1, a relatively short, high temperature synthesis. The use of different Si sources does not affect the formation of sodalite, *e.g.* fumed silica (recipe 1) or 98% precipitated silica (recipe 2). However, under short reaction time, gel preparation makes a difference to sodalite formation in samples. The powder pattern of the as-synthesised zeolite of recipe 3 shows a mixture of zeolite A and sodalite. By dissolving the Si source thoroughly in the gel, *i.e.* recipe 1 & 2, a pure sodalite phase is achieved.

Figure 3.4(b) shows the powder pattern of zeolites formed under a long, relatively low temperature condition 2. A trace of zeolite A is present in all samples when the synthesis is performed at a lower temperature. This can be seen as small peaks in the diffraction pattern below $10^\circ 2\theta$. However, comparing the powder patterns of recipe 3 in figure 3.4(b) to figure 3.4(a), the intensity of the zeolite A peaks are largely reduced. It implies that even at low temperature, a longer reaction time favours the formation of sodalite.

In the long, high temperature condition 3, a single sodalite phase is formed using all three recipes regardless of the batch composition or gel preparation (figure 3.4(c)). These results indicate that there is a transformation of zeolite A to sodalite depending on reaction time and temperature, which will be discussed in section 3.3.

Figure 3.4(d) shows the powder patterns of as-synthesised zeolite using recipe 3 under four different conditions. Comparing the samples made using a microwave method to the hydrothermal synthesis using an oven, sodalite is formed regardless of the methods being used. The purity depends on temperature and time of crystallisation. However, the synthesis time is highly reduced with microwave methods. Batch

composition is known to affect the size of the crystalline product[57], but in the above study, difference in batch composition does not affect the formation of sodalite phase.

It is known that the use of different silica sources affects the nucleation step, the size distribution of the as-synthesised zeolite crystals, and the as-synthesised zeolite phase. In a study reported by Twu et al. [107], they synthesised zeolite X and Y using two different silica source, and characterised the gel using Raman spectroscopy. The two silica source used were Ludox and N-brand, which were colloidal SiO_2 particles suspended in water and a sodium silicate solution respectively.

In the zeolite X synthesis, zeolite X was synthesised regardless the silica source being used. However, Raman spectroscopy suggested the initial reaction between the two silica sources and the aluminate source was different. Ludox solution consists of SiO_2 particles covered with OH groups, and by reacting with aluminate source, forming a core-shell like particle with an aluminum hydroxide sheath, only monomeric silica species was observed. N-brand silicate solution, however, consists of polymeric silicate species such as trimeric cyclic silicate and dimeric silicate [108]. When it reacted with aluminate source, Si–O–Al bonds were formed immediately and no excess aluminate ions were observed. Although Ludox and N-brand reacted differently with aluminate source, similar solid and solution-species were formed after 2-3 hours of heating, and zeolite X was synthesised regardless the Si source being used. Use of different silica source also affects the rate of crystallization of zeolite X. Zeolite X was crystallized after 8 hours of heating in the Ludox system while minimum of 12 hours of heating was required in the N-brand system. Zeolite X nuclei were formed after 5.5 hours of heating in the Ludox system.

When Twu et al. synthesised zeolite Y with an aging step of 24 hours, zeolite P (with GIS framework topology) and zeolite Y were formed using N-brand and Ludox respectively. Raman data showed that the spectral differences between Ludox and N-brand synthesis were only significant in the first hour of the aging process. Only monomeric silicate ions were observed in the Ludox system, but monomeric, dimeric, as well as oligomeric silicate species were observed in the N-brand system. Additional experiments by mixing the Ludox and N-brand containing gel provided evidence that the formation of zeolite P using N-brand was due to the presence of the polymeric silicate species in the very early stage of the aging step - tetrameric Si-O chains were formed which are the important building units for GIS framework, and zeolite P was formed. Thus, the reaction between the aluminate species and the silicate species initially present in the silica source affects the formation of the as-synthesised zeolite phase.

The study of Twu et al. may explain why the use of precipitated silica and fumed silica had no effect on the as-synthesised zeolite phase in the microwave syntheses described in this section. Both precipitated silica and fumed silica are in solid forms, and form SiO₂ particles with OH groups attached on the surface when mixing in an alkaline solution, which is very similar to the Ludox system. Monomeric silicate species are dominant and there are very few polymeric silicate species.

Twu et al. showed that in their zeolite X synthesis, different silica sources influence the nucleation process. This is also supported by the study reported by Hamilton et al. [109] and Tekin et al. [110]. Hamilton et al. synthesised zeolite NaX crystals using 11 different silica sources. Their results showed that the choice of silica source affects

the crystallization time, the final average crystal size and the impurity zeolite phases. Cab-O-sil, a type of fumed silica, produced the largest zeolite X crystals but less zeolite X nuclei, and required the longest crystallization time. Sodium metasilicate nonahydrate, however, produced the smallest zeolite X crystals with the shortest crystallization time. The effect of different metal ion impurities presence in the silica sources were also tested and had no effect on the crystal size and the purity of the as-synthesised zeolite NaX.

The effects of using different silica sources are not limited to zeolite syntheses with FAU framework topology. Mohamed et al. [111] reported the effect of four different silica sources on the crystallinity of nanosized ZSM-5 zeolite. It was found that ZSM-5 crystals synthesised using fumed silica had the highest crystallinity and surface area, while using sodium metasilicate produced quartz material. When colloidal silica was used, the crystal obtained had the highest average crystal size but the lowest surface area.

The morphology and crystal size of two selected zeolite samples were studied by SEM, as shown in figure 3.5 on the following page. Both samples were synthesised under condition 1 in figure 3.3, but two different recipes were used. When fumed silica was used and the $\text{Na}_2\text{O}:\text{SiO}_2$ ratio kept low to around 3:1 (recipe 1), aggregates of highly crystalline particles were obtained (figure 3.5(a)). No such morphology was reported in the literature. When precipitated silica was used and the $\text{Na}_2\text{O}:\text{SiO}_2$ ratio increased to about 7.5:1 (recipe 3), spherical sodalite particles with sizes about 10 μm were synthesised, as well as some cubic zeolite A crystals (figure 3.5(b)). Close observations on these spherical sodalite crystals indicated that each of them were composed by

inter-growth of smaller disc-like plates. Huang et al. [112] reported a similar sodalite morphology when studying the effect of ethanol in sodalite crystallization. Such morphology was observed when a low concentration of ethanol was used.

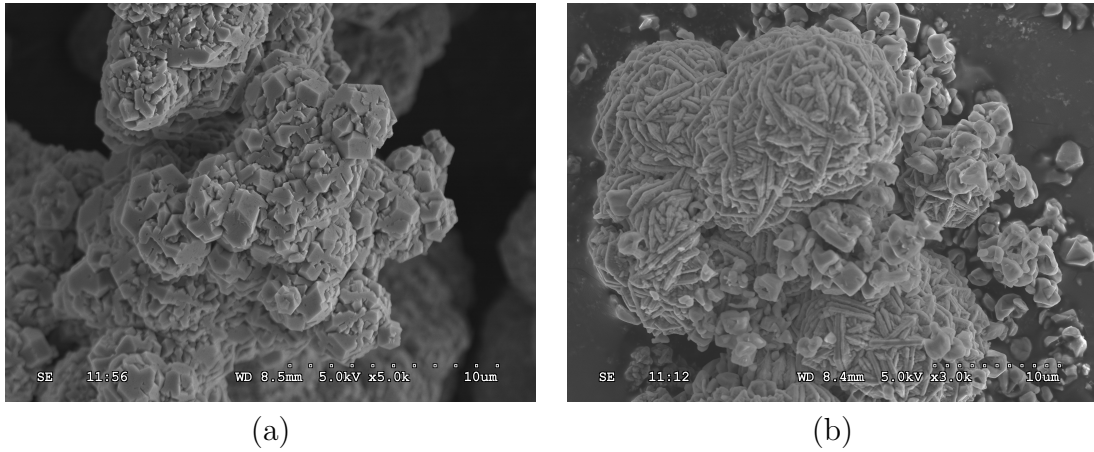


Figure 3.5: SEM images of zeolite samples synthesised under condition 1 using (a) recipe 1 (b) recipe 3

3.3 Transformation between LTA framework and SOD framework

I mentioned in section 3.1 and 3.2 that the formation of zeolite A and sodalite phase heavily depends on the synthesis conditions. In order to have a better understanding between the formation of LTA and SOD framework, a series of samples were synthesised hydrothermally using the same method described in section 3.1 at different reaction temperature and time.

The powder patterns of as-synthesised zeolite A with no OSDA at various temperatures are shown in figure 3.6 on the next page. Pure zeolite A phase was formed when treated hydrothermally for 24 hours at 40 °C, 50 °C and 60 °C. When the temperature was increased to 70 °C, a mix of zeolite A and sodalite was observed. The

sodalite 110 peak can clearly be seen around $14^\circ 2\theta$. The amount of sodalite in the as-synthesised sample increases from 70°C to 95°C . The sample synthesised at 95°C for 24 hours consisted mostly of sodalite. When the reaction time increased from 24 hours to 48 hours at 95°C , single phase sodalite was synthesised. These data show that zeolite A can be synthesised at temperatures as low as 40°C without OSDA.

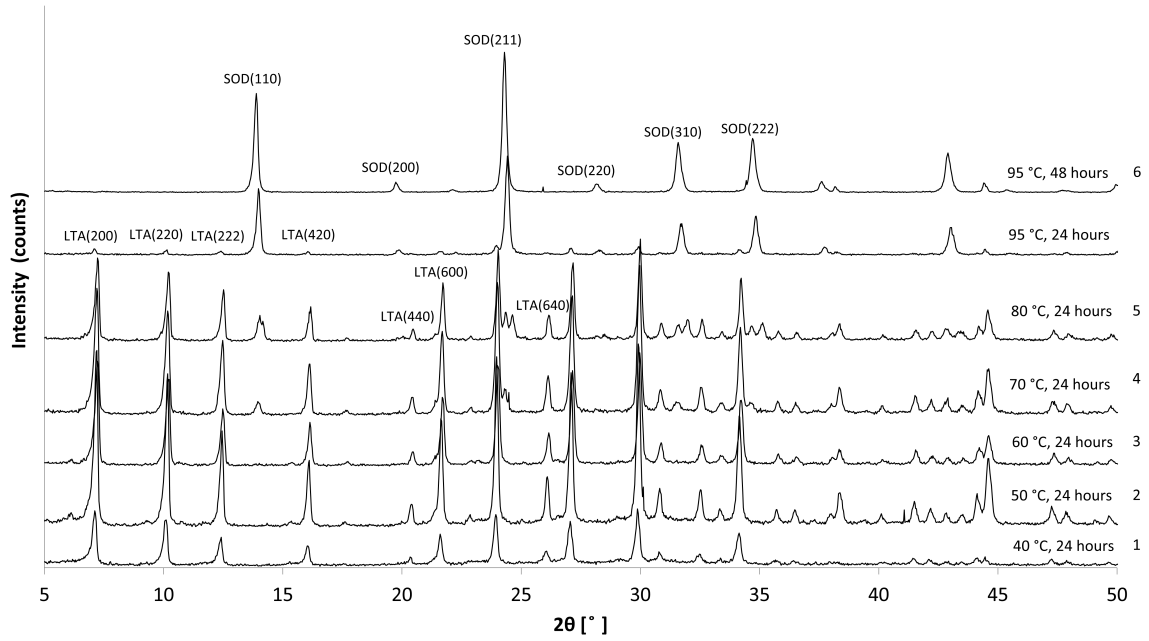


Figure 3.6: Powder pattern of as-synthesised zeolite samples at different temperature and reaction time.

The transformation from the LTA framework to the SOD framework with increased temperature has been reported previously [14, 21, 112–114]. Both zeolite A and sodalite are formed by β -cages stacked in different ways. To make the SOD framework, β -cages are stacked on top of each other in a simple cubic arrangement via single four-rings (S4R). The LTA framework is made in a similar manner with a cubic arrangement of β -cages, but with additional space between the β -cages – D4R units. This makes zeolite A (framework density 14.7 T/nm^3) more open compared to

sodalite (framework density 16.7 T/nm³), so it is reasonable to expect that sodalite will preferentially form with increased temperature[14, 21, 112–114]. Increasing the duration of hydrothermal treatment also favors the formation of sodalite at high temperature.

Table 3.2: SS MAS NMR of as-synthesised zeolite samples (see appendix for spectra)

Sample	Phase	Temp °C	Time hour(s)	Si ppm	Al ppm	Na ppm
1	Zeolite A	40	24	-84.9, -89.5	58.6	-2.4
2	Zeolite A	50	24	-84.5, -85.4, -86.5, -89.3	58.8	-1.9
3	Zeolite A	60	24	-86.5, -89.4, -91.1	58.6	-3.4
4	Zeolite A, Sodalite	70	24	-83.5, -86.6, -89.4, -94.6	58.5	-3.1
5	Zeolite A, Sodalite	80	24	-83.5, -86.5, -89.3	58.5	-3.1
6	Sodalite	95	48	-83.8, -85.2	63.7, 65.3	4.0, -4.1

To study the change of Si and Al local environment during the transformation, the as-synthesised zeolite samples were characterised by solid state MAS NMR. Table 3.2 summarizes the chemical shift of all samples being characterised. Since some of the zeolites were synthesised at temperatures as low as 40 °C, it is difficult to identify specific local Si environments for each of the Si chemical shifts. The presence of silanol signals is also expected for some of these zeolite samples, especially at low temperatures, and it was confirmed by ²⁹Si cross-polarization (CP) MAS NMR (appendix C.2.2). It is interesting to see that there was one signal around -89.4 ppm which was present in all samples with zeolite A (Table 3.2, sample 1-5). This signal was suggested by Ren et al. as an intrinsic signal for the LTA framework [115]. This peak is usually attributed to Si(4Al) species in zeolites [4]. Fan et al. [57] reported that when micro-sized sodalite crystals were synthesised, only one signal at -85.5 ppm was observed. However, there was an extra signal around -83.0 ppm for nanometer-sized crystals. Since both signals were observed in sample 6, it is highly probable that

nanometer-sized sodalite crystals were being synthesised (figure 3.7 on the following page).

^{27}Al and ^{23}Na MAS NMR spectra of as-synthesized zeolite samples at 40 °C, 50 °C, 60 °C, 70 °C and 80 °C (sample 1-5) show only one Al and one Na local environment respectively (appendix C.2.3 and C.2.4 (a) - (e)). This indicates that Al were tetrahedrally coordinated in the framework associated with Na ions. Sodalite (sample 6), however, showed an extra broad ^{23}Na signal at 4.0 ppm.

For single phase zeolites, the Si/Al ratio can be calculated by using equation 2.4 mentioned in chapter 2. For zeolite samples synthesised hydrothermally with no OSDA at 50 °C (sample 2) and 95 °C (sample 6), the estimated ratio was 1.17 ± 0.16 and 1.10 ± 0.10 respectively. The error arises from the identification of Si local environments and the presence of silanol signals. For comparison, the suggested Si/Al ratio for zeolite A with no OSDA, and for sodalite, is 1 [52, 116].

The morphology of selected as-synthesised zeolite samples were characterised using SEM, as shown in figure 3.7 on the next page. Although the powder pattern of the zeolite sample synthesised at 50 °C showed a single phase, aggregates of small crystals less than 0.2 μm without defined shape were observed. At temperatures of 70 °C and 80 °C, a mixture of faceted cubic and truncated zeolite A crystals, as well as sodalite crystals with undefined shape were obtained. Sodalite crystals with hexagonal faces formed at 95 °C. Most of these crystals were less than 1 μm in size.

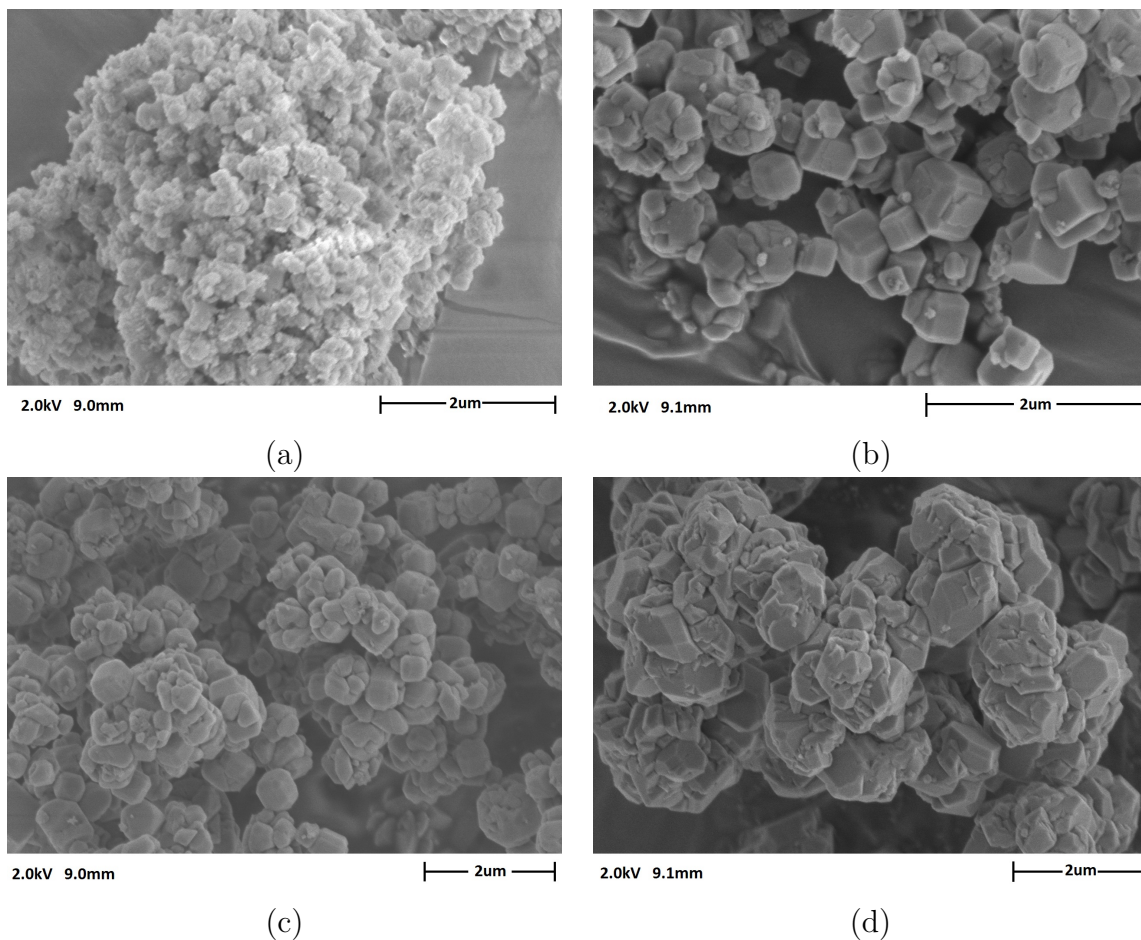


Figure 3.7: SEM images of as-synthesised zeolite samples, (a) 50 °C, (b) 70 °C, (c) 80 °C for 24 hours, and (d) 95 °C for 48 hours

3.4 Synthesis of Linde Type N zeolite with no OSDA

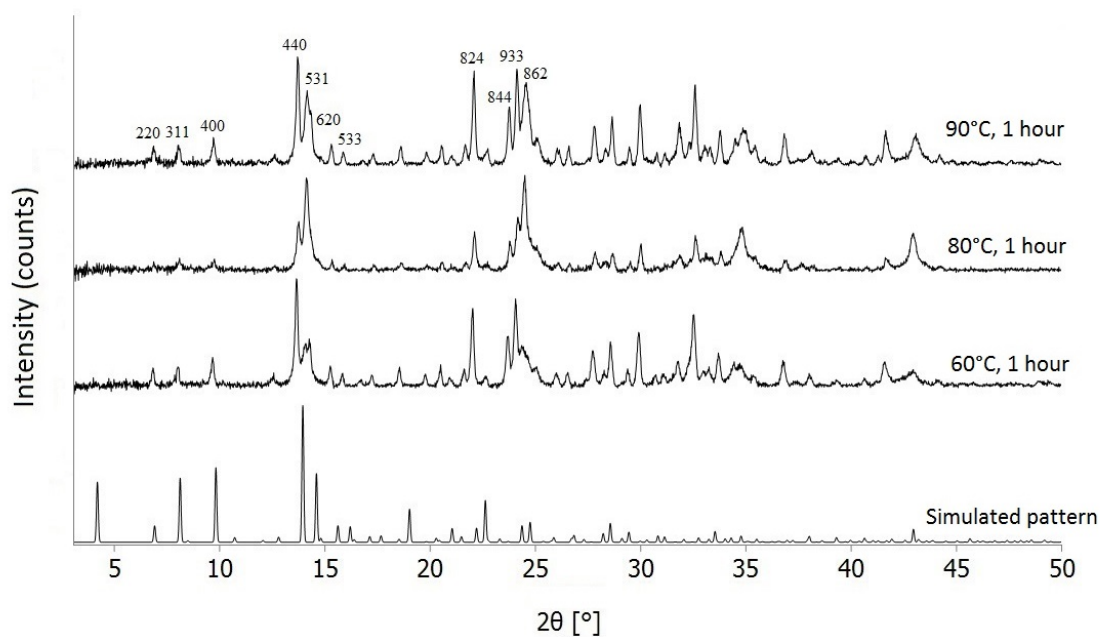
3.4.1 Microwave synthesis of Linde Type N zeolite

In section 3.1, zeolite A was synthesised using a microwave method. When this synthesis was repeated using the same reagents and method of preparation, but with a different gel composition, Linde Type N zeolite was synthesised instead of zeolite A. The Linde Type N zeolite synthesis used the same volume of Ludox HS-30 (2 ml) and water (40 ml), with double and triple the amount of sodium aluminate (2.05 g),

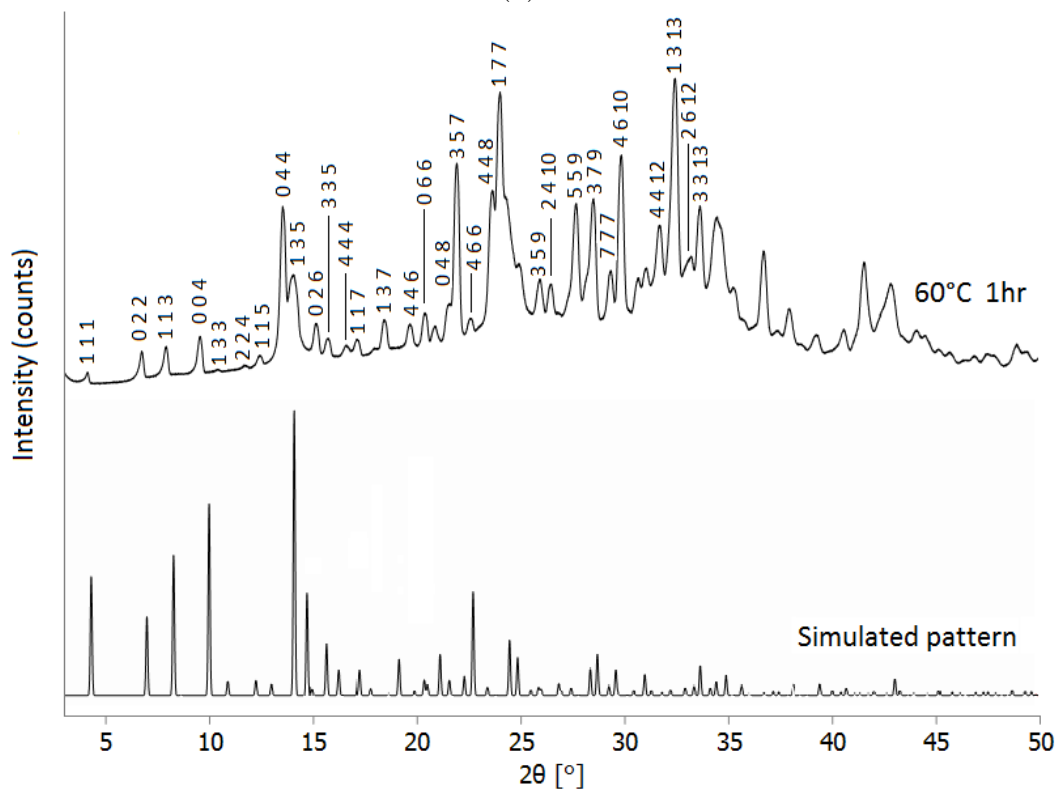
and sodium hydroxide (21 g) respectively. The batch composition was $\text{SiO}_2 : \text{Al}_2\text{O}_3 : 22\text{Na}_2\text{O} : 200\text{H}_2\text{O}$. All syntheses were microwave treated for an hour at 40 °C, 60 °C, 80 °C, 90 °C, 100 °C, and 120 °C respectively. Two more samples were synthesised using fumed silica instead of Ludox HS-30 at 60 °C and 90 °C.

The powder pattern of selected as-synthesised zeolite samples are shown in figure 3.8 on the following page and figure 3.9 on page 50. When the gel was microwave treated at 40 °C, no zeolite phase was observed. Linde Type N zeolite started to form at 60 °C, and up to 90 °C (figure 3.8(a)). Transformation between Linde Type N zeolite and sodalite occurred between 90 °C and 100 °C. At 100 °C and above, single phase sodalite was formed (figure 3.9). The calculated unit cell parameter of Linde Type N zeolite synthesised at 60 °C was $a = 36.724(4) \text{ \AA}$, which is bigger than the value, $a = 35.622 \text{ \AA}$, reported in the “Database of Zeolite Structures”. The increase in cell parameter may correspond to trapped water in the cages of the zeolite which was present during the microwave synthesis. The use of fumed silica has no effect on the as-synthesised zeolite phase and Linde Type N zeolite is formed (see appendix C.1 for powder pattern).

^{29}Si MAS NMR spectrum (appendix C.3.1 on page 111, figure C.6(a)) of the Linde Type N zeolite sample synthesised at 90 °C shows two major signals at -85.3 ppm and -86.3 ppm, with -83.7 ppm contributing to silanol species. Since there is no NMR data reported for Linde Type N zeolite in the literature, it is difficult to compare the Si local environment for each of these signals. Both ^{27}Al and ^{23}Na (appendix C.3.1 on page 111, figure C.6(c), (e)) gave two signals. For ^{27}Al MAS NMR, no penta or octahedral coordinated aluminum were observed in the zeolite framework. The



(a)



(b)

Figure 3.8: Powder patterns of as-synthesised zeolite samples without OSDAs using microwave methods. (a) Linde Type N zeolite forms above 60 °C, (b) A high resolution powder pattern of as-synthesised zeolite sample at 60 °C.

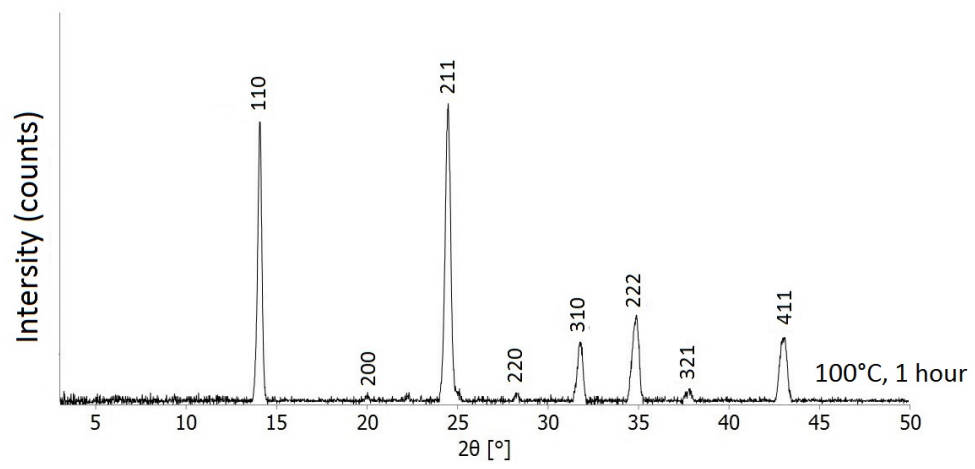


Figure 3.9: Powder pattern of as-synthesised zeolite samples. Sodalite forms at and above 100 °C

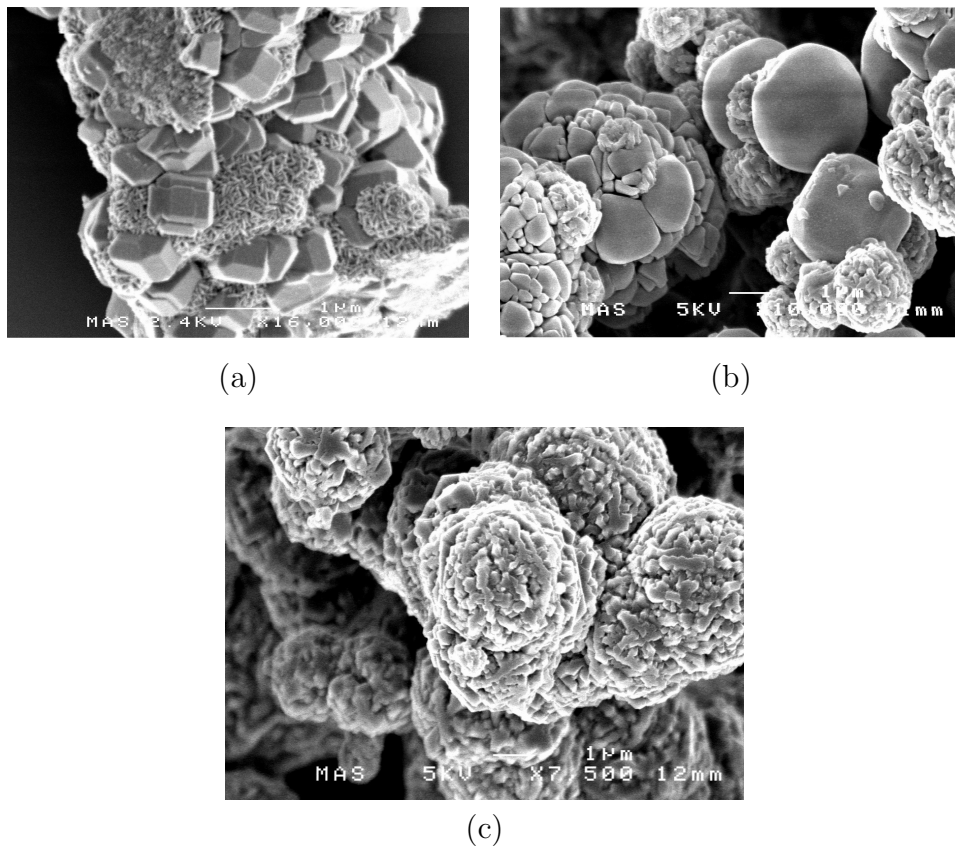


Figure 3.10: SEM images of as-synthesised zeolite samples, (a) at 60 °C (b) at 90 °C (c) at 100 °C

presence of two ^{27}Al environments may be a result of minor framework distortion.

SEM images of as-synthesised zeolite samples at 60 °C, 90 °C, and 100 °C are shown in figure 3.10 on the preceding page. At 60 °C, Linde Type N zeolite formed as truncated cubic crystals associated with spheres formed by inter-growth of smaller disc-like plates (figure 3.10(a)). The truncated cubic crystals grow into aggregates and eventually to 2 μm spheres with a smooth surface at 90 °C (figure 3.10(b)). Uniform sodalite crystals with size 3 μm were observed at 100 °C, as shown in figure 3.10(c).

3.4.2 Hydrothermal synthesis of Linde Type N zeolite

To compare the microwave synthesised Linde Type N zeolite samples in section 3.4.1, a Linde Type N sample was synthesised using hydrothermal method with no OSDA. The method is based on the patent described by Duecker et al.[66]. 10 g of sodium hydroxide was dissolved in 25 ml of deionized water followed by 0.95 g of aluminium hydroxide and stirred at 95 °C for 1 hour until a clear solution was formed. 2.18 ml of sodium silicate solution was then added and shaken vigorously for 1 minute. The resulting gel was transferred into a 60 ml polypropylene bottles and heated at 100 °C for 1 hour, then washed with distilled water until pH 7 was attained, and dried in an oven at 100 °C overnight.

Figure 3.11 on the next page is the powder pattern of the hydrothermal synthesised Linde Type N zeolite sample. The calculated unit cell parameter is $a = 35.400(2)$ Å, which is close to the suggested value, $a = 35.622$ Å. No impurity is observed from the powder pattern.

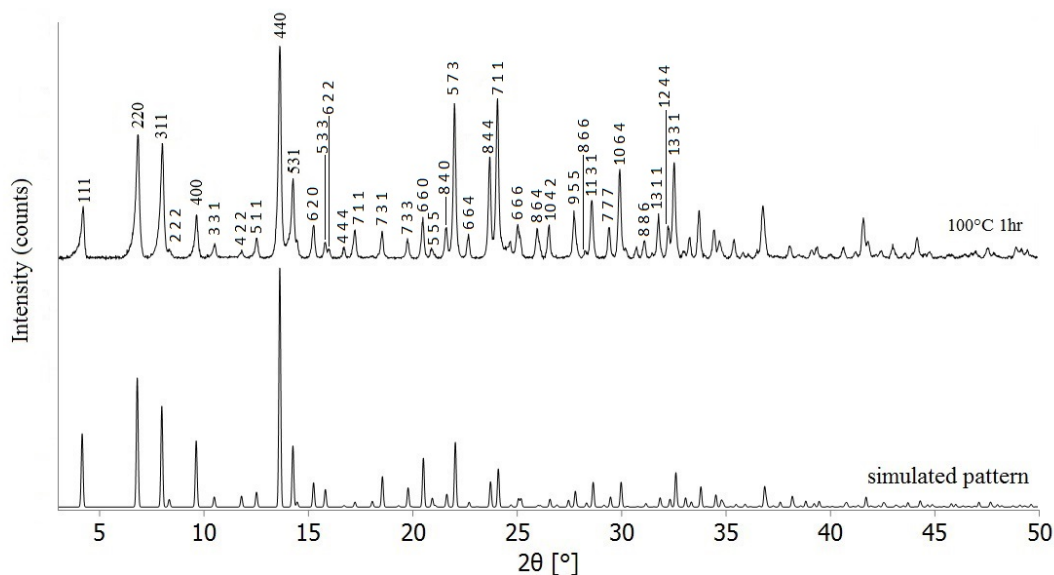


Figure 3.11: Powder pattern of as-synthesised Linde Type N zeolite with no OSDA using hydrothermal method.

Table 3.3: SS MAS NMR of hydrothermal synthesised and microwave synthesised Linde Type N samples

LTN samples	Chemical Shift(s) / ppm		
	Si	Al	Na
Hydrothermal	-84.80, -86.65, -87.10, -88.95, -90.57, -92.13	55.05, 59.54	7.15
Microwave	-83.70, -85.30, -86.30	60.60, 63.53	2.10, -4.81

Table 3.3 summaries the chemical shifts of the hydrothermal and microwave synthesised Linde Type N samples. Compared to the microwave synthesised samples, the ^{29}Si MAS NMR spectrum of the hydrothermal synthesised Linde Type N sample (appendix C.3.1 on page 111, figure C.6(b)) gave four major signals at -87.10 ppm, -88.95 ppm, -90.57 ppm, and -92.13 ppm, with two relatively low intensity signals at -84.80 ppm and -86.65 ppm. The four strong signals can be assigned to the Si(4Al) and Si(3Al) local environments, however, individual signals cannot be precisely assigned to the two local environments. Since two morphologies were observed in this Linde Type N zeolite sample (figure 3.12 on the following page), it is very likely that

one morphology gives the signals at -87.10 ppm and -90.57 ppm, while the signals at -90.57 ppm and -92.13 ppm belong to the other morphology. More characterizations are necessary before a conclusion can be made. Although two signals were observed on the ^{27}Al MAS NMR spectrum (appendix C.3.1, figure C.6(d)) at 55.05 ppm and 59.54 ppm, both are tetrahedrally coordinated Al species. The ^{23}Na MAS NMR (appendix C.3.1, figure C.6(f)) gave only one signal at 7.15 ppm, indicating a uniform distribution of extra-framework Na cations.

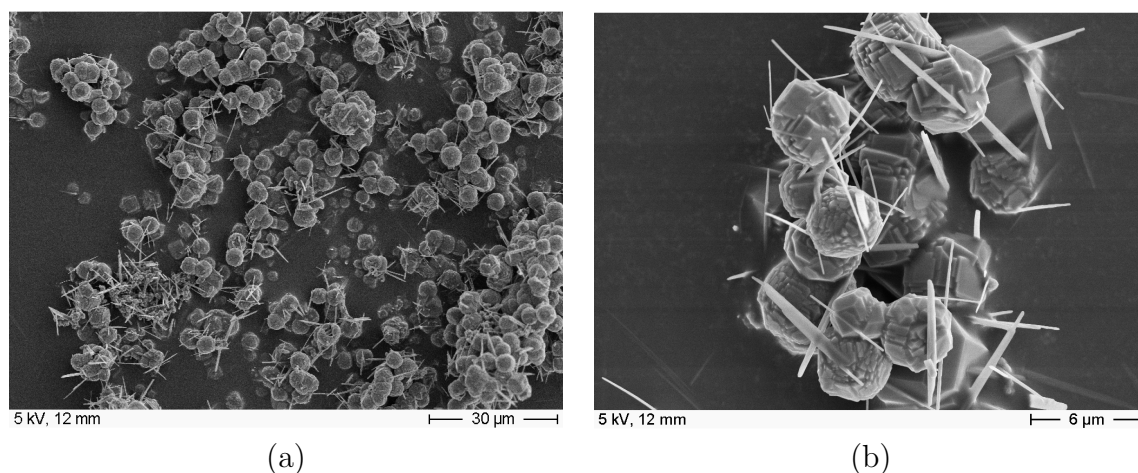


Figure 3.12: SEM images of hydrothermal synthesised Linde Type N zeolite samples at 100 °C, 1 hour.

Figure 3.12 shows the SEM images of the hydrothermal synthesised Linde Type N zeolite. Two morphologies were observed. The majority of the crystals were intergrowths of smaller cubic crystals, which eventually formed aggregates with an average size of 4 μm . Another morphology being observed is the elongated rod with lengths as long as 6 μm . The SEM images presented are known to be the first for Linde Type N zeolite, as none have been reported in the literature.

3.5 Summary

This chapter shows that zeolite synthesis with no organic structure directing agent (OSDA) is challenging, and requires precise control of synthesis conditions. Transformation of zeolite frameworks with similar building units is likely to happen without OSDAs, for example, zeolite A is synthesised hydrothermally at 40 °C but sodalite is formed when the temperature increases to 95 °C. At low temperature, frameworks with lower densities are more likely to form, and *vice versa*. By merely changing the method of crystallization from hydrothermal to microwave, Linde Type N zeolite is synthesised at 60 °C instead of zeolite A. The synthesis of Linde Type N zeolite using a microwave method is new and is the first to be reported in the literature.

Chapter 4

β -cage capacity of water and methanol molecules in siliceous zeolite Y

This chapter is a theoretical study about siliceous zeolite Y using the data obtained from the high pressure study by Colligan et al.[81]. The chapter will start by looking for the flexibility window of siliceous zeolite Y, and to see if the framework will remain in its flexibility window under pressure. The occupation of water and methanol molecules in the beta-cages is then investigated to explain some experimental observation regarding site occupancy. The intrinsic flexibility window of the framework will be distinguished from the newly defined extrinsic window limited by host-guest steric interactions to end the chapter. The study in the chapter has been published in [117].

4.1 Preparation of zeolite Y structure for geometric simulation

In this study, the input is an all-atom crystal structure in P1 symmetry, in this case a single unit cell of the FAU framework containing 192 tetrahedral units (192 Si and 384

framework oxygen atoms) using the Rietveid refined high pressure experimental data obtained on siliceous zeolite-Y by Colligan et al. [81] using methanol-ethanol-water (16:3:1) as a pressure transmitting fluid. The structure is modeled with fixed cell parameters and periodic boundary conditions. Inter-atomic bonding in the SiO_4 unit is represented using a tetrahedral template [118] with a Si-O bond length of 1.61 Å. Framework oxygen atoms are assigned a steric radius of 1.35 Å [119]. Although the geometric simulation method is capable of modelling both SiO_4 and the larger AlO_4 tetrahedra, the input structure in this case is refined as a siliceous structure, and so only SiO_4 units are used in the modelling. A siliceous structure has no interaction between charge-balancing cations and framework oxygen atoms.

A cell parameter can then be imposed on the framework, either from theory or from experimental data. The extra-framework sites can also be populated with a chosen distribution of molecules. Geometric relaxation of the structure reveals whether the framework can accommodate the extra-framework content without distortion of the tetrahedral units. In this case, the structure is “stress-free” within the simplified physical model, lying within its flexibility window. If the structure cannot accommodate without distortions, then it is intrinsically stressed. The a parameter was exposed to a precision of 0.01 Å, e.g. a reported window edge on expansion of 23.46 Å signifies that the structure relaxes at this value but not at $a = 23.47$ Å. The criteria to consider the tetrahedral units as effectively undistorted is for all mismatches between atomic positions and template vertices to be less than 0.001 Å.

A major point of interest in this study is the steric limitation of β -cage occupancy by water and methanol molecules. Given the simplified nature of the geometric simulation, these molecules were represented using a united atom approach. Water molecules are

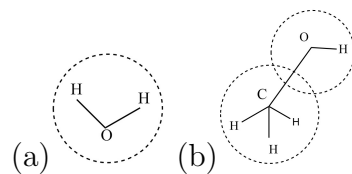


Figure 4.1: Models used in geometric simulation. (a) water molecule (b) methanol molecule

represented as a molecular sphere with a radius of 1.39 Å based on the inter-oxygen distance in water [120]. The larger methanol molecule is represented as a diatomic molecule consisting of a methyl sphere of radius 2.00 Å and a hydroxy sphere of radius 1.39 Å, connected by a bond of 1.40 Å, as shown in figure 4.1 [121, 122].

The behaviour of porous materials under compression can be strikingly different when the pressure transmitting medium contains small molecules that are capable of penetrating the pores and channels of the structure, compared to the case when the medium consists of larger molecules (such as silicone oil) which cannot occupy void spaces within the material [123]. Since the β -cages in siliceous zeolite Y are much more confined than the “supercages” making up the main channel network, the supercage contents are neglected, and the occupation of the β -cages is the main focus.

4.2 Intrinsic flexibility window in FAU framework

I started the simulation with the empty framework structure as refined by Colligan et al. at ambient pressure ($a = 24.24$ Å), and then explored greater cell volumes by increasing the a cell parameter to identify the point at which over-extension of the Si–O bond becomes inevitable, thus defining the upper limit of the flexibility window.

The lower cell volumes are also being explored by decreasing the a parameter to identify the point at which collisions between codimeric framework oxygen atoms can no longer be resolved without distortions of the tetrahedral geometry, therefore defining the lower limit of the window. The intrinsic window obtained lies between $a = 24.46 \text{ \AA}$ and $a = 22.50 \text{ \AA}$. The wide range of the flexibility window and the position of the cell parameter under ambient conditions near the expanded edge are plotted in figure 4.2 along with the ranges of compression observed experimentally.

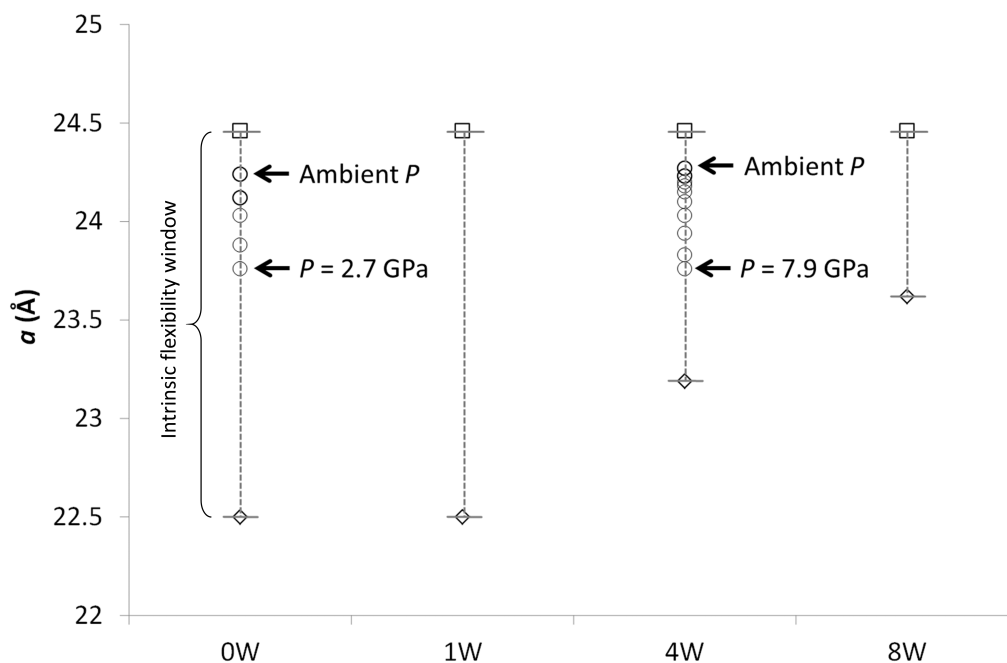


Figure 4.2: Flexibility windows of the FAU framework with a varying water content in the β -cages: 0, 1, 4 or 8 water spheres per cage. The upper (squares) and lower (diamonds) limits of the flexibility window for each case are shown and the extent of the window is shown with a dashed bar. For the 0 water case, circles show experimental data points during compression in silicone oil; for the 4 water molecules case, circles show experimental data points during compression in methanol-ethanol-water. The upper and lower pressure limits of the experimental data are indicated by labelled arrows.

During compression experiments by Colligan et al. without penetrating media, the structure starts to display significant peak broadening at pressures above 2.2 GPa, which is interpreted as the onset of amorphization. At this stage the framework lies

well within the theoretical limits of the flexibility window, with $a = 23.76$ Å at 2.7 GPa as shown in figure 4.2. This observation matches a recent result on silicalite [44], with amorphization occurring while the framework lies within the flexibility window. During compression in the modelling, steric contacts between codimeric framework oxygen atoms first occur when the a parameter reaches 23.00 Å. This indicates that, experimentally, amorphisation in the empty framework sets in well before the framework oxygens would be forced into contact.

In the geometric simulations, Si–O–Si bridging angles are not explicitly constrained. However, in practice the zeolite structures do display a preference for angles in the vicinity of 145° [119] and substantially smaller angles would indicate a degree of strain in the framework. I have therefore examined the angular geometry of the input crystal structure, and of the structure geometrically relaxed under ambient conditions ($a = 24.24$ Å) and at the experimental onset of amorphisation ($a = 23.76$ Å). Four crystallographically distinct populations of bridging angles are identifiable in siliceous zeolite Y. The input structure displays bridging angles of 137° , 149° , 126° and 148° (all values reported to an accuracy of 1°) with a mean around 140° ; essentially the same values are tabulated by Colligan et al. [81]. When the structure is geometrically relaxed under ambient conditions, the four populations become much more similar, with values of 144° , 142° , 139° and 141° . This suggests that the low (strained) values in the crystal structure may be an artefact of the refinement by Colligan et al. At the onset of amorphisation, the values in the relaxed structure are 154° , 129° , 127° and 132° , with a mean around 135° , indicating that a considerable angular strain would exist in the structure at this point and may be the driver of amorphisation.

In the case of silicalite, the framework becomes geometrically stressed during compression with penetrating media [44]. In siliceous zeolite Y, however, the framework remains within its intrinsic flexibility window even with penetrating pressure media, as the smallest cell parameter recorded ($a = 23.76 \text{ \AA}$ at 7.9 GPa) lies well above the limit of the intrinsic window at $a = 22.50 \text{ \AA}$. This difference may be due to the lower framework density of faujasite compared to silicalite (13.3 T nm^{-3} vs. 18.4 T nm^{-3}).

4.3 Steric limits on water occupancy in β -cages

In the experimental investigation by Colligan et al., extra-framework content was notionally modeled as ‘water’ sites. At various stages of compression, the β -cage was refined with one, four or eight water sites, though with partial occupancies less than 1. At low pressures there is a single extra-framework site, Ow(1), at the center of the β -cage, located at the special symmetry position $(1/8, 1/8, 1/8)$. At pressures from 2.7 GPa upwards, this primary site moves off the special position and becomes a tetrahedron of partially occupied sub-sites, Ow(4). As thermal factors could not be refined for these sites, their exact positions should not be over-interpreted; rather, they represent a zone of extra-framework density. At pressures from 3.2 GPa upwards a second extra-framework site, Ow(5), in the β -cage is also occupied. Full population of all extra-framework sites in the modelling corresponds to placing eight water spheres in each β -cage, a level of cage occupation which exceeds that observed experimentally. I have modelled the structure with β -cage contents of one, four and eight water molecules initially placed on extra-framework water sites. The flexibility windows obtained are shown in figure 4.2 on page 58.

A single water molecule per β -cage can be accommodated without affecting the intrinsic flexibility window. As water occupancy increases, the flexibility window narrows, giving an extrinsic flexibility window controlled by host–guest interactions in the β -cages. The sum of partial site occupancies seen experimentally at higher pressures corresponds roughly to the occupation of four water molecules per β -cage. However, even with eight water molecules per cage, the extrinsic flexibility window is wider than the experimentally observed range of cell parameters, indicating that cage occupancies greater than those observed experimentally are sterically possible.

Colligan et al. treated all extra-framework sites as water sites, and made the following comment: ‘There are distances shorter than the van der Waals contacts between Ow(4) and Ow(5) sites in the β -cages...but given the partial occupancies, these will not be simultaneously occupied.’ However, in the case of primary sites, the distance between the sub-sites is approximately 1.6 Å, and the partial occupancy of these subsites is 0.5 or higher for pressures from 2.7 to 5.7 GPa. These partial occupancies imply that at least two of the Ow(4) and Ow(5) sub-sites in each cage are occupied; and yet the 1.6 Å distance between sub-sites is quite incompatible with a water–water contact distance of 2.8 Å. Indeed, the inter-sub-site distance is closer to a typical value for an inter-atomic bond.

The sites as refined within the β -cage form a central tetrahedron of Ow(4) subsites spaced 1.6 Å apart, surrounded by a complementary outer tetrahedron of Ow(5) subsites lying in the 6-ring apertures connecting the β -cage to the supercage (figure 4.3(a)). The Ow(4) sites are in steric clash amongst themselves while the Ow(5)

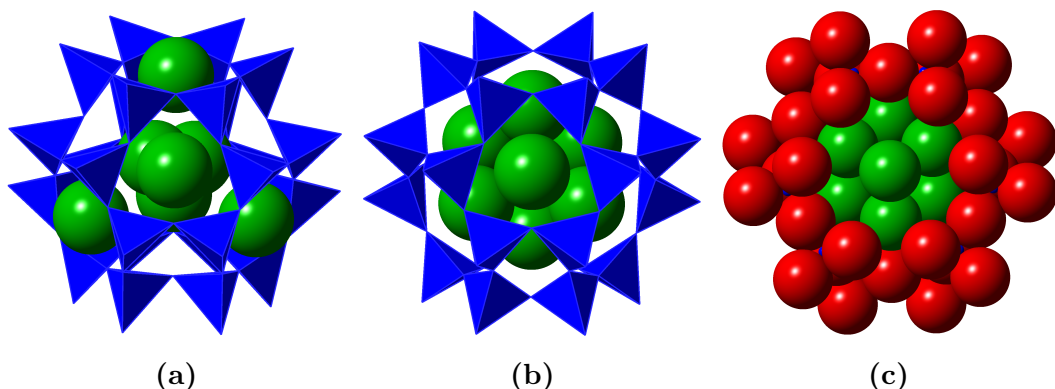


Figure 4.3: (a) A β -cage of faujasite from the crystal structure as refined by Colligan et al. (a tetrahedral framework view), showing the locations of the eight water sites (spheres), (b) A β -cage after geometric relaxation, showing the tetrahedra of the framework and the relaxed locations of eight water spheres, (c) As in (b), with the atoms of the framework shown in space-filling representation; one six-ring of the β -cage has been removed to show the occupation of the interior. The view is in all cases along a crystallographic [1,-1,1] direction.

sites are in a steric clash with framework oxygen atoms in the six-ring. Four water molecules in the simulation, lying initially on the Ow(4) subsites, sterically repel each other to a contact distance of 2.8 Å. Eight water molecules lying initially on the Ow(4) and Ow(5) subsites resolve their steric clash in the simulation, taking up an almost cubic arrangement within the β -cage, as shown in figure 4.3(b). The contrast between the refined extra-framework site positions in figure 4.3(a) and those that are geometrically possible, figure 4.3(b), is very evident.

4.4 Steric limits on methanol occupancy in β -cages

The results of section 4.3 make it doubtful that water molecules in the β -cage can fully account for the extra-framework density observed in the experiments. The presence of a methanol molecule in the β -cage, however, would provide a natural explanation for the presence of two closely adjacent non-hydrogen atoms (C and O) on two

of the Ow(4) sub-sites during compression with a methanol–ethanol–water pressure transmitting fluid. I have therefore investigated the capacity of the β -cages to accommodate methanol molecules as well as water molecules. When introducing methanol molecules into the cage, we initially place the ‘hydroxy’ and ‘methyl’ spheres on two Ow(4) sub-sites in the centre of the cage.

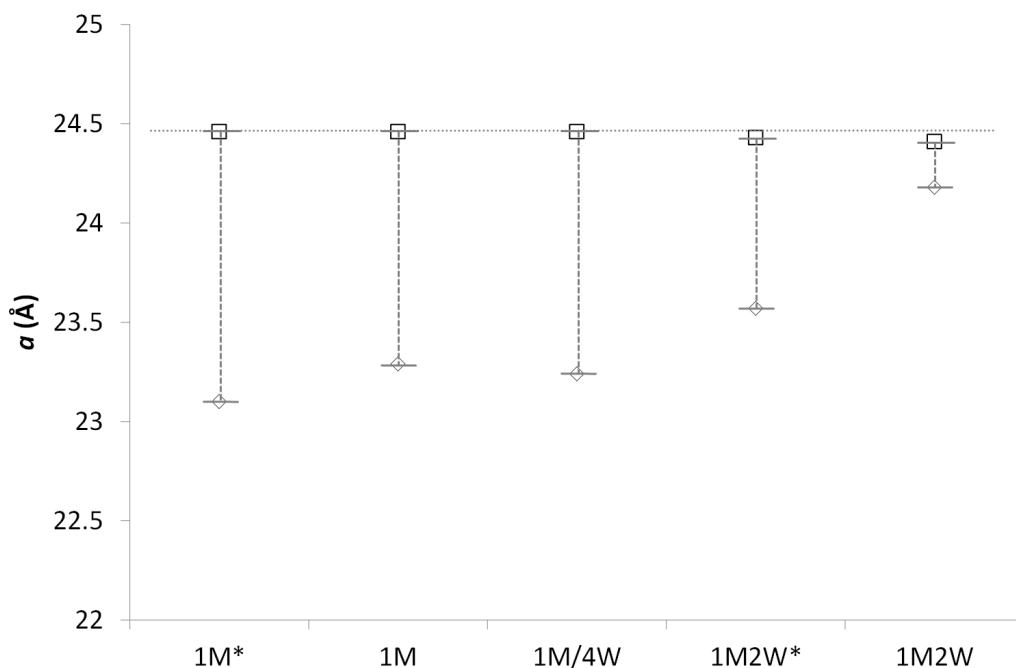


Figure 4.4: Flexibility windows of the FAU framework with varying methanol and water content in the β -cages. 1M* = 1 methanol in one cage, other cages empty; 1M = 1 methanol in each cage; 1M/4W = 1 methanol in one cage, four water molecules in all other cages; 1M2W* = 1 methanol and 2 water molecules in one cage, other cages empty; 1M2W = 1 methanol and 2 water molecules in each cage. The upper (squares) and lower (diamonds) limits of the flexibility window for each case are shown and the extent of the window is shown with a bar. A finely dotted line highlights the contraction of the upper edge of the window in the latter two cases.

Figure 4.4 shows the flexibility windows obtained with methanol in β -cages. Placing a single methanol molecule in one β -cage and leaving the others empty allows the framework to relax over a window from $a = 24.46$ Å to $a = 23.10$ Å. Placing a single methanol molecule within each of the eight β -cages in the unit cell also allows

the framework to relax over an only slightly narrower window, with the lower limit at $a = 23.29$ Å. A structure with one methanol molecule in one cage and four water molecules in each of the others relaxes down to $a = 23.24$ Å. These data suggest that a single methanol molecule is almost interchangeable with four water molecules in terms of β -cage contents.

Two methanol molecules cannot be placed in a single β -cage without introducing stress into the framework. However, some water molecules can share a cage with a methanol molecule. Placing a single methanol molecule and two water molecules in one β -cage and leaving the others empty allows the framework to relax over a window from $a = 24.43$ Å to $a = 23.57$ Å. Here an interesting effect is seen with the cage content causing the flexibility window to become narrower at both the extended and compressed edges; a structure at the limit ($a = 24.46$ Å) of the empty framework is unable to accommodate the cage contents, and must contract slightly to allow the cage to adapt. A similar but a much more marked effect is seen if a single methanol molecule and two water molecules are placed in each of the eight β -cages in the unit cell. In this case the window narrows to the range from $a = 24.41$ Å to $a = 24.18$ Å. This dramatic narrowing illustrates the collective nature of framework flexibility. The β -cages do not accommodate their contents in isolation, but rather through collective motions of the framework polyhedra, which are transmitted to adjacent cages. This behaviour can be considered as a form of an ‘internal auxetic’ effect; near the expanded edge of the flexibility window, expansion of the entire framework effectively contracts the β -cages, preventing them from accommodating bulky contents.

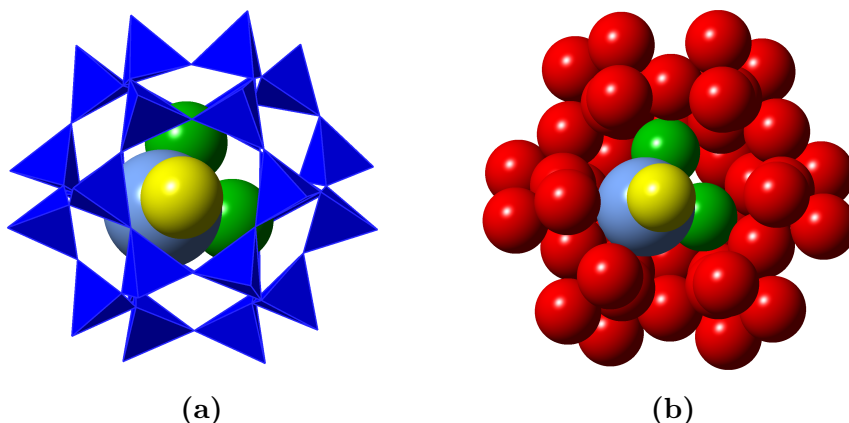


Figure 4.5: (a) β -cage of faujasite, showing the tetrahedra of the framework after relaxation with cage contents of one methanol and two water molecules (spheres). The methanol hydroxy group is the sphere nearest the centre of the image. (b) As in (a), showing the oxygen atoms of the framework in space filling representation. One side of the cage has been removed to view the interior. Both figures are viewed along a crystallographic $[1,-1,1]$ direction.

The geometry of the β -cage containing one methanol and two water molecules is shown in figure 4.5. Note particularly the substantial reorientations of the framework tetrahedra in figure 4.5(a) compared to figure 4.3(b), illustrating the importance of framework flexibility in adapting the cage geometry to bulky contents.

From the result of geometric simulation in section 4.3 and section 4.4, the experimental data of Colligan et al. may provide evidence for the entry of methanol molecules into the β -cages of the FAU framework during compression. This would account for several features of the β -cage occupancy which are difficult to explain if water is the only molecule occupying the β -cage. One of these features is the 50% partial occupancy of the Ow(4) subsites lying only 1.6 Å apart. This concentration of heavy-atom (non-H) sites is sterically forbidden for water molecules but is easily explained by the methanol C and O atoms effectively occupying two adjacent Ow(4) sub-sites. Another is the location of the Ow(5) subsite in an apparent clash with framework oxygen atoms in the 6-ring, and a net occupation of extra-framework

sites in the β -cage corresponding to around four water molecules, when sterically up to eight water molecules could be accommodated without clashes. A disordered arrangement with methanol molecules in some β -cages and varying number of water molecules in others would account for these data. Steric limitations mean that no more than one methanol molecule is able to occupy a β -cage, as two methanol molecules would inevitably cause geometric stress in the framework.

4.5 Access to the β -cage through the six-ring pore

The result of the geometric simulation and the experimental data of Colligan et al. suggested that the β -cage, under certain pressure, is occupied by a methanol molecule. This leaves a fundamental question to be addressed which is the accessibility of the β -cage interior to methanol molecules, as the relatively large methyl group must pass through the small radius of the six-ring aperture. In general, the available aperture depends on the local geometry of an individual six-ring, which may vary considerably; the statistics of such apertures across large structural models can be investigated using Delaunay triangulation [124]. However, the maximum free aperture will be displayed when the six-ring has a regular hexagonal geometry, as any deviation will bring some pair of opposing oxygens closer together, and therefore this limiting case is being investigated.

The aperture can be considered as a hexagon of oxygen sites whose edge length is the edge length of the regular SiO_4 tetrahedron, which is $l_E = 2.63 \text{ \AA}$ (for a Si–O bond length of $l_b = 1.61 \text{ \AA}$ and O–Si–O angle = 109.5° , $l_E = \sin(1/2)(109.5^\circ) * 1.61$

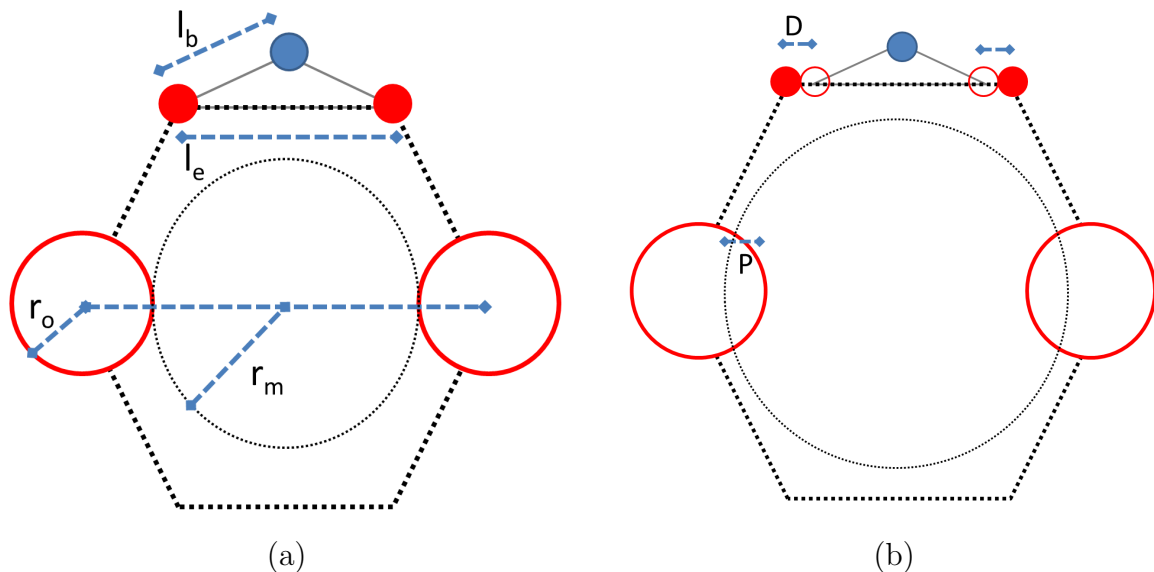


Figure 4.6: (a) Relationship between Si-O bond length l_b , six-ring aperture edge length l_E , framework oxygen radius r_O and the radius, r_M , of the largest molecule that can pass through an unstrained six-ring aperture. (b) Distortions in tetrahedral bonding, D , and steric overlap, P , when larger molecules pass through.

$\text{\AA}^2$). The distance between opposite oxygen centres will be twice the edge length, and the free aperture is this distance less twice the radius of a framework oxygen atom, r_O ; this is $2l_E - 2r_O = 5.26 - 2.70 = 2.56 \text{ \AA}$, the diameter of the largest molecule that could pass without strain in the 6-ring (see figure 4.6(a)). Comparing this to the diameters of the water group ($2.78 \text{ \AA}$) and of the methyl group ($4.0 \text{ \AA}$), both molecules would be excluded from passage through an unstrained six-ring aperture. Therefore, it is necessary to consider what degree of strain is required to permit the molecules to pass.

Two parameters will be needed to describe this situation: the tetrahedral strain D involved in stretching the O-O distance to increase the tetrahedral edge length, and the overlap P as atoms approach more closely than the sum of their radii. If D is the displacement of a framework oxygen atom from its ideal vertex in the tetrahedron,

the edge length is now $l_E^* = l_E + 2D$, and the distance between opposite oxygen vertices in the strained six-ring will now be given by $2l_E^*$. If a molecule with a radius r_M is passing through the aperture, this distance must be equal to $2r_O + 2r_M - 2P$. These parameters are illustrated in figure 4.6(b).

The strain required by equating D and P is estimated, so that all deviations from the ideal geometry, steric or bonding, are equal in magnitude. Setting $P = D$, then $2(l_E + 2D) = 2r_O + 2r_M - 2D$, hence $D = (1/3)(r_O + r_M - l_E)$. The passage of a water group with $r_M = 1.39 \text{ \AA}$ requires a distortion of $D = 0.03 \text{ \AA}$. Using the methyl radius $r_M = 2.00 \text{ \AA}$, a required strain of $D = 0.24 \text{ \AA}$ is obtained. This degree of compression requires the methanol and framework oxygen groups to approach to about 90% of their contact distance, presenting a significant but not insuperable barrier to entry. The appearance of the multiple Ow(4) site within the β -cage at a pressure of 2.7 GPa may therefore mark the point at which the pressure is sufficient to drive methanol, the major component of the pressure-transmitting medium, into the β -cages of faujasite.

4.6 Chapter summary

The influence of explicitly present extra-framework contents is addressed by the “flexibility window” concept. Low loadings of water within the faujasite β -cage do not affect the flexibility window, which on compression is limited by collisions among codimeric framework oxygen atoms, as in the empty framework. Higher loadings of water or methanol lead to a different behaviour in which the flexibility window on compression is limited by collisions between the framework oxygens and extra-framework contents. Therefore the intrinsic flexibility window of the empty framework and the

extrinsic window at higher loadings can be distinguished.

An unexpected feature of the extrinsic window is that it can be narrower than the intrinsic window not only in compression, but also in extension. It is intuitive that the presence of extra-framework content should naturally impose a steric limit on the window in compression. The effect on extension is more subtle; near the expanded edge of the window, the cages in the structure lack the freedom to adapt to the shape of bulky contents such as a combination of methanol and water molecules.

Analysis of structural data on the siliceous faujasite framework under compression, using geometric simulation, indicates that the framework remains within its flexibility window over a wide range of pressures, with or without penetrating pressure-transmitting media. The onset of amorphization during compression without penetrating media occurs while the framework is well within its flexibility window. The geometric simulations indicate that the distribution of the extra-framework content in faujasite within the β -cages at higher pressures (2.7 GPa and above) may be accounted for the presence of methanol molecules within some of the β -cages.

Chapter 5

Synthesis and framework flexibility of zeolite EMC-2

In this chapter, I will first describe the synthesis of zeolite EMC-2 using an organic structure directing agent - a crown ether molecule named 18-crown-6. The chapter will then move on to a theoretical study by geometric simulation to see if the 18-crown-6 molecule, which occupies specific cages of the EMT framework, will affect the flexibility window [125].

5.1 Synthesis of zeolite EMC-2

Zeolite EMC-2 was synthesised using 25.32 g colloidal silica (Ludox HS-30, 30 wt% SiO₂, Aldrich), 2.41 g sodium aluminate (Al₂O₃ 50-56%, Na₂O 40-45%, Sigma-Aldrich), 2 g sodium hydroxide solution (50% in H₂O, Sigma-Aldrich), and 13.14 g deionised water. Crown ether (18-crown-6, Aldrich) was used as an organic structure directing agent [82]. Sodium hydroxide solution was first added to deionised water, followed by sodium aluminate and 18-crown-6. The solution was stirred for an hour under ambient condition. Colloidal silica was then added and stirred vigorously for another 30 minutes. The resulting gel was incubated for 24 hours at room

temperature, sealed into a 64 ml stainless steel autoclave, and placed into an oven for 12 days at 110 °C. The as-synthesised zeolite was washed with deionised water to remove excess crown ether. The sample was then dried in an oven for 24 hours at 120 °C. Calcination was done at 300 °C under vacuum for 6 hours using a tube furnace (Lenton) with the following program setting: ramp at 1 °C per minute from 20 °C to 300 °C with dwelling for two hours at 100 °C and 200 °C respectively, followed by a 2 °C per minute drop down to ambient condition.

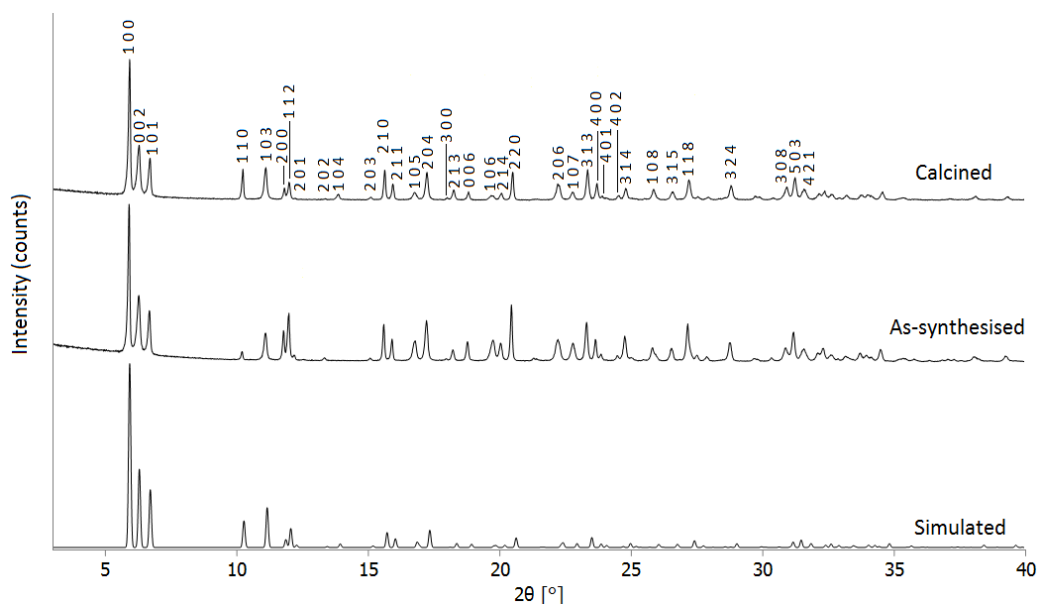


Figure 5.1: Powder pattern of as-synthesised and calcined zeolite EMC-2.

The powder patterns of the as-synthesised zeolite EMC-2 before and after calcination are shown in figure 5.1. The powder pattern of the calcined zeolite EMC-2 remained almost unchanged, compared to the sample before calcination. The hexagonal unit cell parameters of the as-synthesised and calcined zeolite EMC-2 are $a = 17.761(4)$ Å, $c = 28.029(8)$ Å, and $a = 17.769(5)$ Å, $c = 28.010(8)$ Å respectively, which is close to each other, and very closed to the suggested value reported by the

“Database of Zeolite Structures” - $a = 17.215 \text{ \AA}$, and $c = 28.082 \text{ \AA}$. Elemental analysis of the as-synthesised zeolite sample shows that there is 8 wt% of carbon, indicating the presence of crown ether in the pores of the zeolite. However, after calcination, a significant drop of carbon content is observed - only 0.11 wt% remains in the sample suggesting a successful calcination.

Four Si local environments are observed in the ^{29}Si MAS NMR spectrum of the calcined sample (figure 5.2) [126]. Chemical shifts at -88.98 ppm, -94.38 ppm, -100.25 ppm, and -106.03 ppm can be assigned to the local Si(4Al), Si(3Al), Si(2Al), and Si(1Al) environments respectively. The calculated Si/Al ratio is 1.89 (65.39% Si), which is lower than the suggested 79% Si by Delprato et al. [82]. ^{27}Al MAS NMR shows only a single peak at 59.29 ppm indicating all aluminium atoms are tetrahedrally-coordinated to Si atoms.

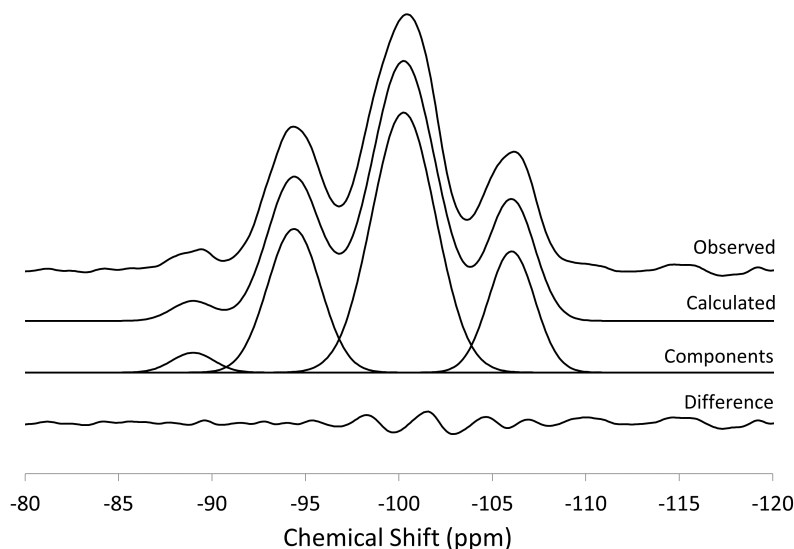


Figure 5.2: ^{29}Si MAS NMR of calcined zeolite EMC-2.

The morphology of zeolite EMC-2 before and after calcination is shown in figure

5.3. It is synthesised as hexagonal plates. No change in morphology is observed before and after calcination. Crystals are uniform in shape and approximately $2.5\ \mu\text{m}$ in size.

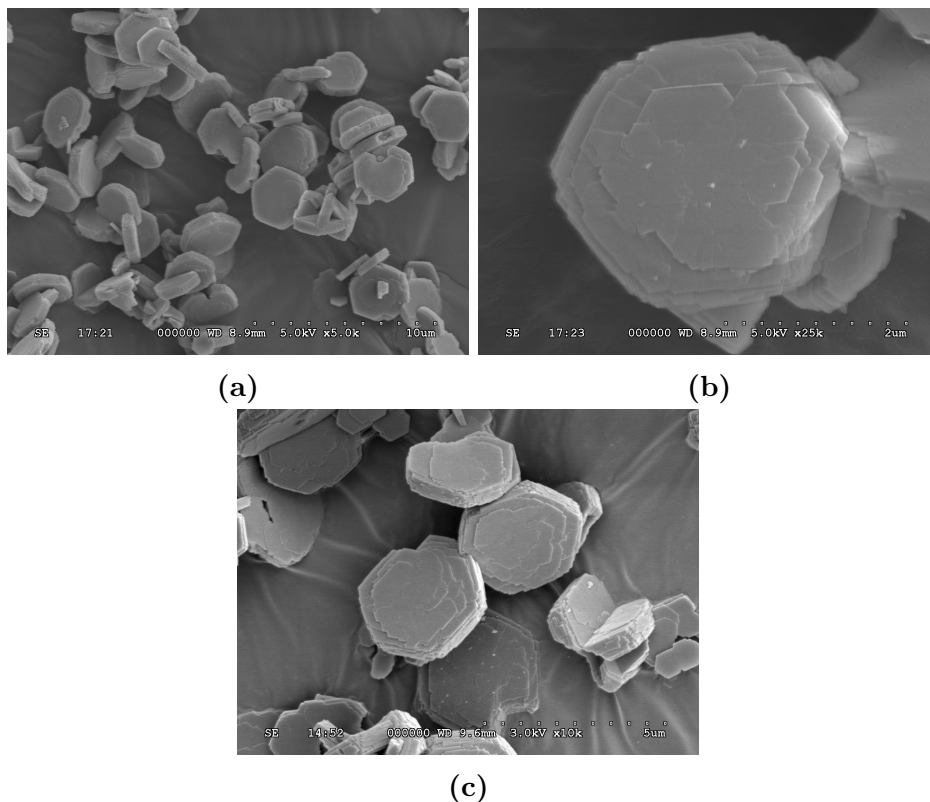


Figure 5.3: SEM images of zeolite EMC-2: (a) as-synthesised, (b) close-up of the as-synthesised sample, (c) calcined

5.2 Flexibility window in EMT zeolite framework

For the synthesis of zeolite EMC-2, crown ether (18-crown-6) is regarded as an essential organic structure directing agent [82]. The center of the 18-crown-6 ether ring can accommodate cations such as sodium and form the 18-crown-6/Na complex. It is concluded that such a complex matches the geometry of the smaller supercages present which leads to development of the EMT framework [49, 127]. In this section,

geometric simulation is used to study the flexibility window of the hexagonal EMT framework in both its calcined (empty) and crown-ether containing (as-synthesised) forms, and determine whether crown ether controls an extrinsic flexibility window in EMT zeolite framework.

5.2.1 Preparation of EMT structure for geometric simulation

The all-atom input structure comprises a single EMC-2 (EMT) unit cell in P1 symmetry, using the coordinates obtained by Baerlocher et al. through Rietveld refinement [48]. Each unit cell contains 96 tetrahedral units and the hexagonal unit cell parameters of the ambient structure are $a, b = 17.37 \text{ \AA}$, $c = 28.36 \text{ \AA}$. The framework was modelled with T–O bond length of $1.63 \text{ \AA}$ to reflect the presence of a small proportion of aluminium in the structure. The results are not sensitive to the bond length: use of a shorter bond length of $1.61 \text{ \AA}$, for pure silica, in this case slightly contracts the window but does not change its shape or character. The steric radius of oxygen in the framework, a key controlling parameter in the intrinsic flexibility window, was set at $1.35 \text{ \AA}$ as is conventional [119].

In the study of Baerlocher et al. [48], the as-synthesised crystal structure has well-resolved 18-crown-6 ether molecules in the smaller *t-wof* cavities; in the crystallographic average structure, each cavity contains a superposition of two such molecules with 50% occupancy. Since there is room in the cavity for only one molecule, its orientation - facing up or facing down - is random. For the input structure in my simulation, a single copy of the ether molecule was retained in each of the two *t-wof*

cavities in the unit cell, one in each of the two possible orientations. The bond lengths and angles in the crown ether are taken from the input structure. Bonds are assigned in GASP between the central Na ion and its three coordinating oxygens to maintain the geometry of the complex. Since the hydrogen atoms in the CH₂ groups of the ether are not resolved, a suitable effective radius must be assigned to the carbon atoms by considering the closest approach between an ether C and a framework O atom in the crystal structure and this distance is 2.95 Å. A radius of 1.60 Å (C–O contact distance - radius of O atom = 2.95 Å - 1.35 Å) is therefore assigned to the ether carbons, so that the ether is just in contact with the framework initially. Rotation is permitted around all C–C and C–O bonds in the molecule, and the ether is not tethered to the framework so it is able to move and flex in response to changes in the cage geometry.

The presence of crown ether is detectable in the larger *t-wou* cages. However, these molecules are partially disordered and only some of the heavy atoms are resolved, indicating both positional and orientational disorder. Given this disorder and the larger size of the cavity, the modeling of crown ether molecules in the *t-wou* cages was not attempted, but rather the disordered molecules were neglected, so as all other water and sodium ions. This study therefore makes use of two input structures, one with crown ether molecules present in the *t-wof* cavities, and one without any extra-framework content which represents the empty framework.

5.2.2 The flexibility window of EMT framework

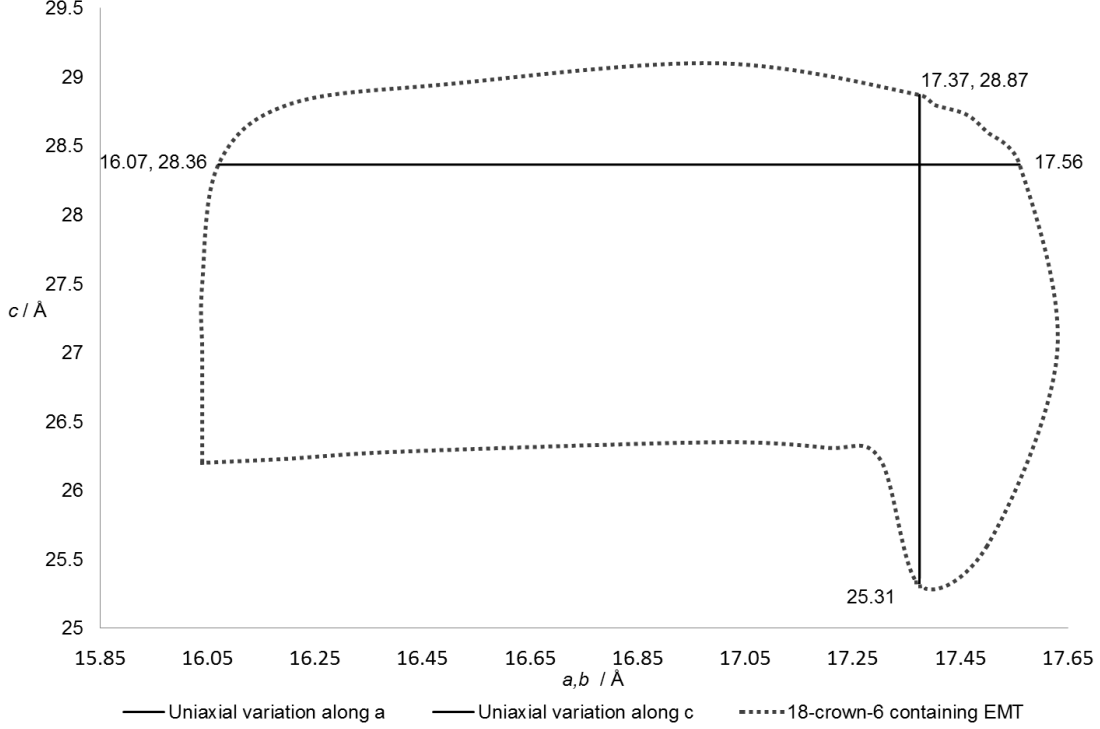


Figure 5.4: Extent of the flexibility window for the EMT framework during variation of the a and c parameters

Since EMT is a hexagonal structure, its flexibility window is defined by variations of the two independent cell parameters, $a(=b)$ and c . An initial investigation of the intrinsic flexibility window in EMT framework comprised the exploration of uniaxial variation of the parameters to an accuracy of 0.01 Å. The a parameter can be expanded slightly to 17.56 Å, corresponding to a 2.15% increase in unit cell volume, before the onset of extension in the Si–O bonds. In compression the parameter can be reduced substantially to 16.07 Å, reducing the initial ambient unit cell volume by 16.89%. For uniaxial variation along the c parameter, a similar trend is observed. The parameter can be extended to 28.87 Å, equivalent to a 1.78% expansion in unit cell

volume, compared to a 10.76% decrease in volume on compression to 25.31 Å. These limits, represented as solid, linear lines in figure 5.4 on the previous page, describe the uniaxial confines of the intrinsic flexibility window for empty EMC-2.

Having established the preliminary limits to EMT framework flexibility, the next step was to determine points lying along the perimeter of the flexibility window. The results are depicted in figure 5.4 as dotted lines. The window has an almost rectangular shape in the a, c plane, showing that there are substantial areas of phase space within which the parameters can be independently varied. In detail, however, the window has a strikingly nontrivial, “speech-bubble” shape, showing that at the limits of compression, there are complex interactions between the mechanisms of compression along different directions.

The next step was to carry out the same exploration of the flexibility window with Na^+ /crown ether complexes present in the *t-wof* cages of the EMT framework. The crown ether is a bulky molecule which effectively fills one side of the *t-wof* cage, with the sodium ion and its coordinating ether oxygens lying in the mid-plane of the cage. The structure with crown ethers present is shown in figure 5.5 on the following page. As noted, the ether carbon radius was chosen so that the ether is already in steric contact with the framework in the input structure. Therefore a substantial contraction of the flexibility window would be expected when the ether OSDA was included in the simulation. The result obtained is in fact entirely different: the EMT framework with crown ethers included displays an identical flexibility window to the empty framework. The window illustrated in figure 5.4 thus also applies to the framework with ethers present. The ether molecule has sufficient geometric flexibility

that it can adapt to the contraction of the *t-wof* cage during the simulations, and the flexibility window remains under the control of intrinsic framework factors. A striking example of this adaptation is illustrated in figure 5.6 on the next page, which shows the structure at the limit of compression of the *c* and *a* parameters. The cage itself displays substantial compression, and the ether molecule is in steric contact with the surrounding framework, yet the molecule can adapt to its surroundings so that it does not limit the contraction of the framework, and the degree of steric overlap remains on the order of 0.01 Å or less.

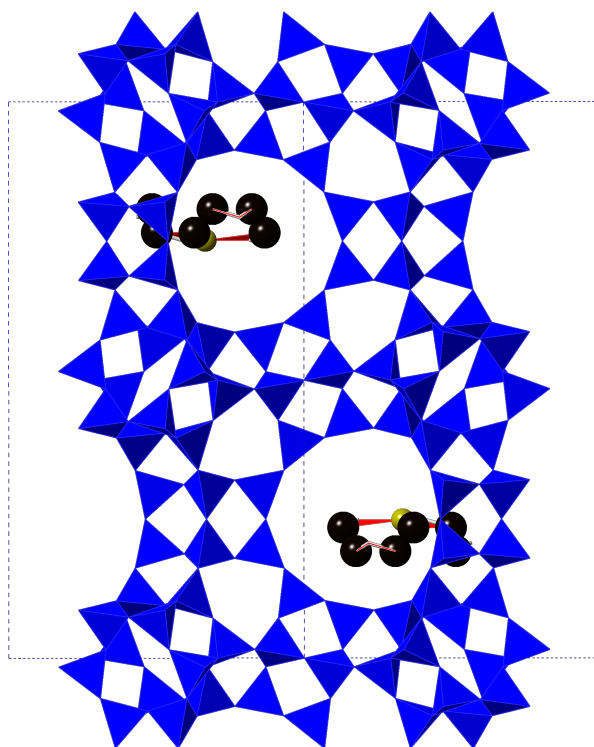


Figure 5.5: EMT framework under ambient conditions showing the location of well-resolved crown ether molecules in the *t-wof* cages

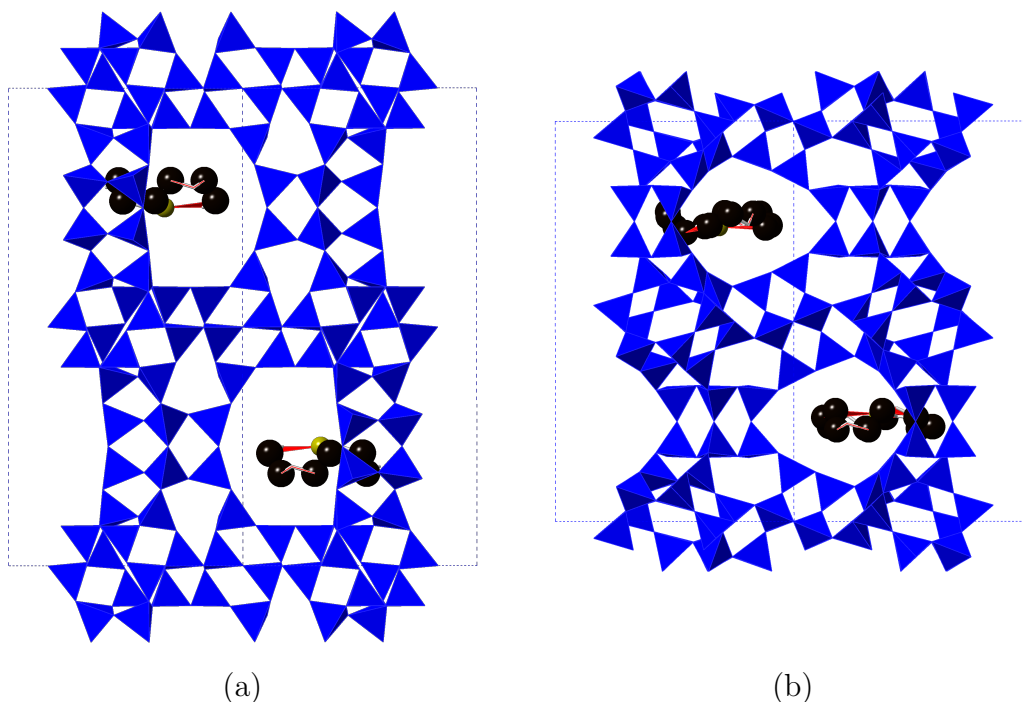


Figure 5.6: (a) EMT framework at the limit of geometric compression of the *a* parameter; (b) EMT framework at the limit of geometric compression of the *c* parameter.

5.3 Chapter summary

Zeolite EMC-2 is synthesised using crown ether, 18-crown-6. The powder pattern of the calcined form is identical to the as-synthesised zeolite sample. ^{29}Si MAS NMR shows four Si local environments, and all Al are tetrahedral-coordinated in the framework. Hexagonal crystals are observed using SEM with an average size of $2.5\ \mu\text{m}$.

The geometric simulation reveals that the intrinsic flexibility window, by varying the *a* and *c* parameters, is in a “speech-bubble” shape. No difference between extrinsic and intrinsic flexibility window is observed when the simulation only includes crown ether molecules in the *t-wof* cages; the ether molecule has sufficient geometric flexibility which can adapt to the contraction of the *t-wof* cages.

Chapter 6

Framework flexibility of sodalite under pressure

In this chapter, I will first describe the preparation of two different forms of sodalite - the hydroxy form and the sodium bromide form. High pressure experiments were done using these two samples. The frameworks response differently to the compression depending on the pressure transmitting media being used during the experiments. Such behaviors can be explained by geometric simulation of four SOD frameworks with various composition, which results will be present at the end of this chapter.

6.1 High-pressure experiment

Two different forms of sodalite were prepared before the high pressure experiment: Na-sodalite (Na-SOD) with no OSDA and NaBr-sodalite (NaBr-SOD) with bromide ion following recipes modified from Stem et al. [52], with batch composition $\text{Al}(\text{OH})_3:\text{SiO}_2:5\text{NaOH}:41\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3:\text{SiO}_2:12.5\text{NaOH}:7.5\text{NaBr}:144\text{H}_2\text{O}$ respectively. In the synthesis of Na-SOD, aluminium hydroxide and fumed silica were dissolved separately in water with sodium hydroxide, and heated to 95 °C. The silica solution and aluminium hydroxide solution were then mixed together and stirred vig-

orously for 5 minutes. The gel was put in an oven at 95 °C for 24 hours. The synthesis of NaBr-SOD was the same as Na-SOD, *e.g.* temperature, reaction time, starting material, but using sodium bromide as a template. The as-synthesised zeolites were then dehydrated under vacuum to remove water.

Figure 6.1 shows the powder patterns of the as-synthesised Na-SOD and NaBr-SOD zeolites. Both samples have no impurity, the only difference is that NaBr-SOD has a bromine ion that sits inside the β -cage while Na-SOD is relatively empty.

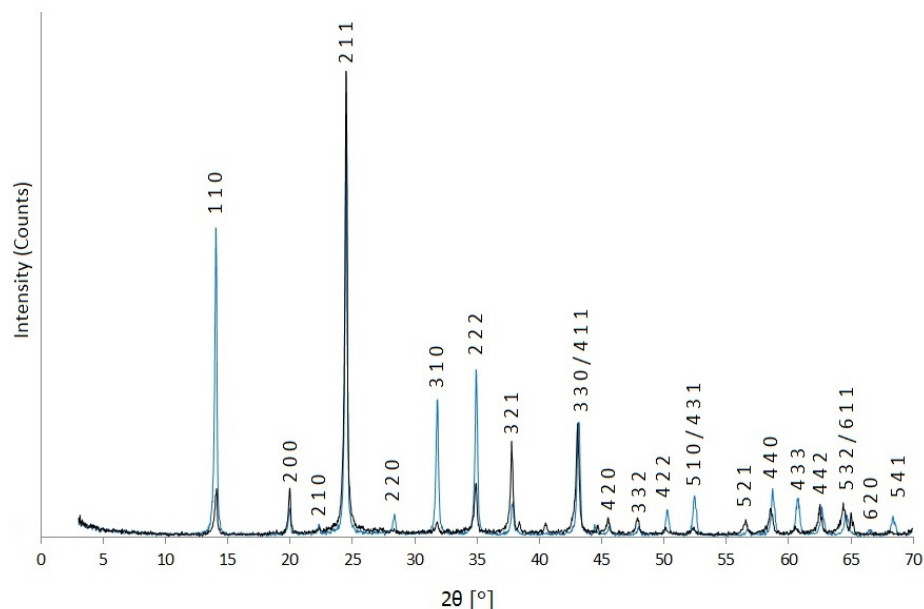


Figure 6.1: Powder patterns of as-synthesised Na-sodalite (Blue) and NaBr-sodalite (Black).

High-pressure neutron diffraction experiments were carried out on PEARL beamline, ISIS (a time-of-flight neutron diffractometer with Paris-Edinburgh (PE) cell) to observe the response of framework under varying pressures. Ethanol/methanol mixture and fluorinert (C_6F_{14}) were used as pressure transmitting media. Ethanol/methanol mixture is a penetrating medium which enters the SOD framework while fluorinert re-

mains outside the framework and is a non-penetrating medium. A lead pellet inside the gasket was used for pressure calibration. For the experiment with NaBr-SOD using an ethanol/methanol mixture, 15 pressure points were measured from ambient pressure up to 6 GPa. For Na-SOD, 4 pressure points were measured using the ethanol/methanol mixture, and 7 pressure points for fluorinert.

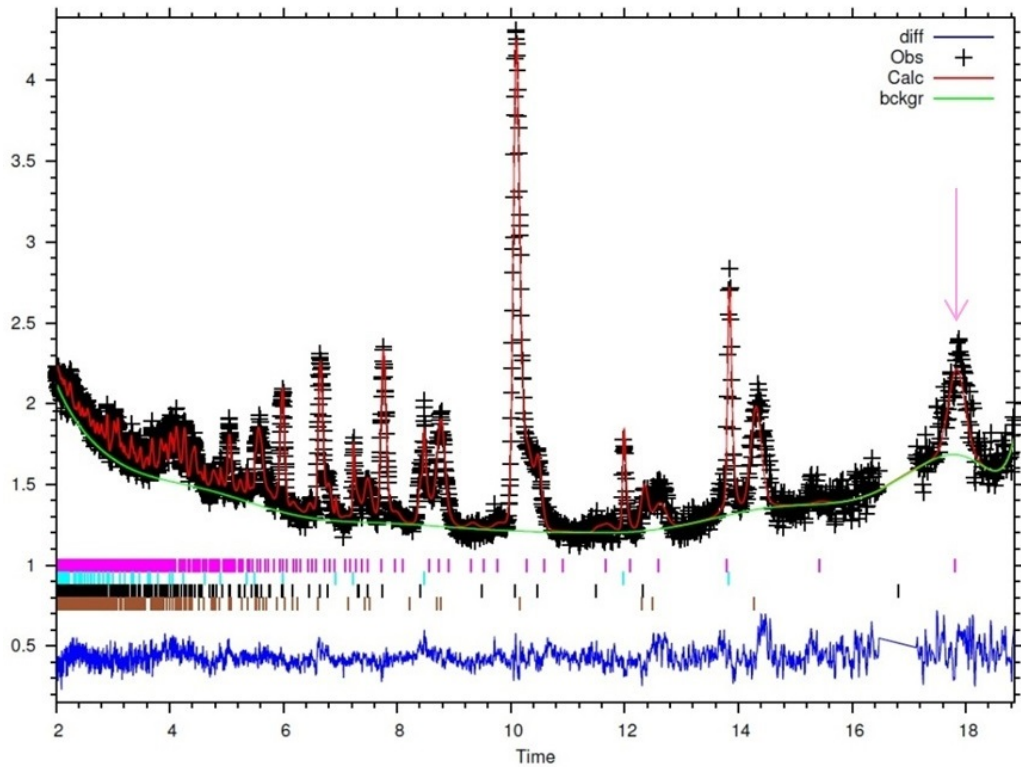


Figure 6.2: GSAS refinement of the experimental Na-SOD neutron diffraction data at pressure 0.05GPa. Four phases are fitted here - Na-SOD (pink), lead (blue), alumina of the PE cell and gasket (black), and zirconia surrounding the gasket (brown). Pink arrow indicates the Na-SOD 211 peak, the only peak which does not overlap with other phases.

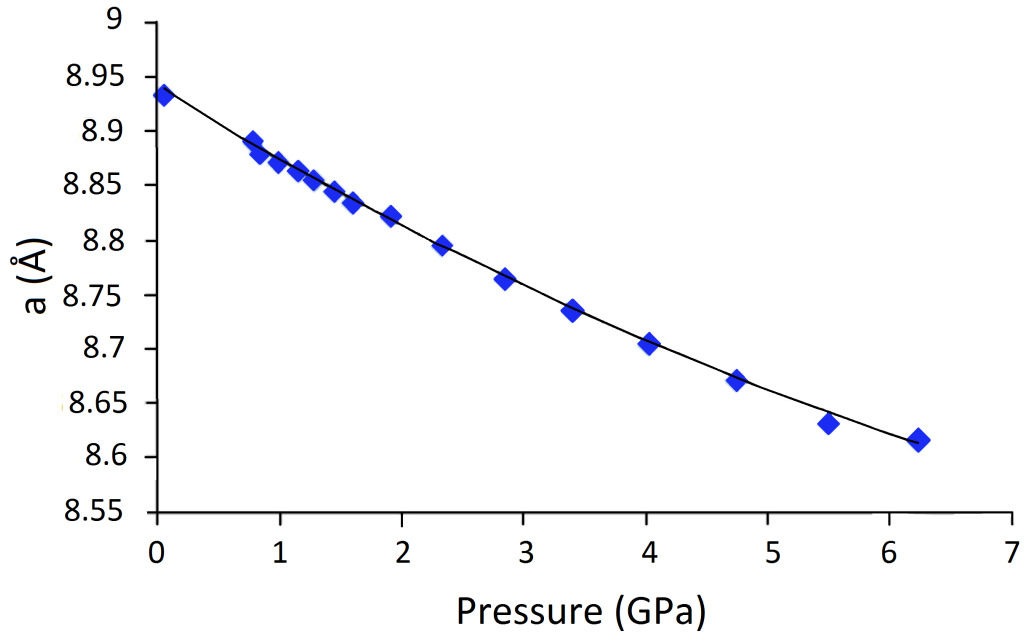
General Structure Analysis System (GSAS) [128] was used to refine all high-pressure data. Figure 6.2 is an example of the Na-SOD GSAS refinement at 0.05 GPa. The neutron diffraction pattern consists of four different phases - Na-SOD (pink), lead (blue), alumina of the PE cell and gasket (black), and zirconia surrounding the gasket

(brown). The Na-SOD 211 peak, labelled by the pink arrow, is the only peak that does not overlap with any other phases. The actual pressure of the sample is calculated using GSAS refinement of a lead pellet and the Birch-Murnaghan equation of state (EOS) [129], as shown in equation 6.1, where P is the pressure (in GPa) experienced by the sample. V_0 , B_0 and B'_0 are the volume, bulk modules, and its derivative at ambient pressure, respectively.

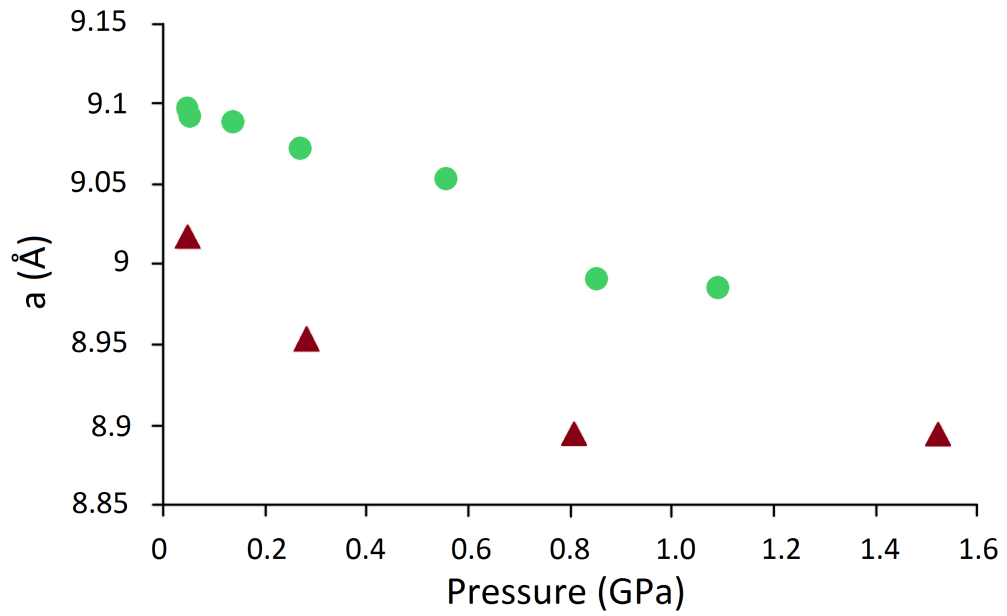
$$P = 1.5B_0 \left[\left(\frac{V}{V_0} \right)^{-7/5} - \left(\frac{V}{V_0} \right)^{-5/3} \right] \left[1 + 0.75 (B'_0 - 4) \left(\left(\frac{V}{V_0} \right)^{-2/3} - 1 \right) \right] \quad (6.1)$$

The cell parameter and volume for NaBr-SOD decreases smoothly with pressure, this can be seen from figure 6.3(a). Figure 6.4(a) shows the time-of-flight diffraction data of NaBr-SOD under varying pressures. The 211 peak can be clearly seen up to 4 GPa. Above 4 GPa, this peak merges with the alumina peak. However, from the powder pattern, it is observed that the zeolite remains crystalline at least up to 4 GPa.

The refined Na-SOD cell parameter under various pressures with methanol/ethanol mixture and fluorinert at 0.05 GPa is 9.02 Å and 9.10 Å respectively (figure 6.3(b)). The difference is due to the internal screening effect of polar molecules inside the framework of Na-SOD. As a result, the framework of Na-SOD shrinks slightly in the presence of the methanol/ethanol mixture, having a smaller cell parameter. It is known that a methanol molecule is small enough to occupy a β -cage (chapter 4). The cell parameter of Na-SOD (red triangles) decreases from 9.02 Å at 0.05 GPa to 8.90 Å at 0.81 GPa, then flattens out. This behaviour is seen because after a certain pressure, the methanol molecules in the β -cage act as scaffolding and the framework cannot

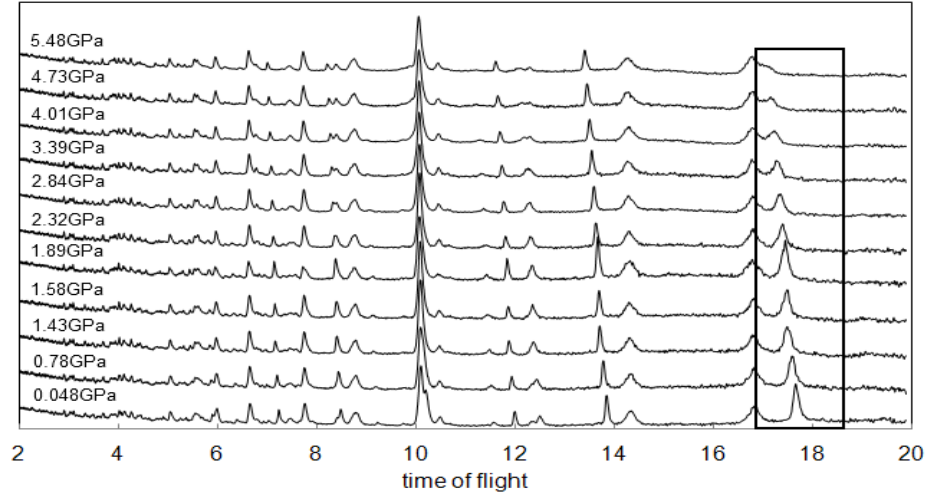


(a)

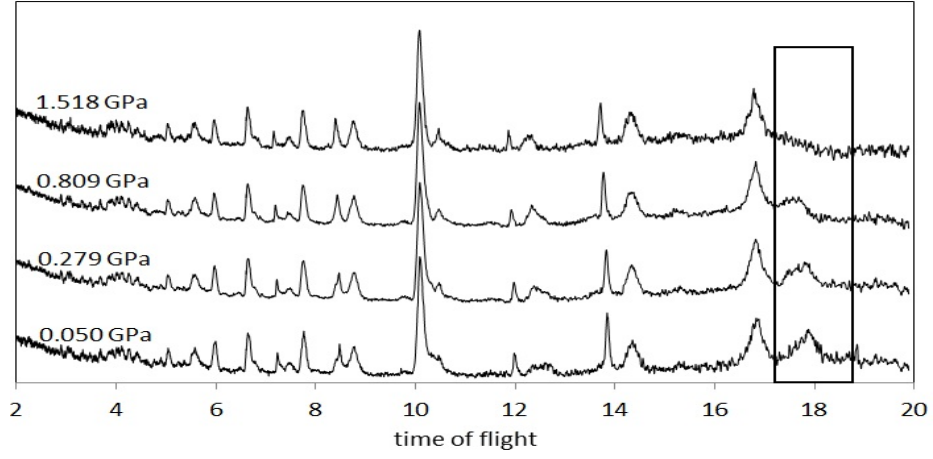


(b)

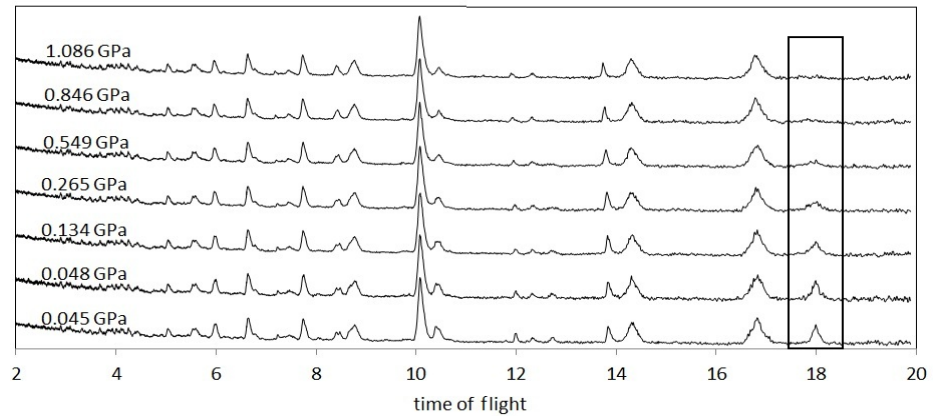
Figure 6.3: Cell parameters vs pressure. a) Cell parameter, a , against pressure of NaBr-SOD with methanol/ethanol mixture fitted to the Birch-Murnaghan equation of state (EOS); b) Cell parameter, a , against pressure of Na-SOD with methanol/ethanol mixture and fluorinert as pressure transmitting media: green circles - with fluorinert, red triangles - with methanol/ethanol mixture. Error bars are not significant compared to the data presented.



(a)



(b)



(c)

Figure 6.4: Time-of-flight neutron diffraction data of: a) NaBr-SOD with methanol/ethanol mixture as pressure transmitting medium, b) Na-SOD with methanol/ethanol mixture, and c) Na-SOD with fluorinert, as pressure transmitting medium.

be compressed around it anymore without distortions. The experimental neutron diffraction data is shown in figure 6.4(b).

A different picture is seen with fluorinert. Unlike the ethanol/methanol mixture, fluorinert is a very bulky molecule that cannot enter the SOD framework. In figure 6.3(b), the cell parameter of Na-SOD (green dots) decreases from 9.10 Å at 0.05 GPa to 9.06 Å at 0.55 GPa and there is a sudden drop between 0.6 and 0.8 GPa. After 0.8 GPa, the framework amorphises, since it is mostly empty without any scaffolding molecules within the β -cage. This manifests in dramatic change in the cell parameter and loss in the intensity of most diffraction peaks can be seen in figure 6.4(c).

6.2 Geometric simulation on sodalite

6.2.1 Preparation of sodalite structure for geometric simulation

The input structure of sodalite for geometric simulation is very similar to siliceous zeolite Y in chapter 4 and EMC-2 in chapter 5. In this case, a single unit cell of SOD framework consists of 12 tetrahedral units (12 Si or Al, and 24 framework oxygen atoms) in P1 symmetry. The structure is modeled with fixed cell parameters and periodic boundary conditions. Inter-atomic bonding in the SiO_4 unit is represented using a tetrahedral template with a Si-O bond length of 1.61 Å. The simulation contains Al tetrahedral units, where the inter-atomic Al-O bond length is set to be 1.75 Å. Framework oxygen atoms, extra framework sodium and bromide ions are assigned a steric radius of 1.35 Å, 1.02 Å, and 1.94 Å respectively.

Several different simulations were done and a summary is shown in figure 6.5. Se-

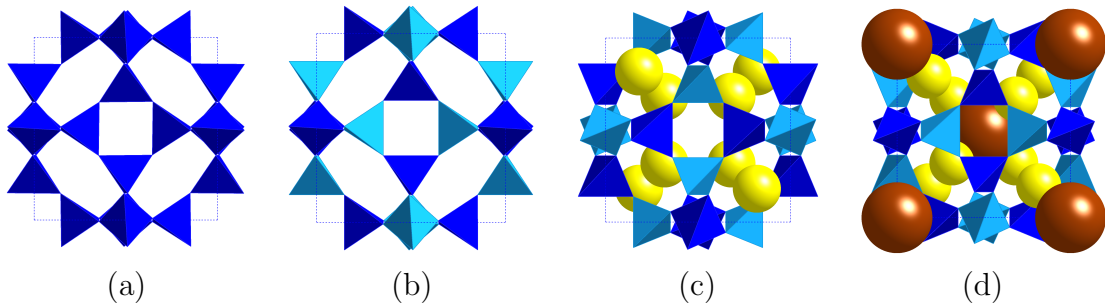


Figure 6.5: Different simulations with SOD frameworks. a) Empty framework with only SiO_4 tetrahedra, b) empty ordered $\text{Si}/\text{Al} = 50/50$ framework, c) Na-SOD framework with Na as yellow spheres, and d) NaBr-SOD framework with Br in brown, and Na ions in yellow. SiO_4 tetrahedral unit is shown in blue and AlO_4 tetrahedra in cyan.

ries 1 (figure 6.5(a)) is a simulation of a hypothetical empty siliceous SOD framework in which all polyhedra are identical and have the Si–O bond length. The simulation cell contains 12 Si atoms and 24 vertex oxygen atoms. In this case, a range of cell parameters is explored for the cubic unit cell, so as to determine the theoretical width of the flexibility window. Series 2 (figure 6.5(b)) is a simulation of an empty ordered Si/Al SOD framework in which alternate neighboring polyhedra have Si–O and Al–O bond lengths. The simulation cell contains 6 Si atoms, 6 Al atoms, and 24 vertex oxygen atoms. This simulation is intended to represent the case where the polyhedra of the ordered framework can rotate freely without steric hindrance from the framework contents. Series 3 (figure 6.5(c)) is an ordered framework with sodium atoms. In this series, the simulation is an ordered Si/Al framework with 8 Na atoms in the β -cage. This exceeded the experimental number of Na atoms, which was 6, but since it was hard to refine the precise position of all Na atoms, an excess number was used. Series 4 (figure 6.5(d)) is a simulation of an ordered Si/Al SOD framework in which sodium and bromine channel contents are explicitly present as spheres. In simulations

containing AlO_4 tetrahedral units, another set of simulation was run. Instead of a rigid tetrahedral AlO_4 template, a “softer” AlO_4 unit is used by setting the internal O–Al–O bond angle free.

6.2.2 The flexibility window of sodalite

Firstly, a simulation is done to locate the flexibility window of the SOD framework in the hypothetical siliceous form, as shown in figure 6.6. As expected, the framework displays a broad flexibility window. The most expanded end of the flexibility window lies at $a = 8.98 \text{ \AA}$; further expansion above this limit causes over-extension of Si–O bonds. As the a parameter is reduced to compress the unit cell, steric contacts between codimeric oxygens first occur at $a = 7.35 \text{ \AA}$, and distortion of the tetrahedra becomes inevitable on compression below $a = 6.50 \text{ \AA}$.

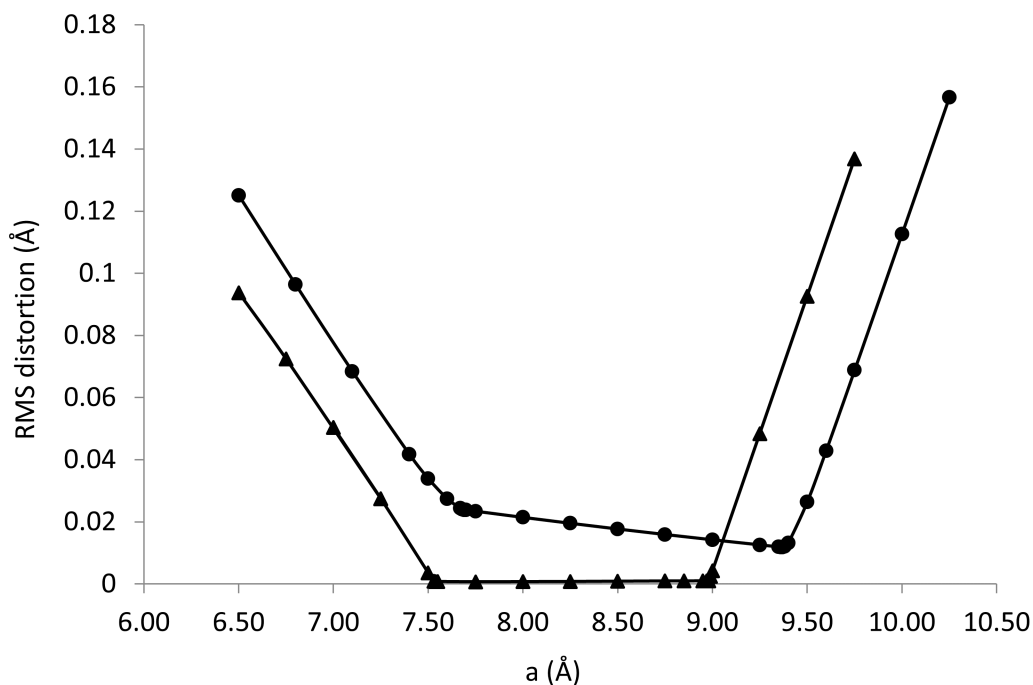


Figure 6.6: Flexibility window of SOD framework in the hypothetical siliceous form (triangles) and the fully ordered Si/Al form (circles) with Al centered tetrahedra geometry.

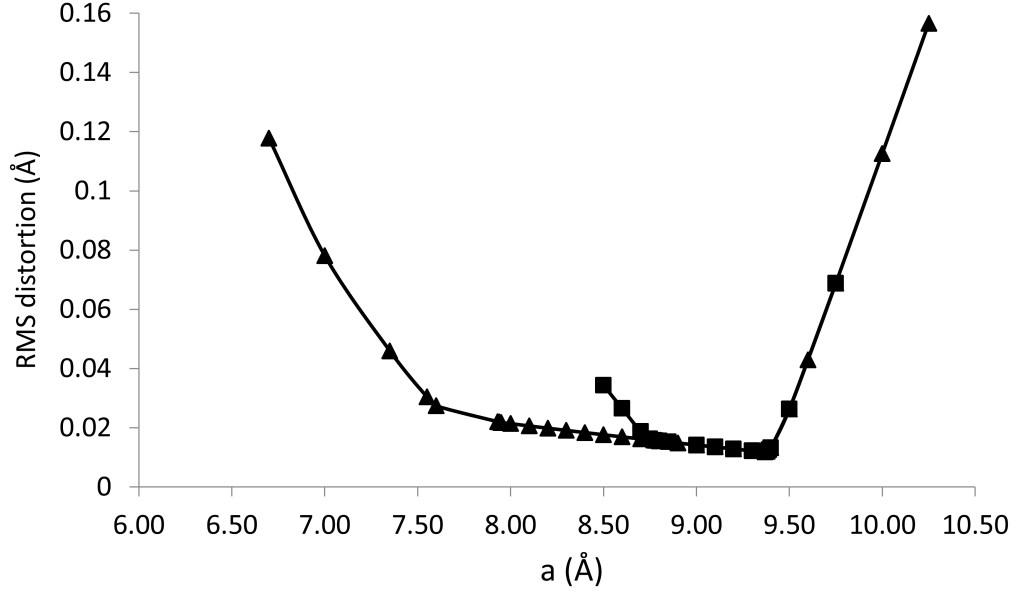


Figure 6.7: Flexibility window of a fully ordered Si/Al SOD framework with sodium ions (triangles) and sodium bromide (squares) with Al centered tetrahedra geometry.

In the cubic SOD framework, every tetrahedral centre lies on a face of the unit cell. The folding mechanism during isotropic compression of the cell involves counter-rotation of adjacent tetrahedra; each tetrahedron rotates in-plane, that is, the axis of rotation for each tetrahedron is perpendicular to the unit cell face. The magnitude of tetrahedral rotation, measured relative to the maximally expanded structure at $a = 8.98 \text{ Å}$, is shown in figure 6.8 on the next page. The tetrahedral rotation is a whole-body measure, calculated by superposing corresponding tetrahedra and finding the best-fit rotation which minimises their mismatch.

Having obtained these data for the hypothetical siliceous SOD framework, the next step is to examine the fully ordered Si/Al SOD framework, distinguishing between Al- and Si-centred tetrahedral units. It is found that this introduction of two differently sized tetrahedra causes intrinsic strain in the framework at all densities. A window

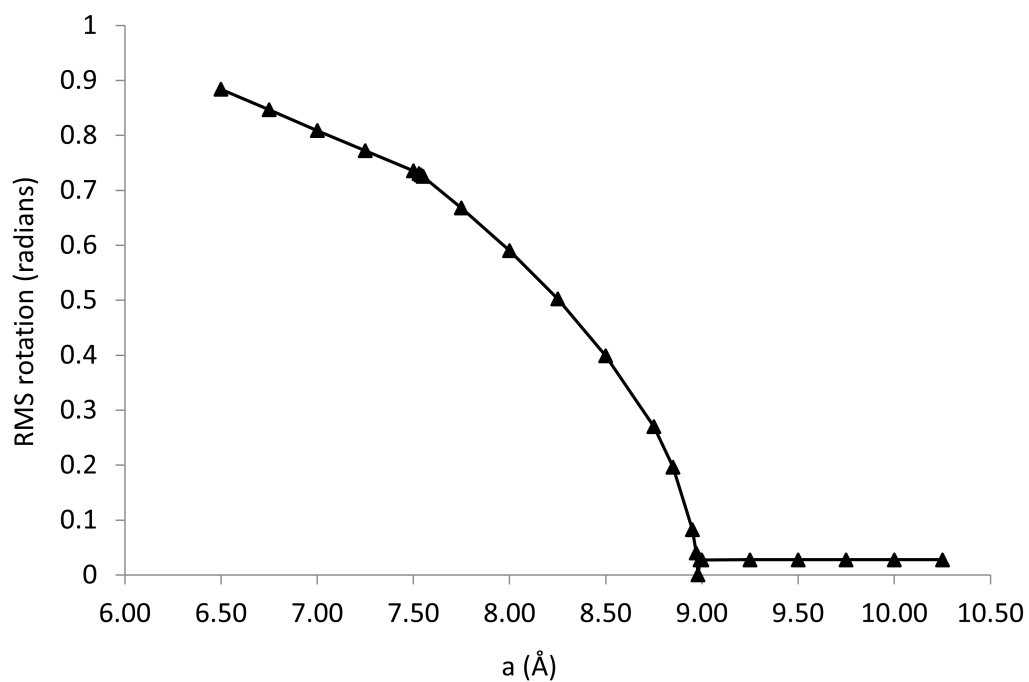


Figure 6.8: RMS rotation of Si tetrahedral units in hypothetical siliceous SOD framework

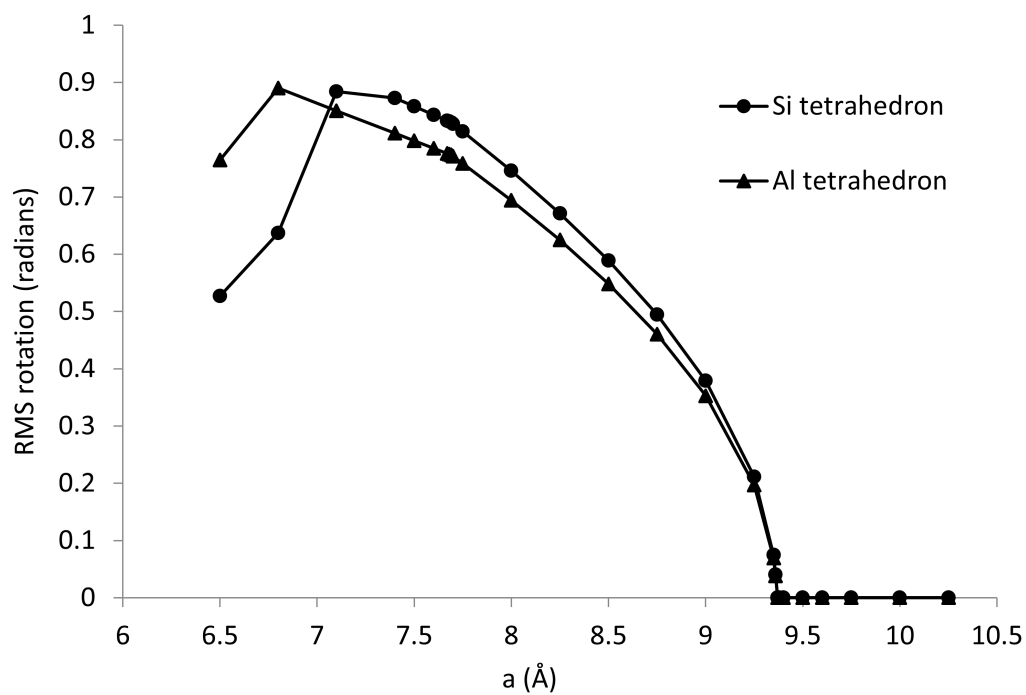


Figure 6.9: RMS rotation of Si and Al tetrahedral units in fully ordered Si/Al SOD framework

can still be defined, distinguishing a central low-strain region from high-strain regions in compression and extension, as illustrated in figure 6.6 on page 88. Within the low-strain region, the strain decreases linearly as the a parameter increases, and is minimised by expansion to $a = 9.37$ Å. The folding mechanism, of in-plane counter-rotations of adjacent tetrahedra, retains the same character as in the hypothetical siliceous SOD framework; however, the magnitude of the rotation is greater for the Si tetrahedra than for the Al tetrahedra, in inverse proportion to their bond lengths, as shown in figure 6.9 on the previous page.

The point of maximum expansion for the fully ordered Si/Al SOD framework lies at a considerably lower density (larger a parameter) than the expanded limit of the pure-silica hypothetical window. This is because Al tetrahedral units are slightly bigger in size compared to Si tetrahedral units, and they are negatively charged which can interact with the extra framework contents such as counter-balancing sodium ions. The flexibility window of a fully ordered Si/Al SOD framework with 8 Na⁺, as shown in figure 6.7 on page 89, is identical to the empty fully ordered Si/Al SOD framework, with the most expanded end at 9.37 Å and the most compressed end at 7.67 Å. When bromide ion is included in the framework (figure 6.7), the flexibility window at the low density end remains unchanged, but is narrowed at the most compressed end to 8.75 Å.

A further step is to reflect the “softer” character of bonding at an Al centred tetrahedron by relaxing the requirement of strict tetrahedral geometry. This is achieved in the simulation using ‘bar’ constraints, which require the same Al–O bond length of 1.75 Å, but do not limit the O–Al–O angle. Since the O vertices in an AlO₄

unit lie further apart than the O–O contact distance of 2.70 Å, this permits some variation of the AlO_4 geometry. With this approach, ordered Si/Al centered tetrahedra SOD frameworks display a true flexibility window analogous to that defined for the siliceous systems, as shown in figure 6.10. The limits of this window correspond closely to those defined for the fully tetrahedral case discussed above, with the most expanded end at $a = 9.37$ Å, and the most compressed end at $a = 7.70$ Å.

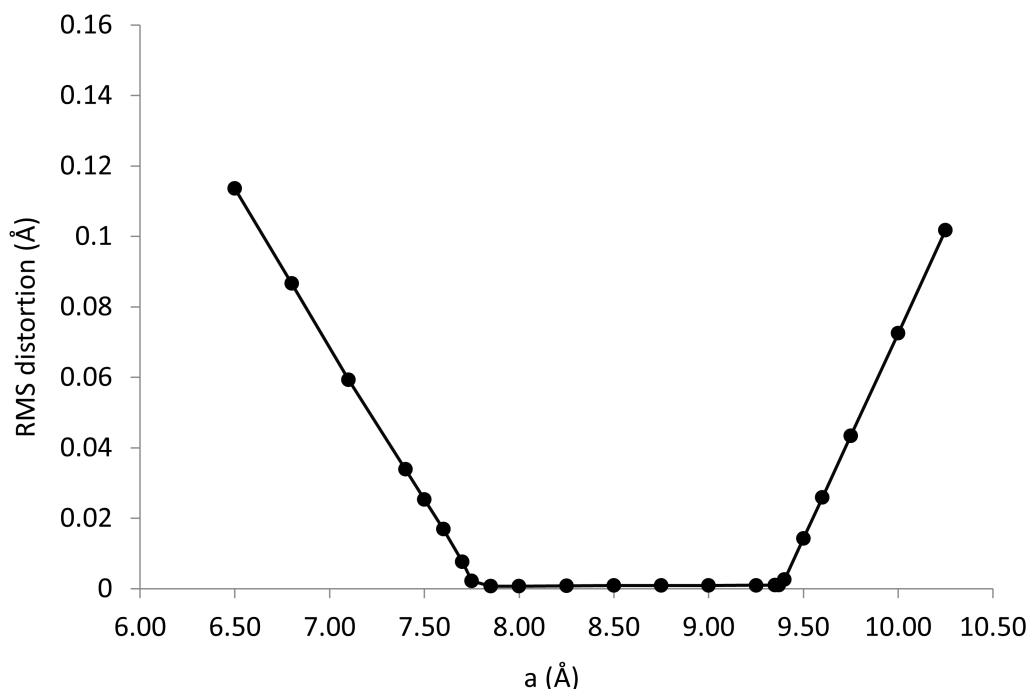


Figure 6.10: Flexibility window of bar-constrained fully ordered Si/Al SOD framework

After simulating the hypothetical siliceous SOD framework and fully ordered Si/Al SOD framework with/without Al tetrahedral bonding geometry, simulation then focuses on the presence of extra framework contents which may affect the flexibility of the SOD framework. It starts by populating a “bar” constrained, fully ordered Si/Al framework with 8 sodium ions in the β -cage. The flexibility window is identical to

the empty fully ordered Si/Al framework (see figure 6.11). The inclusion of 8 sodium ions does not hinder the rotations of Si/Al tetrahedra (see figure 6.12 on the following page).

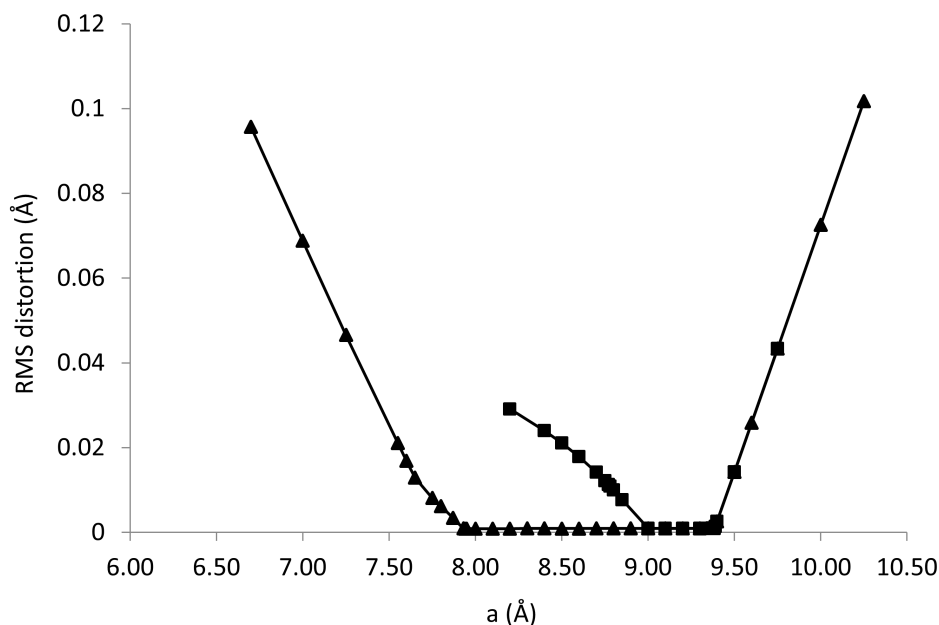


Figure 6.11: Flexibility window of bar-constrained fully ordered Si/Al framework with sodium ions (triangles), and with sodium bromide (squares)

When populating the framework with sodium ions as well as bromide ions, the point of maximum expansion is found at $a = 9.37$ Å, which is identical to the framework with the presence of sodium only (see figure 6.11). However, the most compressed end of the flexibility window lies at 9.00 Å. Further compression of the framework leads to a significant increase of framework distortion, and beyond 8.20 Å, distortion of the tetrahedra becomes inevitable. Figure 6.13 on the next page shows the RMS rotation of bar-constrained, fully ordered Si/Al SOD framework with NaBr. A much shorter range of tetrahedral rotation is observed which is consistent with the flexibility window.

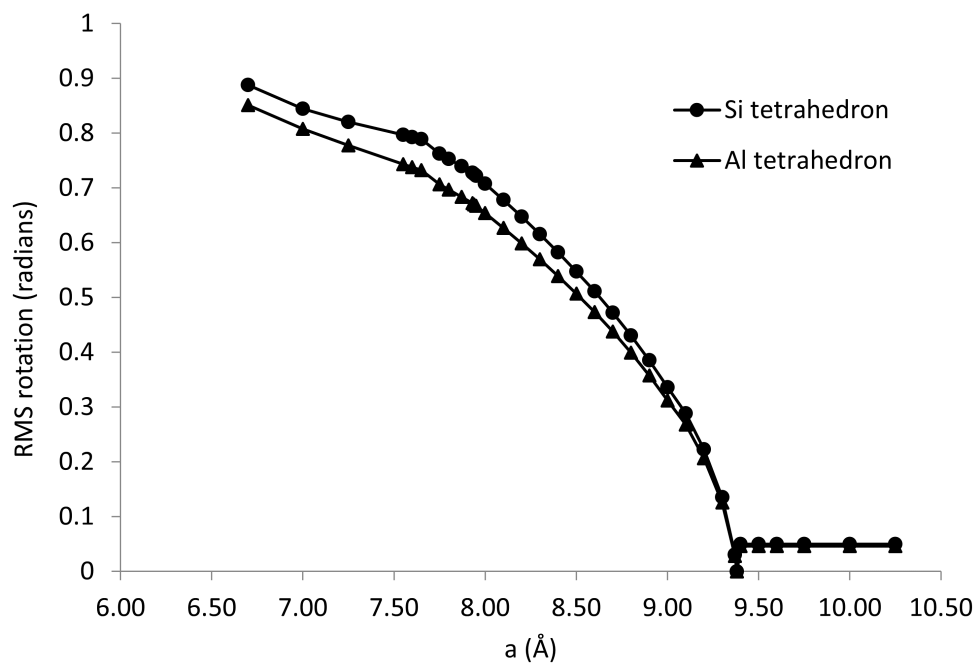


Figure 6.12: RMS rotation of bar-constrained, fully ordered Si/Al SOD framework with 8 sodium atoms in beta-cage

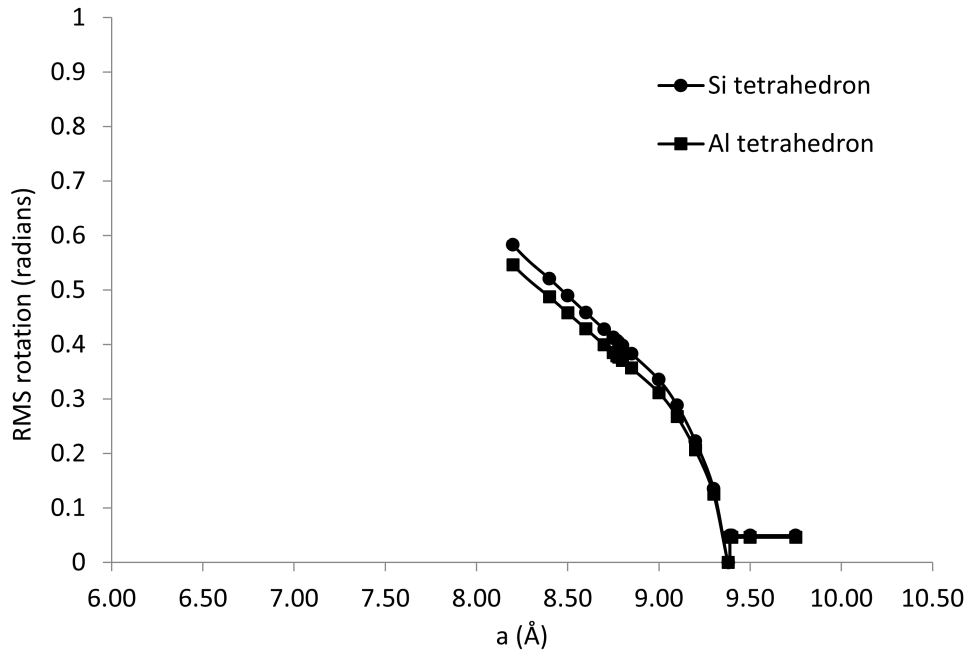


Figure 6.13: RMS rotation of bar-constrained, fully ordered Si/Al SOD framework with sodium and bromide ions

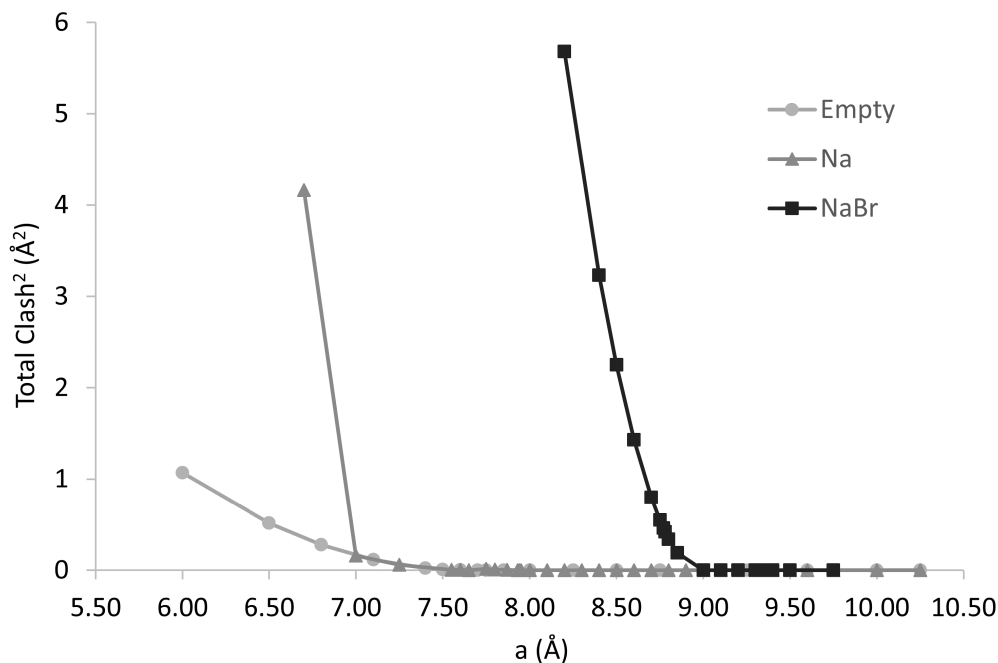


Figure 6.14: Total clash² of empty (circle), sodium (triangle), and sodium bromide (square), bar-constrained, fully ordered Si/Al SOD framework.

When bulky bromide ions are present in the SOD framework, an “extrinsic” flexibility window is observed. It is similar to the case when methanol molecules occupy the β -cages of zeolite Y mentioned in chapter 4. The bromide ion restricts the rotation of the tetrahedral units and the framework is extremely stressed even under moderate compression. With the presence of extra framework contents, steric contacts involving Br^- , Na^+ , and framework O spheres are inevitable. Instead of measuring individual contacts, the “total clash²” is used to measure the sum of all steric contacts involved. Figure 6.14 shows the “total clash²” of empty, Na^+ , and NaBr bar-constrained, fully ordered Si/Al SOD framework. With no extra framework contents, no clash is observed below $a = 7.85$ Å. Clashes between framework oxygen start to build up around $a = 7.75$ Å. With presence of 8 Na^+ , clashes between framework oxygen is first ob-

served at $a = 8.90$ Å, together with extra-framework Na^+ clashes at $a = 7.94$ Å and above. When the framework contains Na^+ and Br^- , steric clashes become significant even at $a = 8.78$ Å. Given the very substantial size of the Br^- , it limits the capacity of the framework polyhedra to rotate, and distortions of the polyhedra become unavoidable.

The results of the geometric simulation can be used to explain some observations of the high pressure experiments. In the experiment of NaBr-SOD using the methanol/ethanol solution as a pressure transmitting medium, the maximum expanded experimental ambient cell parameter is 8.94 Å, which is located towards to the most extended edge of the simulated flexibility window of the tetrahedral-constrained, fully ordered Si/Al framework with NaBr at 9.37 Å. This once again shows that zeolites at ambient condition tend to be maximumly extended. However, the highest experimental pressure point is 6.25 GPa, which is equivalent to $a = 8.62$ Å. Compare to the most compressed end of the simulated flexibility window which is 8.75 Å, the framework at 6.25 GPa is already stressed and being push out of the flexibility window. This can explain the loss of intensity of the sodalite 211 peak in figure 6.4(a) above 4.01 GPa.

In the pressure experiment of Na-SOD using methanol/ethanol solution as pressure transmitting medium, loss of intensity of the sodalite 211 peak is observed at pressure above 0.81 GPa in figure 6.4(b). This is equivalent to $a = 8.90$ Å. The intrinsic flexibility window from the geometric simulation of the tetrahedral-constrained, fully ordered Si/Al framework with 8 Na^+ is between 9.37 Å (the most extended end) and 7.95 Å (the most compressed end). This implies that the experimental

cell parameter can be compressed beyond $a = 8.90$ Å in theory. The difference between geometric simulated and experimental cell parameters can be explained by the “extrinsic flexibility window”. Such window is controlled by the extra framework content present in the framework; in this case, the methanol molecule from the pressure transmitting medium. It is already shown in chapter 4 that methanol molecules can occupy the β -cage. It acts as scaffolding molecules to avoid further collapse of the structure, however, by doing this, it also increases the stress experienced by the framework. This is exactly what is being observed from the high pressure experiment - the framework remains in its flexibility window, but cannot be compressed further.

A similar result is observed when Na-SOD is compressed using fluorinert as pressure transmitting medium. The highest experimental pressure point is 1.086 GPa, equivalent to $a = 8.99$ Å, which is quite a distance away from the most compressed end of the simulated flexibility window with $a = 7.95$ Å. Unlike the methanol molecules which have a scaffolding effect, fluorinert is a non penetrating transmitting medium. It compressed the framework directly with increasing pressure. Since the framework is relatively empty with the absence of bulky extra framework contents, the effect is dramatic. The framework starts to lose its structure at 0.55 GPa (figure 6.4(c)), and the cell parameter remains at $a = 8.99$ Å to the maximum compression point at 1.086 GPa.

6.3 Chapter summary

High pressure experiments were done using two different forms of sodalite - one contains only Na^+ , another with Na^+ as well as Br^- . The frameworks respond differently

when methanol/ethanol mixture was used as a pressure transmitting medium. Collapse of framework structure is observed in Na-sodalite even at small compressions. At high pressure, there is no change in cell parameter due to the scaffolding effect of the penetrating methanol molecules, although the framework remains in its flexibility window, and in theory can be compressed further. Increase in stress in terms of distortion and rotation of framework tetrahedral units is observed from the geometric simulation. However, NaBr-sodalite retains its crystallinity along a wider pressure range. Although the methanol molecules cannot penetrate the framework, the Br^- acts as the scaffolding species in this case and supports the framework against pressure. However, under high pressure, the framework is being pushed out of its flexibility window since it cannot accommodate the stress due to distortion of framework tetrahedral units when framework oxygen atoms start clashing. The experiment of Na-sodalite using fluorinert as pressure transmitting medium is an example to show that the framework cannot hold its structure without any scaffolding species, even when it remains in its flexibility window. The “extrinsic flexibility window” is thus defined, and is controlled by the extra framework contents.

Chapter 7

Conclusion & Future works

The synthesis of zeolite materials without the use of organic structure directing agents requires precise control of synthesis conditions. Syntheses of zeolite A, sodalite and Linde Type N zeolites using hydrothermal and microwave methods have been studied here in depth in order to find new future synthesis methods. Zeolite A can be synthesised at a temperature as low as 40 °C hydrothermally, and with increasing temperature, a transformation to sodalite is observed. Such transformation is explained by the difference in framework density - sodalite is denser compared to zeolite A, so can be synthesised at a higher temperature. The use of microwave methods for zeolite synthesis has reduced the reaction time dramatically, and yet pure zeolite phase can still be achieved by precise control of reaction conditions which can be seen from the sodalite microwave synthesis experiments. It is surprising that, by simply changing the method of crystallization, a new method of synthesising Linde Type N zeolite is found and was reported in this study.

Geometric simulation is used to study the maximum number of water/methanol guest molecules occupying the β -cage of siliceous zeolite Y. It is found that a maximum number of two water molecules and one methanol molecule can simultaneously

occupy the β -cage while the framework structure remains in its flexibility window, i.e. undeformed. The extra framework content of a zeolite framework can have a significant effect to the flexibility window. Methanol molecules penetrating the framework of siliceous zeolite Y under certain pressure have a scaffolding effect which increase the stress experienced by the framework and thus reduce its flexibility window. The same result is observed when NaBr-sodalite is under pressure with methanol/ethanol mixture. These lead to the discovery of the newly defined “extrinsic” flexibility window of zeolite frameworks which is governed by the extra framework contents. However, an exception is observed in the case of zeolite EMC-2. The ether molecule occupies the *t-wof* cages, having no effect on the flexibility window and does not limit the contraction of the framework since crown ether has sufficient geometric flexibility that it can adapt to the contraction of the *t-wof* cage.

One of the aims in zeolite science is to synthesise new zeolite framework with useful applications. To achieve this, the knowledge of synthesis conditions which control different zeolite phase is essential. This study already showed that merely changing the synthesis conditions can control the formation of LTA, SOD, and LTN frameworks which sharing a common building unit, the β -cage. These frameworks are only a very small fraction of the existing frameworks being synthesised in the laboratory. It would be interesting to see if similar frameworks relationship existed by doing a systematic study on all existing synthetic zeolite frameworks.

Structural changes of zeolite frameworks under compression depend on their framework building units and the extra-framework contents. Although this study only focused on three different zeolite under compression, significant differences in frame-

works response to the pressure transmitting media and the extra-framework contents were observed. High pressure experiments can apply to all synthetic zeolite frameworks. The change of channel shape and size under pressure may affect the property of zeolites in molecules separation and catalytic reactions, and lead to discovery of new application. Apart from zeolite materials, high pressure studies can also apply to metal-organic frameworks (MOFs), zeotypes such as aluminum phosphate materials (AlPOs), as well as hybrid zeolite-like metal-organic frameworks. These frameworks may behave differently under pressure compared to inorganic zeolite materials.

Appendices

Appendix A

The Bragg's equation

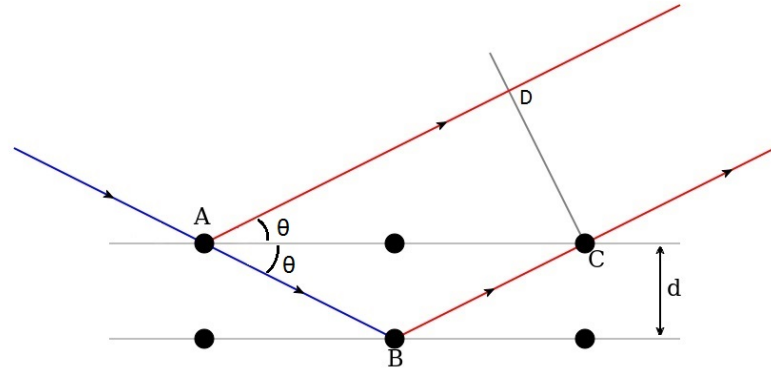


Figure A.1: Graphical representation of Bragg's Law

The path difference of the two reflected ray from two different lattice plane is:

$$(AB + BC) - AD \quad (A.1)$$

For constructive interference to happen, the path difference must equal to any whole number of the wavelength. Therefore:

$$(AB + BC) - AD = n\lambda \quad (A.2)$$

Since:

$$AB = BC = \frac{d}{\sin\theta} \quad (\text{A.3})$$

$$AC = \frac{2d}{\tan\theta} \quad (\text{A.4})$$

Then:

$$AD = (AC)\cos\theta = \frac{2d}{\tan\theta}\cos\theta = \left(\frac{2d}{\sin\theta}\cos\theta\right)\cos\theta = \frac{2d}{\sin\theta}\cos^2\theta \quad (\text{A.5})$$

Thus, substitute the corresponding formula to equation B.2:

$$n\lambda = \frac{d}{\sin\theta} + \frac{d}{\sin\theta} - \frac{2d}{\sin\theta}\cos^2\theta = \frac{2d}{\sin\theta}(1 - \cos^2\theta) = \frac{2d}{\sin\theta}\sin^2\theta = 2d\sin\theta \quad (\text{A.6})$$

which is the Bragg's equation.

Appendix B

Additional information for Chapter 3, Section 3.2

The microwave syntheses in this section are preliminary works to see if single phase Na-SOD can be made using the “CEM Mars 6” microwave reactor, and to find out the optimum synthesis condition. The aim is to make a single phase Na-SOD sample to be used in the high pressure experiment mentioned in chapter 6. It is recommended that precise comparisons should not be made using the data presented in this section, but rather as a reference, mainly because of the presence of multiple variables between experiments and the uncertainties with the microwave reactor.

For those who are planning to replicate the microwave syntheses in this section for precise comparisons, it is recommended to repeat each of the syntheses at least three times (no repeat was done for the data already presented in this section). Moreover, the conditions of microwave syntheses should be altered slightly, for example, condition 1 - 20 mins, 150 °C, condition 2 - 20 mins, 75 °C, condition 3 - 120 mins, 150 °C. The batch composition of recipe 3 should be kept the same as recipe 1 and recipe 2. It is also important not to fill the container more than 50 % of its total volume.

Appendix C

Synthesis of LTA, SOD, and LTN framework zeolites with no organic structure directing agent

C.1 X-ray powder diffraction

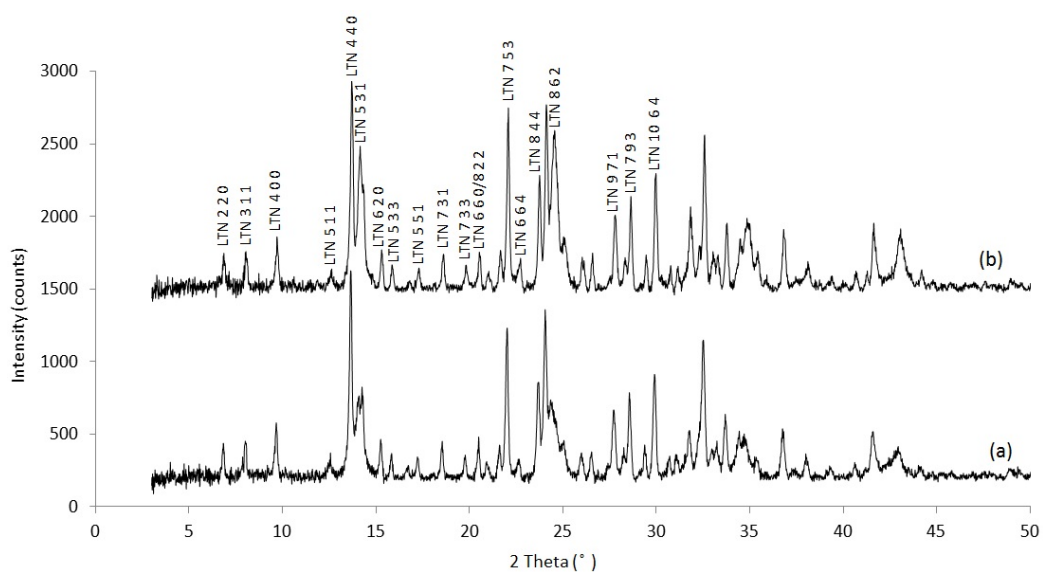


Figure C.1: Powder pattern of as-synthesised Linde Type N zeolite samples using fumed silica.
(a) 60 °C (b) 90 °C

C.2 Hydrothermal synthesis of zeolite A with no OSDAs

C.2.1 ^{29}Si SS MAS NMR

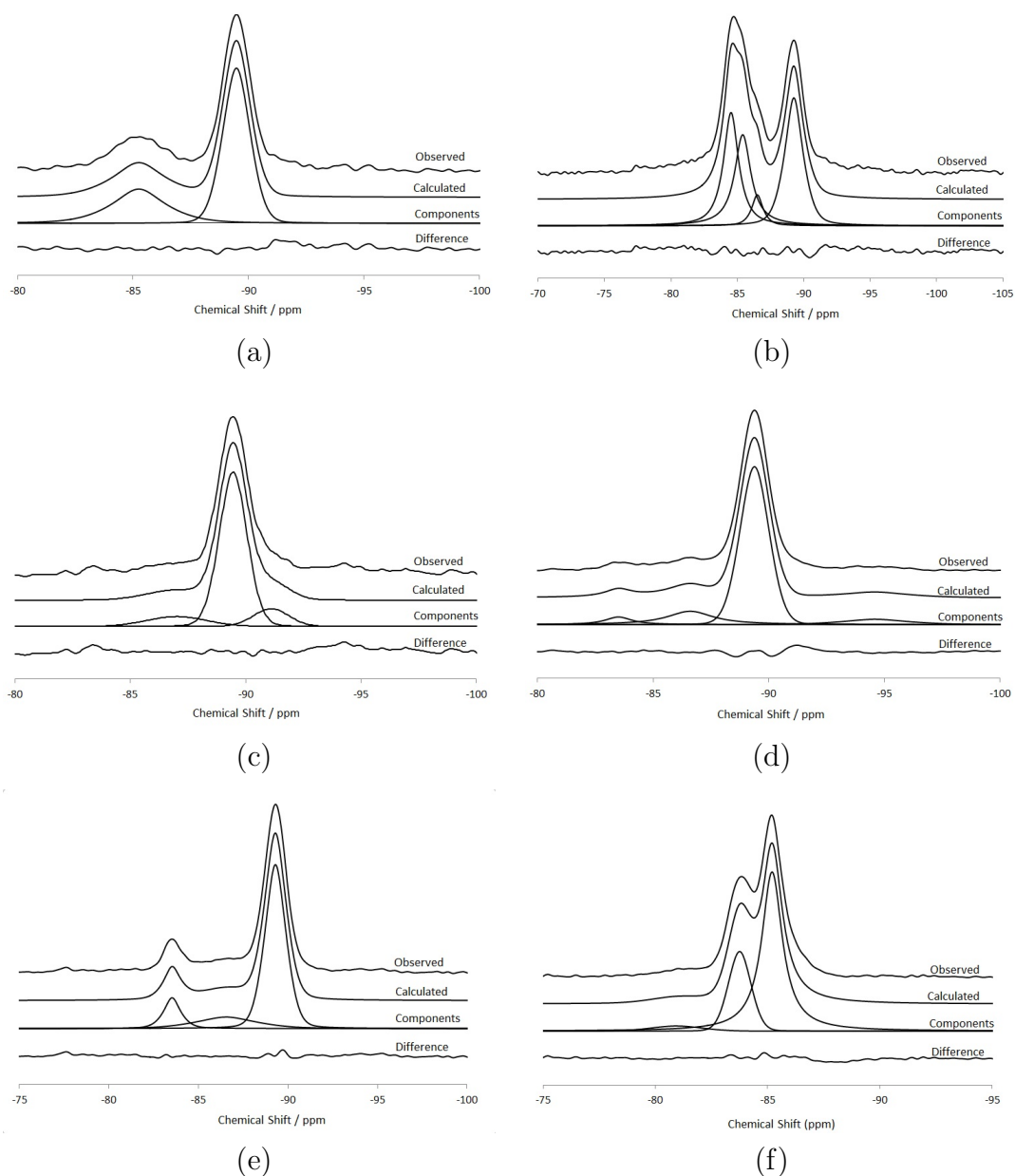


Figure C.2: As-synthesised zeolite samples with no OSDAs at (a) 40 °C (b) 50 °C (c) 60 °C (d) 70 °C (e) 80 °C for 1 hour, (f) 95 °C for 2 hours

C.2.2 ^{29}Si CP MAS NMR

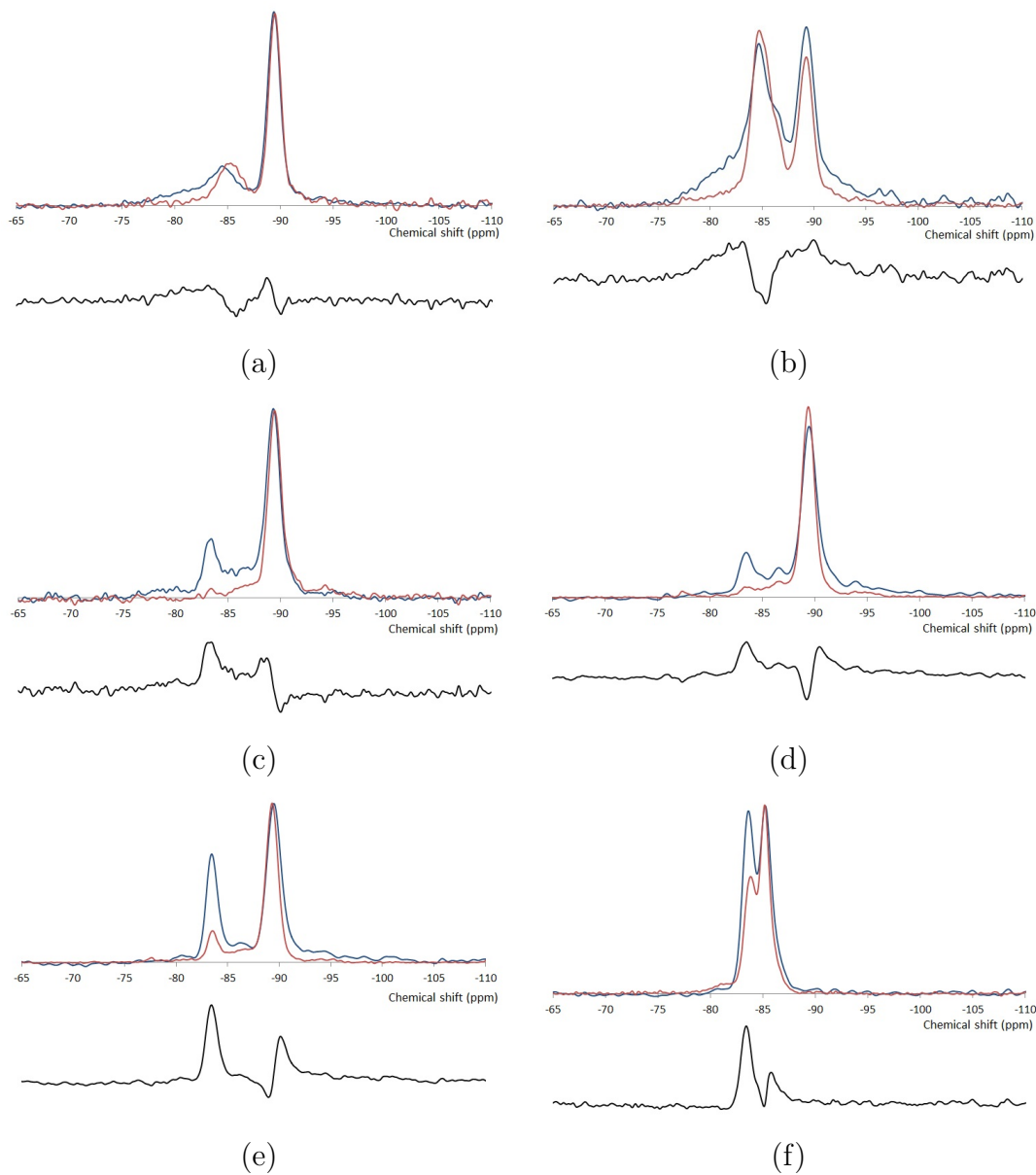


Figure C.3: As-synthesised zeolite samples with no OSDAs at (a) 40 °C (b) 50 °C (c) 60 °C (d) 70 °C (e) 80 °C for 1 hour, (f) 95 °C for 2 hours, red - signal of ^{29}Si MAS NMR, blue - signal of ^{29}Si CP MAS NMR, black - difference between two signals

C.2.3 ^{27}Al SS MAS NMR

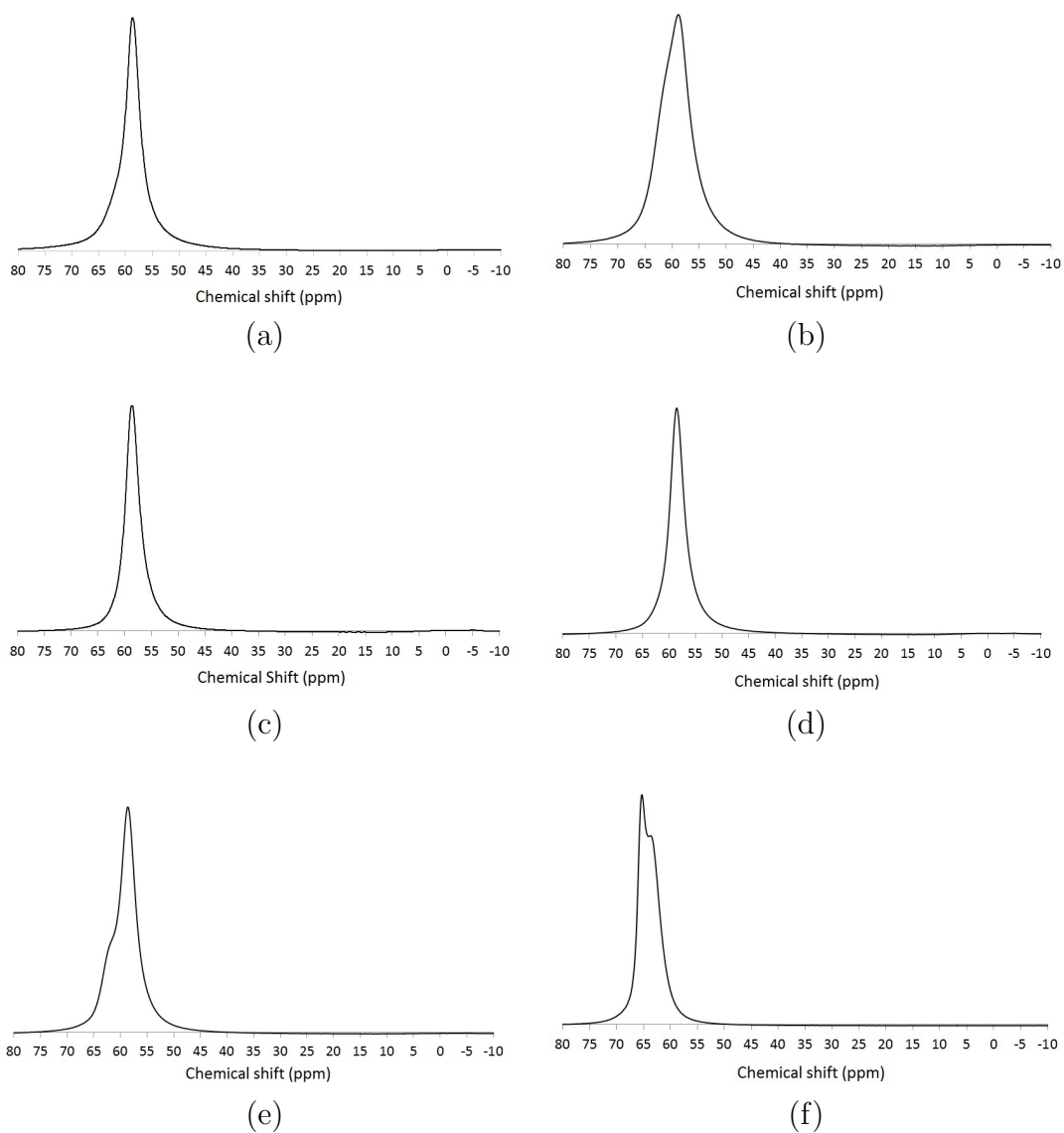


Figure C.4: As-synthesised zeolite samples with no OSDAs at (a) 40 °C (b) 50 °C (c) 60 °C (d) 70 °C (e) 80 °C for 1 hour, (f) 95 °C for 2 hours

C.2.4 ^{23}Na SS MAS NMR

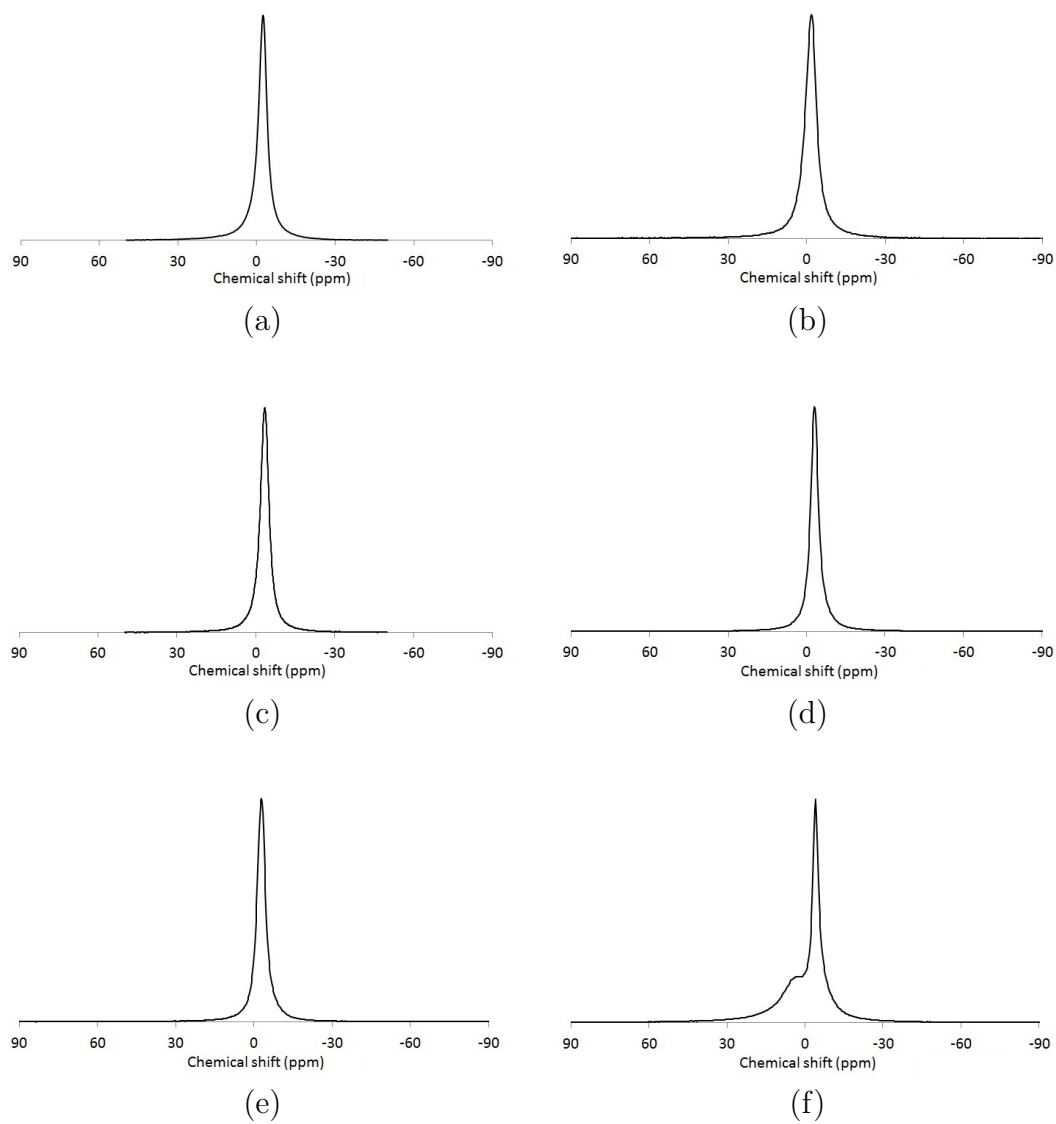


Figure C.5: As-synthesised zeolite samples with no OSDAs at (a) 40 °C, (b) 50 °C, (c) 60 °C, (d) 70 °C, (e) 80 °C for 1 hour, and (f) 95 °C for 2 hours

C.3 Microwave & hydrothermal synthesis of Linde Type N zeolite with no OSDAs

C.3.1 SS MAS NMR

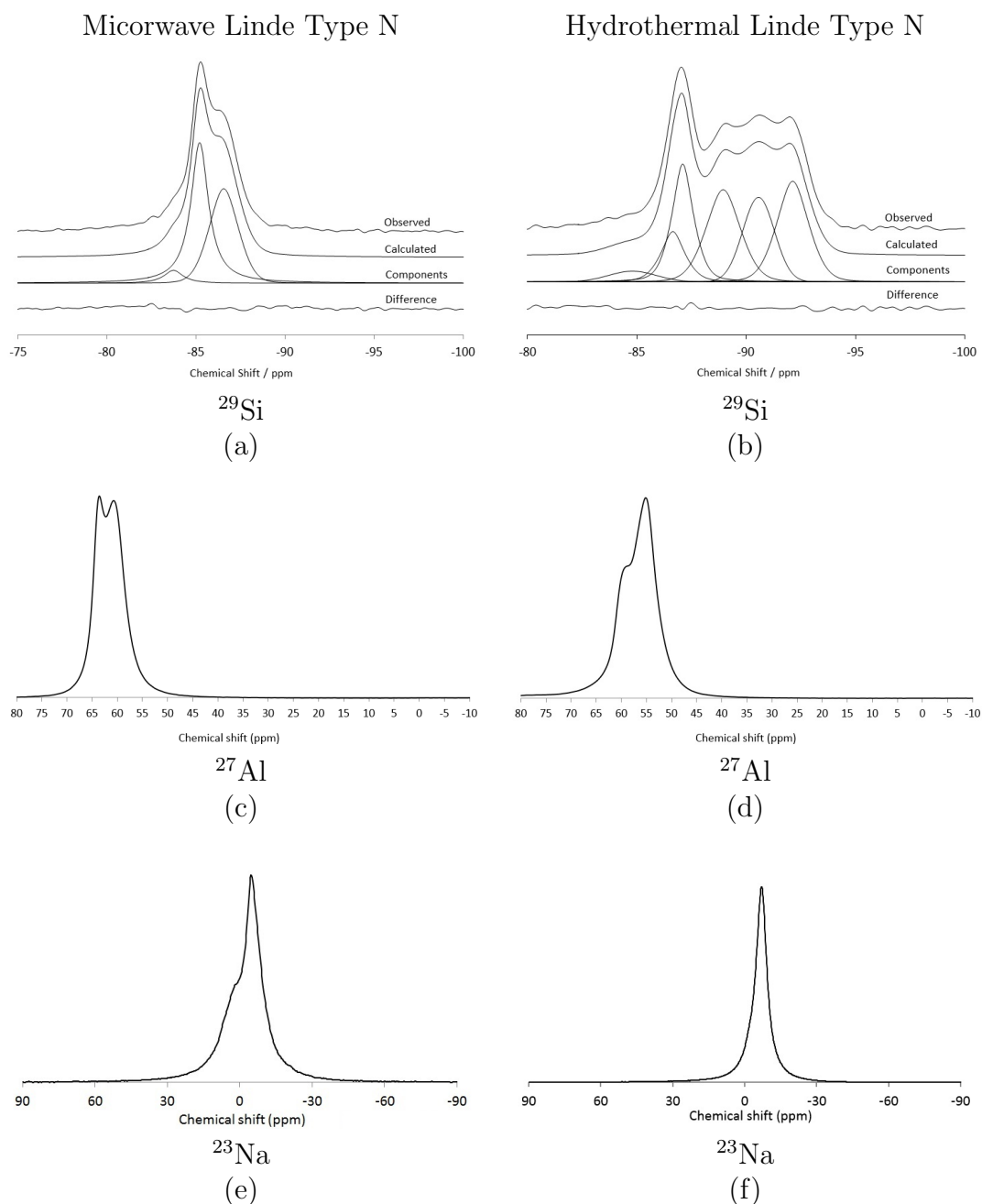


Figure C.6: SS MAS NMR spectra of as-synthesised zeolite sample with no OSDAs. Column left: Microwave synthesis. Column right: Hydrothermal synthesis.

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