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**Highly Dispersed Alkali Metals Confined
in Porous Matrices**

by

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

Master of Science

Department of Chemistry

Carleton University

Ottawa, Ontario

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Abstract

Highly-dispersed alkali metals (Na, K, Rb, Cs) have been prepared by template synthesis via vapour-phase deposition. For this purpose, several templates were synthesized, ranging from microporous H-ZSM-5 zeolite, to mesoporous MCM-41 and SBA-15 ordered silicates. The production of high quality as-synthesized templates were confirmed by porosimetry, powder XRD and solid state NMR. Commercially available Vycor glass was also used as alternative type of mesoporous template.

The level of alkali metal dispersion was controlled by the template pore size and the metal loading. In zeolites with low doping levels the alkali metals exist as isolated clusters of low nuclearity, which eventually merge into extended superstructures as the loading level increases. In mesoporous templates, the formation of thin filaments of the alkali metals is expected (nanowires).

We have used a wide variety of modern characterization techniques, including multinuclear solid-state nuclear magnetic resonance spectroscopy (SSNMR), electron spin resonance (ESR), and powder and single-crystal X-ray diffraction to study the formation and the properties of these nanostructured materials.

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Maria Stancescu

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Chapter I

Nanostructured Materials in Porous Inorganic Matrices

1.1 Introduction

The present day search for smaller, faster, more selective and more efficient products and processes, the ability to design well defined spatial arrangements of pure substances and composite materials, of dimensions in the quantum size regime (from 5 to 100 Å), is becoming essential.¹ Due to their small sizes, these highly-dispersed structures exhibit novel electrical, mechanical, optical and magnetic properties, in contrast to the properties of bulk materials (quantum confinement effects). For example, metals confined in the random channels of diameter 20-100 Å of porous glasses or ceramics exhibit a critical magnetic field, H_c , 50-100 times greater than in the bulk material.² Also, adsorption edge energies of confined CdS microcrystals are significantly larger than in bulk semiconductors,³ therefore the spatial confinement of these materials allows for band gap adjustment.

The complex relationships existing between electrical and optical properties of nanoparticles and their sizes are fully exemplified by so-called semiconductor superlattices.⁴ These are artificially layered structures consisting of two semiconductor materials layered on top of one another. By design of the layer thickness and judicious choice of materials, electrons localize within these quasi-two-dimensional “quantum wells”. The electronic structure of these kinds of devices are controlled, in part, by the band structure of the bulk materials, yet it is unexpectedly different because of the quantum confinement effects. Some applications of semiconductor superlattices include

high electron mobility transistors, non-linear optical superlattices (NLO) and optical transistors (transphasors).

By reducing the dimensionality of a quasi-2D semiconductor, theoretical considerations indicate that quantum size effects are enhanced. For example, strongly enhanced electron mobilities and resonant tunneling have been predicted and observed in the case of quantum wires and quantum boxes.¹ These are, in part, the justification for the continual search in finding new nanostructured materials, and in developing novel synthetic approaches.

Nanostructured materials are generally synthesized using polymers, semiconductors and metals⁵⁻⁷ by a wide variety of methods. The most popular methods include: molecular beam epitaxy (MBE),³² laser ablation⁸, arc discharge (carbon nanotubes)⁹, or template assisted electrochemical¹⁰ and chemical deposition^{11,12} (so-called template synthesis). The latter method is very attractive, since the void dimensions of host templates may confine the size and shape of the guest nanostructure. Suitable templates include micelles of surfactants and polymers¹³, inversed microemulsions¹⁴, porous glasses¹⁵, porous carbon¹⁶, and molecular sieves¹⁷. The template-synthesized nanostructures are either suspended in solution or supported on a solid substrate (i.e. porous host materials). However, supported quantum structures confined in porous host materials are more desirable for practical applications. Zeolites, with their rigorously periodic system of channels and cavities of molecular dimensions, may be considered as ideal host templates within which the guest structure is assembled. Other inorganic porous templates (such as

MCM-41 and SBA-15) with ordered channel structures of larger pore diameter than zeolites and high internal surface areas (700-1000 m²/g) are also suitable supports.

In what follows is a brief overview of porous inorganic materials, followed by the specifics of template-assisted methods used for the production of quantum-confined structures, and finally several examples of such structures.

1.2 General Description of Porous Inorganic Matrices

1.2.1 Classification

Inorganic solids that contain pores with diameters less than 20 Å are considered microporous materials, according to IUPAC definition. Examples of these types of inorganic solids include zeolites and related materials. When the diameter of the pores is in the size range of 20-500 Å, the materials are considered mesoporous. Some typical examples of such materials include pillared layered structures, aerogels, controlled pore glasses (i.e. Vycor glass), and the novel family of molecular sieves called M41S, and M41S related materials (i.e. SBA type mesoporous silica). Inorganic solids with pore sizes larger than 500 Å are considered macroporous materials, for example glasses and some silica gels.

1.2.2 Microporous Matrices: zeolites

The word zeolite has Greek roots and literally means “boiling stone”, an illustration of the thermally induced loss of water noted when natural zeolites are heated. Zeolites are a well-defined class of crystalline inorganic polymers, composed of infinitely extended three-dimensional frameworks of SiO₄ and AlO₄ tetrahedra, with a negative charge

FAU

LTA

LTL

MFI

MOR

SOD

Figure I.1 Some typical zeolite structures: (FAU) faujastite: zeolites X or Y, (LTA) Linde type A zeolite, (LTL) Linde type L zeolite, (MFI) ZSM-5 zeolite, (MOR) mordenite, (LTL) Linde type L zeolite, SOD (sodalite).⁴⁹

associated with each AlO_4 tetrahedron. This charge must be counter-balanced by a inorganic or organic cation. Depending on the type of connection between tetrahedral building blocks, linear or pseudo-linear channels may form, with diameters ranging from 4.2 to 7.4 Å. In other structural types, cages are formed with diameters of 6.4 to 12 Å, and window sizes from 2.3 Å (6-ring) to 13 Å (18-ring). Some typical examples of zeolite structures are shown in Figure I.1.

There are more than 40 known natural zeolites and almost 200 synthetic zeolites. The mechanism of zeolite synthesis is very complex due to many unwanted chemical reactions, in addition to equilibria and solubility variations that occur in the reaction mixture during the crystallization process.¹⁸ Two different pathways for zeolite formation have been proposed: (i) the solution-mediated transport mechanism and (ii) the solid-phase transformation mechanisms, both of which are illustrated in Figure I.2. On the one hand, the solution-mediated transport mechanism involves the diffusion of alumina, silicate, and/or aluminosilicate species from the liquid phase to the nucleation site for crystal growth. Examples of zeolites whose formation follow this mechanism are zeolites Y, S (GME class), and P (GIS class).¹⁹ On the other hand, the solid-phase transport transformation mechanism suggests that the solid hydrogel reorganizes to form the zeolite structure. An example of this type of process is illustrated by the synthesis of mordenite (MOR)²⁰. Some zeolites (e.g. ZSM-5 zeolite) can be crystallized by either one of these two general routes, depending on the source of silica used.²¹

Figure I. 2 Schematic illustration of the (a) solution-mediated transport and (b) solid-phase transformation crystallization mechanisms

Figure I. 3 The pathways of M41S silicates formation (Mobil group proposal).²²

Synthetic zeolites play an important role in petrochemical catalysis, and are widespread used in radioactive waste storage, water treatment, and gas separation. On the other hand, their use as matrices for recognition of atoms, molecules or atomic clusters is a relatively new application. Zeolite frameworks, which may have many different architectures, offer a unique pathway for creating specific spatial arrangements of quantum size particles. By choosing suitable combinations of the zeolite and the semiconducting material, periodic arrays of quantum structures with controlled dimensionality and properties can be designed. The zeolite lattice also provides a stabilizing medium for the confined particles to prevent their agglomeration.¹

1.2.3 Mesoporous Matrices: Ordered Mesoporous Silicates (M41S type)

M41S type materials represent a new family of ordered mesoporous silicates (OMS), discovered by researchers at the Mobil R&D Corporation. These materials were prepared by using long-chain surfactants as templates. Depending on the synthetic conditions, the resulting OMS consists of either a hexagonal phase (P6mm), referred to as MCM-41, a cubic phase (Ia3d) known as MCM-48, or a nonstable lamellar phase (MCM-50).

Regarding the mechanism of formation of OMS, the Mobil group has originally proposed two possible pathways, as illustrated in Figure I.3. The first mechanism suggests that the surfactant molecules self-organize into a liquid crystalline phase, which plays the role of a template. The silicate species polymerize into a rigid shell around the hydrophilic region of the surfactant aggregates. In the second pathway, the silicate species play a more active role in directing the formation of the organic-inorganic mesophase through charge balance interactions with the surfactant ions.²² Two other

mechanisms have recently been proposed.²³ One is based on electrostatic interactions between cationic surfactants (S^+) and anionic inorganic species (I^-).²³ In contrast, the $S^- I^+$ pathway involves the cooperative organization of cationic inorganic species and an anionic surfactant. Another route is based on interactions between surfactants and inorganic ions with similar charges, mediated by small ions (X) with opposite charges (i.e. $S^+ X^- I^+$, $S^- X^+ I^-$, where $X^- = Cl^-, Br^-$, and $X^+ = Na^+, K^+$). In addition to these mechanisms based on electrostatic interactions, a neutral templating mechanism was also proposed ($S^0 I^0$).²³ In this mechanism, the whole organizational process is driven by hydrogen bonding, as the neutral species formed by partial hydrolysis of the silica source (I^0) interacts with the nonionic surfactant (S^0) via hydrogen bonding.

By varying the size of the surfactant molecules and the synthetic conditions, an OMS material with a desired porous structure may be obtained. The pore size in such materials can be fine-tuned over a wide range, from one-tenth to hundreds of angstroms. This fine-tuning of the pores, combined with the relative inertness of their silica-based framework, makes OMS materials a highly versatile porous template with many potential applications, including synthesis of highly-dispersed nanostructures.

1.3 Template-Assisted Fabrication of Nanostructured Materials.

As mentioned earlier, porous inorganic matrices (zeolites) controlled pore glasses (e.g. Vycor glass) and OMS materials are suitable templates for producing well-defined quantum structures. These nanostructures are obtained by a self-assembly process of the guest molecules or atoms within the narrow channels or cages of the lattice host (from angstrom to nanometer sizes). Since the “reaction chamber” has well defined dimensions

and shape, selective access of the guest atoms or molecules to the cages or channels takes place. Common template-assisted methods to fabricate nanostructured materials include: electrochemical deposition (Au, Ag), chemical deposition (sol-gel methods, wet impregnation, polymerization etc.), forcing non-wetting liquids (Hg, Ga, Pb) to enter the zeolite channels by applying pressure, and chemical vapour deposition (alkali metals).

The most extensively studied systems are narrow bandgap semiconductors, such as CdS, CdSe and PbS, confined in zeolites.^{3,33} The synthetic methods required to prepare such materials involve exposure of the calcined ion-exchanged zeolite to a corresponding cation (eg. Cd^{2+} or Pb^{2+}) in a flow of hydrogen sulfide, at 100 °C. It was demonstrated, that at low semiconductor loading, the confined particles have low dimensionality, and therefore are often referred to as “quantum dots”. As the pore filling is increased, a percolation threshold is reached, and a semiconductor superlattice is created by the 3 D interconnection between intrazeolitic quantum dots. Such nanostructured semiconductor superlattices were created inside zeolites X, Y and A, but only in some of the cases was the percolation threshold achieved. PbS nanoparticles and wires were also prepared inside ordered mesoporous silica materials by wet impregnation methods.³

As is the case of semiconductors, metals may also be encapsulated into zeolites by chemical deposition methods. As an example of systems with practical applications are the silver sodalites: Ag/X-SOD (X = Cl, Br, I, OH, CO_3). Silver sodalites are

Figure I.4 The four ions of Na_4^{3+} located within the sodalite cage of Na-Y zeolite²⁸

commonly used in high-resolution imaging and optical data storage.²⁴ Silver particles were also incorporated in Vycor glass.¹⁵ Noble metal nanoparticles (Pt, Au)²⁵ and nanowires (Pt, Au and Ag)²⁶ were prepared using the hexagonal phase mesoporous silica SBA-15 by wet impregnation, followed by reduction with hydrogen. Selenium and tellurium chains were prepared in unidimensional mordenite channels by injecting the melt of these metals under high pressure or alternatively by vapour phase absorption.²⁷

New synthetic strategies are being developed for encapsulation of so-called “molecular wires”, composed of isolated strands of conducting and semiconducting chain structures. Examples include encapsulation of polythiazyl, polypyrrole, and polyaniline into the 1 D channels of mordenite or L-zeolite hosts.¹ Tunable band filling in 1 D solids is achieved either by chemical doping with electrons or acceptors, or by electrochemical oxidation/reduction.

Another example of nanostructured materials obtained by template-assisted methods includes highly-dispersed alkali metals in zeolites. Since alkali metals are highly volatile, they may easily be introduced into porous matrices by chemical vapour deposition. The first example of an alkali metal encapsulated into a porous inorganic matrix was a sodium-loaded NaY zeolite, synthesized in 1966 by Rabo et al.²⁸ On entering a dehydrated Na-Y zeolite, sodium vapour is spontaneously ionized by the intense electrostatic field within the zeolite host. As a result of this process, excess electrons and extra cations are introduced into the zeolitic structure, and Na_4^{3+} clusters are formed (Figure I.4). The adsorption of metal atoms into zeolites bears certain similarities with dissolution of alkali metals in liquid ammonia as suggested in the following reactions:^{29,30}

where e^- are the solvated electrons and M^+ are the solvated ions. At low doping levels, the electrons are stabilized in the sodalite cages as Na_4^{3+} traps, leaving the added Na^+ coordinated elsewhere in the supercages. It has been demonstrated that doping of cage type zeolites, such as types Y or A, with alkali metals yields a variety of interesting species and leads ultimately to an insulator $\rightarrow$ metal transition at high metal loadings.²⁹ In this view, alkali metal-containing zeolites may be considered as potential candidates for a previously proposed model of “quasi 1 D conducting wires embedded in a 3 D porous matrix”.³¹ However, the hypothesis that zeolites can indeed serve as hosts for atomically thin nanowires has not yet been answered.

1.4 Scope of Thesis

It is the aim of this work to synthesize nanostructured alkali metals confined in porous templates having extended 1D channels, like those found in zeolite ZSM-5 and in ordered mesoporous silicates. The properties of these materials, depending on the metal type (Na, K, Ca or Rb) and loading, are to be investigated with a variety of modern characterization techniques, including powder and single crystal X-ray diffraction, multi-nuclear solid-state NMR and ESR spectroscopy. The possibility of an insulator $\rightarrow$ metal transition in these materials at high metal loadings, and further implications of this transition on the properties of these materials will be evaluated.

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Chapter II

Experimental Techniques

2.1 Solid State NMR Spectroscopy

Nuclear Magnetic Resonance (NMR) spectroscopy has become a powerful tool to study a variety of solid materials. It has successfully been applied to porous silicates and aluminosilicates (zeolites), which are ideal for hosting materials for various inclusion compounds. The NMR technique can be used to check the framework structure of the host material before and after loading the guest compound, as well as to probe the incorporation process itself, to detect the species formed inside the voids, or to do quantitative analyses on the incorporated compounds.

2.1.1 Basic Theoretical Concepts

The fundamental property of an atomic nucleus suitable for an NMR spectroscopy analysis is a non-zero nuclear spin I (angular momentum) of a total magnitude $\hbar [I(I+1)]^{1/2}$, where $\hbar$ is the reduced Planck constant, $h/2\pi$. Depending on the number of protons and neutrons in the nucleus, the spin value can be integer or half-integer (0, 1/2, 1, etc.).

A nucleus with non-zero spin has an associated magnetic momentum, μ . The ratio between the magnetic momentum and the angular momentum is called the magnetogyric ratio, γ , a constant characteristic of each magnetically active nucleus:

$$\gamma = \frac{\mu}{\hbar I} \quad (2.1)$$

A nucleus with spin I can adopt $2I+1$ magnetic spin orientations (spin states), each having its own spin quantum number, m_i , in the range $m_i = -I, -I+1, \dots, I-1, I$. Outside the magnetic field the spin states are degenerate, but in the magnetic field the spin states separate in $2I+1$ energy levels, with the largest positive m_i value corresponding to the lowest-energy (most stable) state. This separation of the states in the magnetic field is referred to as the nuclear Zeeman effect. The energy of a given spin state (E_i) is directly proportional to the value of m_i and the magnetic field strength, B_0 :

$$E_i = -\gamma\hbar m_i B_0 \quad (2.2)$$

The selection rule for NMR transitions is that m_i can only change by one unit, i.e. $\Delta m_i = \pm 1$. Thus, the transition energy is given by: ¹

$$\Delta E = \gamma\hbar B_0 \quad (2.3)$$

To detect this transition energy, the energy of electromagnetic radiation applied, $h\nu$, must be equal to ΔE .

$$\Delta E = \gamma\hbar B_0 = h\nu \quad (2.4)$$

In equation (2.4), which gives the fundamental resonance condition for all NMR experiments, ν is the resonance frequency.

NMR spectroscopy involves the adsorption of radio-frequency energy by the nuclear spins as they resonate and reorient in the presence of both the external applied magnetic field and the internal magnetic field produced by internal electronic and magnetic

interaction.² The resonance frequency and reorientation times are sensitive to the local environment of the nucleus. This sensitivity to the local environment, together with a natural isotopic selectivity, enables NMR spectroscopy to provide detailed information about the structure of many classes of materials.³

2.1.2 NMR Interactions in the Solid State

The interaction experienced by a nuclear spin in an applied magnetic field can be described by the nuclear spin Hamiltonian, which consists of a number of terms. Haeberlean³ groups these terms in two categories: external (H_e) and internal (H_i) Hamiltonians.

H_e comprises the Zeeman Hamiltonian (H_z) and radio-frequency Hamiltonian (H_{RF}). H_z is the Zeeman interactions of the nuclear magnetic moment with the applied field and is by far the greatest interaction that dominates the appearance of the spectrum. H_{RF} results from the interaction between the nuclear spin and the time-dependent radio frequency field. H_i depends on the nucleus in question and its environment, and consists of the following terms:

$$H_i = H_{CS} + H_Q + H_{SR} + H_D + H_J \quad (2.5)$$

where H_{CS} is the chemical shift Hamiltonian expressing the shielding of the nuclear spins by surroundings electrons; H_Q is the quadrupolar Hamiltonian representing the interaction of the quadrupole moment of the nucleus with the electric field gradient (EFG) at the nuclear site; H_{SR} is the spin-rotation Hamiltonian describing the coupling of the nuclear spin with the magnetic moment; H_D is the dipolar Hamiltonian, representing the

interaction between spins, and H_J is the indirect spin–spin coupling term which is important only for directly connected atoms in molecules.

NMR interactions in the solid state are anisotropic, and their three-dimensional nature can be described by second-rank Cartesian tensors. These tensors can be diagonalized to yield tensors that have three principal components, which describe the interaction in its own principal axis system (PAS)⁴:

$$H_{\text{PAS}} = \begin{bmatrix} A_{11} & 0 & 0 \\ 0 & A_{22} & 0 \\ 0 & 0 & A_{33} \end{bmatrix} \quad (2.6)$$

Such interaction tensors are pictured as ellipsoids (Figure II.1), with the A_{33} component assigned to the largest principal component. Nuclear spins are coupled to external magnetic fields via these tensor interactions.

In the following section, the discussion will be limited to the description of the chemical shielding anisotropy, dipolar and quadrupolar interactions, since these are the most relevant to the NMR experiments conducted in the present study.

2.1.2.1 Chemical Shift Interaction

The chemical shift interaction is caused by a secondary magnetic field that is produced by the motional screening of electrons. The secondary magnetic field is proportional to the applied magnetic field B_0 , but opposite in direction. The chemical shift Hamiltonian H_{CS} can be expressed as:⁵

$$H_{\text{CS}} = \gamma \hbar I * \bar{\sigma} * B_0 \quad (2.7)$$

Figure II.1 Schematic representation of magnetic shielding ellipsoid

where $\bar{\sigma}$ is a second-rank Cartesian tensor known as the chemical shielding tensor schematically presented in Figure II.1. Three principal components of the tensor are assigned in order of increasing shielding $\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$. The experimentally measurable quantity of the shielding tensor in the laboratory frame is σ_{zz} , which is a linear combination of the principal components, σ_{jj} .⁶

$$\sigma_{zz} = \sum_{j=1}^3 \sigma_{jj} \cos^2 \theta_{jz} \quad (2.8)$$

where θ_{jz} are angles between σ_{jj} and B_0 . The expression (2.7) can be further written as:

$$\sigma_{zz} = \text{Tr}\sigma + 1/3 \sum_{j=1}^3 (3\cos^2 \theta_{jz} - 1) \sigma_{jj} \quad (2.9)$$

The first part of Eq. (2.9) is the trace of the tensor, $\text{Tr}\sigma$, a directionally invariant (isotropic) term given by:

$$\text{Tr}\sigma = (\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad (2.10)$$

The second part of Eq. (2.9) is directionally dependent (anisotropic) and gives rise to chemical shift anisotropy $\Delta\sigma$, which is given by:

$$\Delta\sigma = \sigma_{33} - 1/2(\sigma_{11} + \sigma_{22}) \quad (2.11)$$

When the tensor is axially symmetric because of local molecular symmetry, σ_{33} is defined as $\sigma_{\parallel}$ and $\sigma_{11} = \sigma_{22}$ as $\sigma_{\perp}$. Thus, Eq. (2.10) becomes:

$$\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp} \quad (2.12)$$

In solution, the rapid molecular tumbling results in averaging of the chemical shift terms over all orientations and only the isotropic chemical shift, σ_i , is observed:

$$\sigma_i = 1/3(\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad (2.13)$$

The position of this averaged line in the spectrum is given by:

$$\nu = \frac{\gamma}{2\pi} B_0 (1 - \sigma_i) \quad (2.14)$$

For a single crystal, a single line is also observed whose frequency varies with the orientation of the crystal in the magnetic field. On the other hand, in a polycrystalline powder sample each crystal will exhibit its own spectrum, each resonance position being determined by the orientation of the chemical shielding tensor with respect to B_0 . As a result, the powder pattern spectra for powder samples with different site symmetries will look similar to the ones shown schematically in Figure II.2.

Figure II.2 Schematic powder patterns for different site symmetries ⁶

It has been shown⁷ that when a polycrystalline sample is spun at an angle β to the external magnetic field, B_0 the time average-value of the tensor component along B_0 is:

$$\sigma_{zz} = \frac{3}{2} \sigma_i \sin^2 \beta + \frac{1}{2} (3 \cos^2 \beta - 1) \sum_{j=1}^3 \sigma_{ij} \cos^2 \chi_j \quad (2.15)$$

where χ_j is the angle between the spinning axis and each of the three principal axes. At the “magic angle” ($54^\circ 44'$), when $\cos^2 \beta = 1/3$ and $\sin^2 \beta = 2/3$, σ_{zz} is reduced to the scalar isotropic value σ_i , and thus chemical shift anisotropy is removed.

2.1.2.2 Dipolar Interaction

The dipolar interaction results from the interaction of one nuclear spin with the magnetic field generated by another nuclear spin, and vice versa. Dipolar interactions can be either homonuclear - between like spins or heteronuclear- between unlike spins. The dipolar Hamiltonian for the coupling between two unlike nuclei i and j is⁸:

$$H_D = I_i * \bar{D} * I_j \quad (2.16)$$

where $\bar{D}$ is the dipolar interaction tensor. Eq. (2.15) can be further written as:

$$H_D = 1/2 \gamma_i \gamma_j^2 \hbar^2 r_{ij}^{-3} (I_i I_j - 3 I_{iz} I_{jz}) (3 \cos^2 \theta_{ij} - 1) \quad (2.17)$$

where γ_i and γ_j are the nuclear gyromagnetic ratios; r_{ij} the internuclear distance, I_i and I_j are the spin operators of the two nuclei respectively; θ_{ij} is the angle between r_{ij} and B_0 which is by convention directed along the z-axis.

Essential features of this interaction are: (i) it can be averaged out when $\cos^2 \theta = 1/3$ (i.e. random rotation of molecules in fluids, or rapidly spinning solid samples at an angle

of $54^0 44'$); (ii) it is dependent upon the magnetogyric ratios of each nucleus; (iii) it is strongly dependent on the internuclear distance (inverse cubic dependence), being important only for nuclei in a close proximity.

2.1.2.3 Quadrupolar Interaction

Quadrupolar nuclei are those with spin I greater than $\frac{1}{2}$. They have non-spherically symmetric charge distributions, which gives rise to a nuclear electric quadrupole moment. The nuclear quadrupole interacts with the electric field gradients (EFG) caused by the charges that surround the nucleus. The interaction is dependent upon the distribution of electric charges and the resulting EFG's. The EFG's at the quadrupolar nucleus can be described by the EFG tensor with the three principal components defined such that $V_{11} \leq V_{22} \leq V_{33}$.

The quadrupole moment is usually denoted by eQ and the magnitude of the electric field gradient by eq , where e is the elementary charge. Thus, the size of the quadrupolar interaction experienced by a particular nucleus is a constant, called the quadrupole coupling constant, QCC, which is given by the following relation: ⁹

$$QCC = \frac{e^2 q Q}{h} \quad (2.18)$$

where $eq = V_{33}$

The asymmetry of the quadrupolar interaction is given by the asymmetry parameter, η :

$$\eta = \left(\frac{V_{11} - V_{22}}{V_{33}} \right) \quad (2.19)$$

where $0 \leq \eta \leq 1$.

The quadrupolar interaction, described by H_Q , can be written as a sum of first and second order interactions³:

$$H_Q = H_Q^{(1)} + H_Q^{(2)} \quad (2.20)$$

In the first order, when Zeeman interactions are dominant ($H_Z > H_Q$), the quadrupolar interaction is treated as a perturbation on the Zeeman Hamiltonian. The first-order quadrupolar interaction for a single spin is described by the hamiltonian, $H_Q^{(1)}$ ¹⁰:

$$H_Q^{(1)} = \frac{1}{4} \omega_Q [3 \cos^2 \theta - 1 - \eta \sin^2 \theta \cos 2\varphi] \left[I_z^2 - \frac{I(I+1)}{3} \right] \quad (2.21)$$

where θ and φ are polar angles, I_z is a nuclear spin operator and ω_Q is the quadrupolar frequency (in rad s^{-1}) given by⁷:

$$\omega_Q = \frac{3e^2qQ}{2I(2I-1)\hbar} \quad (2.22)$$

The quadrupolar frequency, ν_Q , expressed in Hz is given by:

$$\nu_Q = \frac{\omega_Q}{2\pi} = \frac{3e^2qQ}{2I(2I-1)h} = \frac{3}{2I(2I-1)} QCC \quad (2.23)$$

Thus, the first order interaction is proportional to QCC. It can also be seen from equation (2.21), that $H_Q^{(1)}$ is dependent on the asymmetry parameter, η , and independent of the applied field. If the quadrupolar interaction becomes larger, as the result of increasing EFG's (H_Q comparable with H_Z , QCC large), the second order quadrupolar

effect $H_Q^{(2)}$ must also be considered. $H_Q^{(2)}$ is proportional to QCC^2/ν_0 (where ν_0 is Zeeman frequency, $\nu_0 = \frac{\gamma}{2\pi} B_0$) and is directly dependent on the applied field.

Figure II.3 shows the effects of the first- and second-order interactions on the energy levels of a spin 5/2 nucleus. The first set of splittings is the result of the Zeeman interaction (H_Z), where the splitting is the same (equal). The second set shows the splitting which occurs when the quadrupole interaction is an order of magnitude smaller than the Zeeman interactions (QCC small), or for integer spins.

Figure II.3 Spin energy diagram for an $I = 5/2$ nucleus in a strong magnetic field ⁹

The energy levels are perturbed by the first order quadrupolar interactions being shifted by the same degree. As a result, the central transition $+1/2 \leftrightarrow -1/2$ is not

Figure II.4 Noninteger quadrupole NMR line shapes ¹¹

(a) $I = 5/2$, all transitions, first order perturbation, $\eta = 0$; (b) $I = 3/2, 5/2$, central transition, second order, $\eta = 0$ (top), $\eta = 1$ (bottom)

affected in the first order. A corresponding quadrupole-split NMR spectrum is shown in Figure II.4 (a). This spectrum consist of a relatively sharp central line at the Zeeman frequency (central transition) accompanied by a set of $2I$ lines (satellite transitions) symmetrically displaced from the central transition. The satellite transitions give broad powder pattern.

The last set of splittings shown in Figure II.3 occurs when the quadrupole interaction is comparable with the Zeeman interaction and thus, the second order perturbations of the

energy levels should be considered. This is the case for most quadrupolar nuclei when QCC is large, often so large that only the central transition is observed, the satellite transitions being broadened beyond the sweep width of the NMR spectrometer.¹¹ The second order effects on central transition are observed as a characteristic powder line shape dependent on the asymmetry parameter, η (Figure II.4 (b)) and in a shifting of the NMR line. This shifting of the NMR resonance with respect to the true isotopic chemical shift, as-called quadrupole induced shift is given by the following relation:

$$QIS = -D_I \left(\frac{QCC^2}{\nu_0^2} \right) \left(1 + \frac{\eta^2}{3} \right) \quad (2.24)$$

with $D_I = 6000$ for $I = 5/2$.

2.1.3 Magic Angle Spinning

Magic angle spinning or MAS is a well-known solid-state NMR technique used to enhance the resolution of powder pattern spectra. Applying MAS it is possible to remove line broadening caused by dipolar and first order quadrupolar interactions, and to reduce the anisotropy of the chemical shifts to their isotropic values. The second order quadrupolar interaction cannot be completely averaged by MAS, but is only reduced, nevertheless the MAS NMR lines being narrowed by a factor of 4.¹²

MAS involves continuous spinning of the sample at an angle of $\theta = 54^\circ 44'$ relative to the axis of the external magnetic field, B_0 . Because all three mentioned interactions (dipolar, first order quadrupolar interactions and chemical shift anisotropy) have a

Figure II.5 Magnetization vector, M_0 , at equilibrium

Figure II.6 Magnetization vector precessing at Larmor frequency

Figure II.7 Relaxation mechanisms⁸

dependence on the $(3\cos^2\theta - 1)$ term, this expression equals zero at the magic angle, and as a consequence the nuclear spin interactions are reduced to their values in solution.

However, the effect of MAS is not to collapse the broad powder pattern observed in static experiments of solids to a single, sharp line as in solution, but rather to produce a regular pattern of narrow spinning side-bands.¹³ The distance between the side-bands (in Hz) equals the rotation speed of the rotor. Spinning side-bands arise when the spinning speed is smaller than the static line width.⁹

2.1.4 The Pulse Fourier Transform Technique

The energy levels approach used previously is not enough to completely describe an NMR experiment. A few other tools are necessary. Among them are the vector model and the rotating framework, both being explained in the following paragraphs.

When nuclear spins are placed in a static magnetic field, B_0 , at equilibrium the magnetic moments are aligned in such a way that when their contributions are added up there is a magnetic field along the direction of the applied field. This is called the bulk magnetization of the sample and is represented by a magnetization vector, M_0 , pointing along the direction of B_0 (along z axis in a fixed axes system, so called laboratory frame) as shown in Figure II.5. If the magnetization vector is tilted away by an angle β from the z axis it executes a precessional motion (Larmor precession) in which the vector sweeps out a cone of constant angle to the magnetic field direction as shown in Figure II.6. The frequency of the Larmor precession is given by $\omega_0 = \gamma B_0$. The projection of the magnetization vector, M_0 , onto the xy-plane at initial moment t_0 will give two

components: an x-component (M_x) of size $M_0 \sin \beta$ and a y-component (M_y) of size $-M_0 \sin \beta$. As the vector is rotating at ω_0 , after time t the angle through which the vector has precessed is given by $\omega_0 t$. The x- and y-components of M_0 become:

$$M_x = M_0 \sin \beta \cos(\omega_0 t)$$

$$M_y = -M_0 \sin \beta \sin(\omega_0 t)$$

It is useful to consider NMR experiments in a rotating reference frame, rather than in a fixed one, since the rotation of the magnetization vector at the Larmor frequency in a frame moving at the same frequency would remove the time dependence of the magnetization vector. The rotating frame is one in which the z' axis is the same as the magnetic field direction, but the x' and y' axes rotate about the z' axis at a frequency ω_0 . Applying an rf pulse of frequency ω_0 , along the x' axis in the rotating frame would be equivalent to applying a static field B_1 along x' . The effect of applying a constant field along x' for a time t , cause M_0 to rotate in a clockwise direction about the x' axis with a frequency $\omega_1 = \gamma B_1$, and M_0 to be displaced from the equilibrium by an angle of $\theta = \gamma B_1 t$.¹ This angle is called pulse angle. Since the spectrometer is designed to detect the signals along y' -axis, tipping M_0 through the angle θ will give rise to a component $M_0 \sin \theta$ along the y' -axis. M_0 attains a maximum when $\theta = 90^\circ$. This pulse is known as the 90° pulse.

Once the rf pulse is removed, the perturbed magnetization will begin to relax back towards its equilibrium condition, causing the signal induced in the coil by oscillating magnetic fields to decay. This signal is called free induction decay (FID). The FID is a

time domain function and after phase sensitive detection and digitization, the FID is Fourier Transformed into a frequency domain function, which is known as the NMR spectrum. In Figure II.7 the two relaxation processes involved in the recovery of the original magnetization are shown.

In the first, the relaxation occurs by the lost of energy from the excited nuclear spins to the surrounding molecular lattice. In this process, called spin-lattice or longitudinal relaxation, the component of the magnetization remaining along the z-axis (M_z) relaxes back to its original value, M_0 , with a constant T_1 .¹⁴

In the second, the relaxation arises from a redistribution of the energy within the spin system. This process, called spin-spin or transverse relaxation, involves the lost of phase coherence of the individual nuclear moments in the $x'y'$ -plane with the time constant T_2 (ignoring magnet inhomogeneity effects).¹⁴

2.1.4 Spin - Echo Pulse Sequence

Broad lines arising from chemical shift anisotropy, dipolar coupling, quadrupolar interactions etc. have rapidly decaying free induction decay's (FID). "Ringing" in the rf coil measuring the FID prevents measurement of the signal until a short time (dead time) after a pulse. As a result the initial part of the FID is not recorded, and distortions are induced into the time domain (TD) spectrum after applying Fourier transformation. The problem can be overcome by using so called spin-echo pulse technique. There are several modifications of the spin-echo sequence depending on the interactions that contribute to the line broadening.

The spin-echo sequence “ $\pi/2_x - \tau - \pi_y - \tau - \text{acquire}$ ” together with the behavior of the transverse magnetization components are depicted in Figure II.8. A $\pi/2$ pulse applied along x' at time 0 causes the magnetization to tip to the positive y' axis. As a result of the inhomogeneity in B_0 the magnetization components dephase during the first τ period.

Figure II.8 The spin - echo pulse sequence

The subsequent π pulse rotates the magnetization components 180° about the pulse axis (y' in this case) so that the components refocus after a further τ period. Choosing a τ delay long enough to include the dead time of the probe, the complete FID can be completely recorded from the true echo maximum.¹⁵

2.1.5 General Aspects of ^{29}Si and ^{27}Al NMR in Silicates and Aluminosilicates

Frameworks

^{29}Si and ^{27}Al NMR provide valuable information on the local structure and symmetry in silicates and aluminosilicates.

To illustrate the structure of building units in silicates, the Q^n notation is commonly adopted, where Q represents the Si atom bonded to four O atoms. The superscript n indicates the connectivity, the number of other Q units attached to the SiO_4 tetrahedron. For aluminosilicates the number of AlO_4 tetrahedra (m) bound to central silicon of a Q^n unit is presented as $\text{Q}^n(\text{mAl})$.¹⁶

2.1.5.1 ^{29}Si NMR

Silicon has one naturally occurring isotope with non-zero spin, ^{29}Si ($I = \frac{1}{2}$). It has low γ and a very low natural abundance of 4.7%, which makes desirable application of high magnetic fields for obtaining ^{29}Si NMR signals. Moreover, the broad and often overlapped resonances observed in the static spectra imply the use of MAS technique for recording highly resolved ^{29}Si NMR spectra.

The characteristic features of the ^{29}Si NMR spectra are: chemical shift, linewidth, and intensity. All these parameters are closely related to the structure of the sample.

Chemical Shift

Chemical shift (δ) depends on the chemical environment of the ^{29}Si nucleus, particular geometry around the Si atom in question and its coordination number.

The particular sensitivity of the ^{29}Si NMR to the chemical environment is described by several empirical relationships between δ and structural parameters in silicates and aluminosilicates. For example, a shift of approximately 10 ppm to a lower frequency is observed for each SiOSi connection in a given Q^n environment, while each replacement of Si with Al in a $Q^n(\text{mAl})$ environment induces a shift contribution of 5 ppm to a higher frequency.¹⁶

The particular geometry around the Si atom (SiOT bond angles, α , - where T is Si or Al; Si-Si distances, $d_{\text{Si-Si}}$; Si-O bond lengths, $d_{\text{Si-O}}$) influences the chemical shifts, low-frequency shifts of δ being observed with decreasing $d_{\text{Si-O}}$ and increasing α and $d_{\text{Si-Si}}$.

Finally, the ^{29}Si NMR chemical shift sensitivity to coordination number is indicated by the large low frequency shifts observed when Si is six-coordinated compared to Si in a four-coordination state.¹⁶

Linewidth

The lines in the static ^{29}Si NMR spectra are often broad due to various spin interactions: (i) chemical shielding anisotropy has the main contribution in the line width; (ii) heteronuclear dipolar interactions between ^{29}Si and ^1H or ^{27}Al , and possible other NMR-active nuclei if they are present in a close proximity to ^{29}Si nuclei; (iii) the presence of paramagnetic impurities.¹⁷

In general, shielding anisotropy and weak heteronuclear dipolar interactions can be fully averaged by MAS. However, the narrowing of the line width by MAS technique is not complete, few other factors may add their contributions, such as: (i) dispersion of

chemical shifts due to structural disorder, distortion or amorphisation of the framework;

(ii) residual dipolar interaction between ^{29}Si and ^1H or ^{27}Al .¹⁶

Intensity

When recorded under appropriate experimental conditions (long enough relaxation delays), the integrated intensities of the peaks observed in the ^{29}Si NMR spectra are directly related to the number of the silicon atoms present in the sample.¹⁶

2.1.5.2 ^{27}Al NMR

Aluminum has only one naturally occurring isotope, namely ^{27}Al , which is quadrupolar with $I = 5/2$. The fast relaxation generally observed for quadrupolar nuclei and its high natural abundance (100%), make ^{27}Al a very favorable nucleus for NMR investigations.

In addition to chemical shift and dipolar interactions mentioned already for ^{29}Si NMR, for ^{27}Al NMR the quadrupolar interactions should be taken into account. The nuclear quadrupolar moment of ^{27}Al nucleus interact with an electric field gradient at the site of the nucleus caused by surroundings ions. For a perfect tetrahedral surrounding of aluminum by four oxygens, the electric field gradient is zero. Any distortion of this tetrahedron, however, cause a field gradient at aluminum and consequently quadrupolar interactions of the aluminum nuclear spins.¹⁸ The effects of chemical shift and dipolar interactions can be totally removed under fast magic angle spinning conditions ($\nu_{\text{rotor}} \geq 7$ kHz), but the quadrupolar interactions can be only reduced. If only isotropic ^{27}Al chemical shift is required, the application of very high B_0 is advantageous. Because the

consequences of the quadrupolar interactions in the ^{27}Al NMR spectra were outlined already and for the purpose of the present work, only two spectral parameters are mentioned below.

Isotropic Chemical Shift

The ^{27}Al MAS NMR spectra are usually simpler than the ^{29}Si spectra counterpart since only one tetrahedral environment, namely $\text{Al}(\text{OSi})_4$ exists in the zeolite framework (Al-O-Al linkage is forbidden in the zeolite framework according to Loewenstein).^{10,17} The extra-framework Al atoms are usually octahedral units $[\text{AlO}_6]$, and rarely pentahedral units $[\text{AlO}_5]$. The observed shifts are about +50 to +80 ppm for $[\text{AlO}_4]$, about -10 to +20 ppm for $[\text{AlO}_6]$ and about +30 to +40 ppm for $[\text{AlO}_5]$.¹⁷

Line intensity

The ^{27}Al line intensity is affected (apart from the usual experimental difficulties) by: (i) the very strong quadrupolar interactions at some ^{27}Al sites, interactions which may broaden the lines beyond detection; (ii) excitation of satellite transitions of which extent depends the spectral intensities changes of the central transition.

2.1.6 Alkali Metals NMR

The NMR spectra of alkali metal nuclei in bulk metals are dominated by the Knight shift interaction between nuclear spins and conduction electrons. The Knight Shift refers to the relative shift, in NMR frequency, for atoms in metal compared with the same atoms in a nonmetallic environment.¹⁹

Table II. 1 Spin properties of alkali metals nuclei ²⁸

Isotope	Spin	Natural Abundance (N) (%)	Magnetogyric Ratio (γ) ($\times 10^7$, rad T ⁻¹ s ⁻¹)	Quadrupolar Moment (Q) ($\times 10^{-28}$ m ²)
⁶ Li	1	7.42	3.966	-8 $\times 10^{-4}$
⁷ Li	3/2	92.58	10.396	-4.5 $\times 10^{-2}$
²³ Na	3/2	100	7.076	0.12
³⁹ K	3/2	93.1	1.2484	5.5 $\times 10^{-2}$
⁴¹ K	3/2	6.88	0.6852	6.7 $\times 10^{-2}$
⁸⁵ Rb	5/2	72.15	2.5829	0.247
⁸⁷ Rb	3/2	27.85	8.7532	0.12
¹³³ Cs	7/2	100	3.5089	-3 $\times 10^{-3}$

2.1.6.1 Lithium

Lithium has two NMR active isotopes ^6Li and ^7Li , both quadrupolar. ^7Li has spin $I = 3/2$, a relatively low quadrupolar moment ($-8 \times 10^{-4} \times 10^{-28} \text{ m}^2$) and a high natural abundance (93%), which renders the registration of the ^7Li NMR spectra relatively simple. By contrast, ^6Li ($I = 1$) has both low natural abundance and low magnetogyric ratio, which makes ^6Li NMR spectra more difficult to record.¹⁷

2.1.6.2 Sodium

The ^{23}Na nucleus, the only naturally occurring NMR active nucleus of sodium, has a spin $I = 3/2$, and a large quadrupolar moment ($0.12 \times 10^{-28} \text{ m}^2$) as shown in Table II.1. Because of the large quadrupolar moment, the ^{23}Na nucleus has a significant second-order quadrupolar shift and will give rise to broad NMR lines with characteristic shapes. The second-order quadrupolar doublet pattern is often only narrowed, but not reduced, to a single line under MAS conditions, even at the highest magnetic field strength of 11.7 T.¹⁶

2.1.6.3 Potassium

Potassium has two NMR active nuclei ^{39}K and ^{41}K . The ^{39}K nucleus has a spin $I=3/2$, high natural abundance (93.1%), a relative large quadrupole moment ($5.5 \times 10^{-2} \times 10^{-28} \text{ m}^2$) and a very low magnetogyric ratio ($\sim 1.3 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$). The latter spin property makes ^{39}K difficult to study by NMR at low magnetic fields (i.e. its resonance frequency in a 400-MHz field is around 18 MHz), but higher magnetic fields would make the ^{39}K NMR spectrum easier to be recorded. The ^{41}K nucleus is also quadrupolar ($I = 3/2$), having a

quadrupole moment even larger than the ^{39}K nucleus and a low natural abundance (6.98%). All of these make ^{41}K impractical for NMR studies.

2.1.6.4 Rubidium

Rubidium has two NMR active nuclei ^{85}Rb and ^{87}Rb , both quadrupolar. The ^{87}Rb nucleus has a spin $I=3/2$, relatively high magnetogyric ratio ($\sim 8.8 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$), but its low natural abundance (27.85%) and the large quadrupolar moment ($0.12 \times 10^{-28} \text{ m}^2$) make the recording of the ^{87}Rb NMR spectra not easy to attain. The ^{85}Rb nucleus is even more difficult to study using NMR techniques, its large spin number ($I = 5/2$) rendering to larger quadrupolar effects, and its low magnetogyric ratio ($\sim 2.6 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$) demanding a larger magnetic field strength.

2.1.6.5 Cesium

The only NMR active nucleus of Cesium, namely ^{133}Cs , has a 100% natural abundance, a spin number of $I=7/2$, and a low quadrupole moment ($-3 \times 10^{-3} \times 10^{-28} \text{ m}^2$). As a consequence the lines of the solid-state ^{133}Cs NMR spectra are only relatively broad owing to quadrupolar interactions, and the shift range is sufficiently large to resolve distinct lines of ^{133}Cs nuclei in different structural surroundings, even without the application of MAS.¹⁷

NMR line widths of a quadrupolar nuclide are related to Q^2 (Q is the electric quadrupolar moment) and to the spin of the nucleus (I) through the line width factor (l) defined by:

$$l = Q^2 \frac{(2I+3)}{[I^2(2I-1)]} \times 10^{56} \text{ m}^4 \quad (2.25)$$

Since ^{133}Cs nucleus has a large spin ($I=7/2$), but a small electric quadrupolar ($Q = -3 \times 10^{-3} \times 10^{-28} \text{ m}^2$), its linewidth factor will be small ($l = 1.2 \times 10^{-6} \times 10^{56} \text{ m}^4$), the smallest of any quadrupolar nuclide, and therefore ^{133}Cs line widths are relatively narrow compared to those of other alkali metals.⁶

2.2 Electron Spin Resonance (ESR) Spectroscopy

Electron spin resonance (ESR) spectroscopy, also known as electron paramagnetic resonance (EPR), is a spectroscopic technique that uses microwave radiation to detect spin-state changes in substances containing unpaired electron spins (paramagnets). The spin state changes can be induced by a few milliwatts of microwave power when a sample is placed in a magnetic field of about 3480 gauss at corresponding frequencies ($\sim 9.5 \text{ GHz}$).

The ESR technique is closely related to the NMR technique, the main differences being the target species to be detected (unpaired electrons versus nuclei) and the type of electromagnetic radiation used to induce the absorption process (microwave versus radio frequency radiation). Another difference arises from the natural abundance of the species analyzed by each technique: ESR is very specific since paramagnets are relatively rare in nature, while NMR is more general, many nuclei being highly abundant in nature.

Regarding its limit of detection, the ESR technique is remarkably sensitive, being able to detect molar concentrations of paramagnetic species in the range of 10^{-1} to as low as 10^{-12} M .²⁰

2.2.1 Basic Theoretical Concepts

The interactions measured by the ESR technique are: (1) interactions between the electron spin and the applied magnetic field (Zeeman interactions); (2) spin orbit coupling; (3) electron spin - nuclear spin interactions (hyperfine and superhyperfine interactions); and (4) spin-spin interactions. Below, only the Zeeman and the electron spin-nuclear spin interactions are described.

Zeeman Interactions

In the presence of a magnetic field, B_0 , a molecule or ion having one unpaired electron has two electron-spin energy levels, described by the Hamiltonian:

$$H = g\mu_B B_0 M_S \quad (2.26)$$

where g is a proportionality factor ("g factor"), μ_B is the Bohr magneton, and M_S is the electron spin quantum number ($\pm 1/2$).

The allowed transition has the condition $\Delta M_S = 1$, so the resonant condition is given by:

$$\Delta E = h\nu = g\mu_B B_0 M_S \quad (2.27)$$

where ν is the frequency of the microwave radiation and h is the Planck constant.

An ESR spectrum is obtained by monitoring the microwave adsorption as the magnetic field is changed, and a typical spectrum is shown in Figure II.9. The appearance of the spectrum (first-derivative of the adsorption) arises from the detection technique, which is sensitive to the slope of the adsorption curve.²¹

Figure II.9 The appearance of the ESR spectrum ²²

In the ESR spectrum, the g factor is an important value to determine because all of the other factors are either constant ($h/\mu_B = 714.484 \text{ GHz}^{-1}$) or set (i.e. $\nu \sim 9.2 \text{ GHz}$). The g factor can be calculated using the following formula:

$$g = (714.484 \text{ GHz}) \times \nu / B \quad (2.28)$$

Electron Spin - Nuclear Spin Interactions

When the unpaired spin interacts with the neighboring nuclear magnetic dipole, the effect of this interaction should be considered. The total system would be described by:

$$H = g\mu_B B_0 M_S + A M_S I \quad (2.29)$$

where A is the hyperfine coupling constant and I is the nuclear spin number.

The effect of these electron spin-nuclear spin interactions can be observed in the ESR spectrum as an important feature - hyperfine structure - the splitting of individual lines

into components. The spacing between the lines (A) is dependent on the strength of the interactions.²¹ The hyperfine structure is a sort of fingerprint which helps to identify the paramagnet, and A , the hyperfine coupling constant, can be used to map the molecular orbital occupied by the unpaired electron.²³

2.3 X-ray Diffraction

2.3.1 Basic Theoretical Concepts

The X-ray diffraction technique is used for the identification of the crystalline materials and to determine their crystal structure.²⁴ The technique is based on the diffraction phenomenon, due to the interference caused by an object in the path of waves. This interference will occur only when the dimensions of the diffracting object are comparable to the wavelength of the radiation. The X-rays have wavelengths comparable to the bond lengths in the molecules and the spacing of atoms in crystals (about 0.1 Å, and as a result, they are diffracted by them.

The Origin of X-rays

X-rays are electromagnetic radiation of wavelength 0.1-100 Å produced in an evacuated tube by applying an electrical current to a wire filament that ejects electrons. The electrons are accelerated across a high potential and then allowed to strike a metal target. X-rays are generated as a result of the interaction of the incident electrons with the inner core of the target metal, in which the 1s electrons are expelled. The vacant 1s level is immediately filled with an electron from an outer orbital (2p or 3p) and the energy released in the transition appears as X radiation.²⁴

Diffraction of X-rays

Treating the diffraction of X-rays by crystals as “reflections” from lattice planes separated one from each other by the distance d , Bragg formulated the following condition in order for constructive interference to occur:

$$2d\sin\theta = n\lambda \quad (2.30)$$

where θ is the angle between the incoming X-ray beam and the lattice planes, λ is the wavelength of the X-ray radiation, and n is the order of reflection.

A diffraction experiment will generally not produce diffraction patterns when using an arbitrary setting of a single crystal in a monochromatic X-ray beam, and as a result, very little information can be obtained. This problem can be overcome by continuously varying θ or λ over a range of values to satisfy Bragg’s law. Practically this is done by: (i) using a powder or a polycrystalline specimen (Powder X-ray Method) or by rotating the crystal (Single Crystal X-ray Method) in a monochromatic beam of X-rays; (ii) using a range of X-ray wavelengths (synchrotron radiation).

In the following sections only the first two methods will be briefly discussed since they are the only ones applied in this study.

2.3.2 Powder X-ray Diffraction (PXRD)

The idea behind this method is that in powdered samples there will always be some crystallites oriented in such a way as to satisfy the Bragg’s condition. Each crystallite behaves like a single crystal and may diffract one beam. All crystallites can be seen as single crystals, that have all possible orientations, diffracting all possible beams. This

results in many coaxial cones of diffracted beams emanating from the samples, one cone for every diffracted beam. The cone half-angles are 2θ . Measuring 2θ and knowing the wavelength of the X-ray, the d spacing can be calculated using Bragg's law. The reflections are digitized and the result is a powder x-ray diffractogram, a plot of intensities of diffracted beams versus 2θ . Comparing the diffraction pattern with known data from a database an identification of the material is possible.

As dictated by Bragg's law, the larger the diffraction angle, the smaller the length scale probe. As related to the present work, two consequences are as follow: (i) wide angle x-ray diffraction (WAXD) was used to determine the crystal structure on the atomic length scale (as is the case of the ZSM-5 zeolite); (ii) the small-angle x-ray diffraction (SAXD) was used to probe large length scale structures such as mesoporous materials of the MCM family (only hexagonal structures in our materials).

The d spacing for the hexagonal structure is given by: ²⁴

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (2.31)$$

where a, c are the parameters of the hexagonal cell, and h, k, l are Miller indices.

Knowing d_(hkl), the diffraction conditions for the hexagonal structure are:

$$\frac{d_{(100)} : d_{(110)}}{d_{(100)} : d_{(200)}} = \frac{\sqrt{3}}{2} \quad (2.32)$$

2.3.2 Single Crystal XRD (SC XRD)

Single crystal X-ray diffraction is the method of choice for the crystal structure determination. If large enough crystals of good quality are available, this method allows

measurements of the intensities and the position of the X-ray reflections with high precision. The index triple (h,k,l) can be determined from the position of the reflection, and the appropriate intensity can be assigned to it. The intensity of the reflection depends on various factors, such as: (i) polarization factor - angular dependence of intensity scattered by electrons; (ii) structure factor – dependent on the position of atoms in the unit cell and their scattering power; (iii) temperature factor – dependent on thermal vibrations of atoms, which decrease the intensities of diffracted beams and increase the background scattering; (iv) extinction - reduced diffracting power due to nearly perfect crystals.²⁵

The structure of a crystal is solved and refined using various crystallographic software packages and the data sets obtained from several ten thousand reflections collected during an SC XRD experiment.

2.4 Nitrogen Physisorption (Porosimetry)

Nitrogen physisorption is one of the most popular techniques used to study the pore sizes and surface area of porous materials. This method is based on the effect of condensation of nitrogen in the pores of the material at a constant temperature by increasing the nitrogen relative pressure. The correlation of pore size with pressure can also be conducted in the reverse way, by decreasing the nitrogen relative pressure and emptying the pores. The equilibrium relationship between the amount of nitrogen adsorbed or desorbed and the given pressure at constant temperature produces the sorption isotherm. From the sorption isotherm not only pore size distribution, but also

other valuable information such as the type of interaction between adsorbate and adsorbent phases and eventually the class of the porous material, can be obtained.

Figure III.10 IUPAC classification of nitrogen adsorption and desorption isotherms²⁵

According to the IUPAC classification, there are six types of isotherms (Figure II.10) corresponding to adsorbents that are microporous (type I), nonporous (type II, III, VI) or mesoporous (type IV and V).²⁶ OMS (ordered mesoporous materials) materials are porous materials that give rise to nitrogen adsorption isotherms of type IV with or without hysteresis loop. The hysteresis loop is formed when nitrogen condensation and

evaporation within the pores occur at different relative pressures. The existence of a hysteresis loop in the isotherm indicates the presence of mesopores, whereas the shape of the hysteresis loop is related to the shape of the mesopores. Roughly, a vertical hysteresis loop indicates cylindrical mesopores, whereas a horizontal hysteresis loop indicates inkbottle-type mesopores.²⁷ Because part of this study was focused in investigating the Cesium deposition inside the mesopores, it was important to know their shape.

For the analysis of the nitrogen physisorption data several methods are available, between which the BET (Brunauer-Emmet-Teller) and the BJH (Barret-Joyner-Halenda) methods.²⁵ The BET method is based on a kinetic model of the adsorption process put forward by Langmuir,^{26,27} in which the surface of a solid is regarded as an array of adsorption sites. A state of dynamic equilibrium was postulated in which the rate at which molecules arriving from the gas phase and condensing on the bare sites is equal to the rate at which molecules evaporate from occupied sites.²⁷ The BJH method uses the adsorption or desorption branches of the nitrogen isotherms to calculate: the surface area, the pore size and the adsorbed volume. In the present work, we used the total volume of the pores to estimate the maximum amount of Cesium metal that can occupy the void spaces of MCM's materials or Vycor glass.

2.6 References

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Chapter III

Alkali Metal-Loaded ZSM-5 Zeolite

3.1 Introduction

As mentioned in the introductory chapter, alkali metals dispersed in zeolites have attracted particular attention because of the unusual species which can form inside the void spaces. The nature of such species depends greatly on the pore structure and cationic form of the zeolite used. In cage zeolites, such as X, Y or A, isolated alkali metal clusters have been found. On the other hand, channel zeolites might be expected to have extended chains of alkali atoms present. In this work we have used H-ZSM-5 zeolite with its porous channel structure to verify this hypothesis.

H-ZSM-5 zeolite synthesized in our lab was dehydrated and then loaded with different amounts of Na, K, Rb or Cs metal via vapor deposition at elevated temperatures. The corresponding alkali metal exchanged-ZSM-5 zeolites were also prepared, dehydrated and used as references in the spectroscopic techniques performed. As well, a Cs-loaded Li-ZSM-5 sample was synthesized in order to compare the framework stability of H-ZSM-5 vs. Li-ZSM-5 upon loading with the same amount of Cs metal.

^{23}Na , ^{87}Rb or ^{133}Cs NMR and ESR spectroscopy were used to identify diamagnetic and paramagnetic alkali metal species. Interaction of the zeolite with the alkali metals was followed with ^1H MAS NMR, as well as with ^{27}Al and ^{29}Si MAS NMR and powder XRD to confirm retention of the framework crystallinity. When the quality of the metal loaded-ZSM-5 crystals permitted (Rb/ZSM-5, and Cs/ZSM-5), SC-XRD analyses were performed for crystal structure determination.

3.2 Experimental Section

3.2.1 Samples Preparation

3.2.1.1 ZSM-5 Synthesis

A ZSM-5 zeolite with a unit cell composition $H_{3.7}[Si_{92.3}Al_{3.7}O_{192}]$ (Si/Al = 25) was prepared via the “fluoride method”.^{1,2} The original method was modified to use a completely soluble Al source. This method was chosen for two main reasons: (i) defect-free crystals could be prepared; and (ii) the protonated form of the product could be obtained simply by calcination of the template without additional ion exchange.²

The starting materials were: (i) Ludox AS-40 colloidal silica (Aldrich, 40 wt. % suspension in water) as a silica source; (ii) aluminium chloride hexahydrate (Anachemia, 99.99% Al) as Al precursor; tetrapropylammonium bromide (TPABr) (Aldrich, 98%) as the template for reaction; (iii) ammonium fluoride (Aldrich, 98%) as the solubilizing agent for the other reagents and (iv) distilled water. The synthesis gel composition was as follow:

Si: Al:F:TPABr: H₂O = 1:0.04:1:0.2:40

Two solutions (A and B) were prepared separately in two beakers under stirring at 40 °C. Solution (A), 0.68 g of Al precursor was dissolved in a solution of 3.85 g of TPABr in 20 ml water. Solution (B), 2.67 g of NH₄F were dissolved in 23 ml water. The two clear solutions (A and B) were combined rapidly after cooling them to room temperature under vigorous stirring. 10.63 g of Ludox AS-40 silica sol was then added dropwise under agitation to the solution and stirred for 1 hour. The resulting gel was transferred into Teflon-lined stainless steel autoclaves, and aged hydrothermally at 175 °C. The crystal

formation was periodically checked by optical microscopy. The crystals sizes ranged from 40 -100 μm after 4 days, and up to about 200 μm after 6 days. When the crystals attained the desired size, the autoclaves were quenched and solid and liquid phases separated. The solid product was washed with distilled water and air-dried overnight. The template was removed by calcination at 550 $^{\circ}\text{C}$ in air for 6 hours.

Three different batches were prepared: one with crystal sizes of about 100 μm which was used in preparing Cs-loaded, Li-exchanged ZSM-5, and Cs₁₀/Li-ZSM-5 samples, another with crystal sizes of about 200 μm which was used to prepare the Rb-loaded and Rb-exchanged ZSM-5 samples, and the last with crystals sizes of about 150 μm for Na-loaded, Na-exchange ZSM-5 and K-loaded samples.

3.2.1.2 Ion-Exchanged ZSM-5 Synthesis

The starting material was the protonated form of ZSM-5 (H-ZSM-5) obtained as described in the previous section. The weakly acidic suspension (pH = 4-5) of H-ZSM-5 in distilled water was repeatedly treated with a 1 M solution of LiOH, NaOH, RbOH or CsCl under stirring at room temperature until neutralization (pH = 7) as indicated by pH paper. The liquid was then decanted and the crystals were collected on a filter paper, washed several times with distilled water, and dried in air overnight. Thus prepared zeolites were named Li-ZSM-5, Na-ZSM-5, Rb-ZSM-5 and Cs-ZSM-5.

3.2.1.3 Preparation of the Alkali Metal-Loaded ZSM-5

Alkali metal-loaded samples were synthesized by a direct reaction of the dehydrated H-ZSM-5 zeolite with known amounts of alkali metal via vapour-phase deposition in sealed, evacuated reaction vessels.

Figure III.1 Vacuum setup used for dehydration of porous templates : 1-power supply; 2-transformer; 3-temperature controller; 4-oven; 5-thermocouple; 6-vessel stopcock assembly; 7-vacuum installation; 8-cold trap; 9-diffusion pump; 10-oil pump; 11-pressure controller.

The reaction vessel, consisting of a central chamber (70 mm length and 25 mm o.d.) with an attached access tube (140 mm length and 10 mm o.d.) and two side arms (25 mm length and 5 mm o.d.), was made from quartz glass. Quartz was used instead of Pyrex in order to avoid interference from the sodium nuclei present in Pyrex when conducting ^{23}Na NMR on samples containing sodium and to ease the symmetrical sealing-off process of the side arms, which is crucial for MAS experiments.

Before use, the reaction vessel was soaked in detergent, rinsed abundantly with tap and then distilled water, and held in an oven at 120 $^{\circ}\text{C}$ for a few days. The same cleaning procedure was applied to all reaction vessels used in the experiments.

The vessel with the vacuum stopcock assembly is shown in Figure III.1(6). The whole set up was weighed empty and after adding the zeolite powder. The amount of H-ZSM-5 zeolite before dehydration (~ 0.5 g) was determined by weight difference. The set up with the added zeolite powder was then connected to a vacuum line and evacuated slowly for 2 hours at room temperature. Then it was heated gradually (1 $^{\circ}\text{C}/\text{min}$ with a 4 h ramp at 120 $^{\circ}\text{C}$) in a Hoskins cylindrical furnace connected to an Omega CN-2010 Programmable Temperature Controller to 450 $^{\circ}\text{C}$ and held at this temperature for 48 h under a pressure of less than 10^{-4} torr. Supplementary treatment of the zeolite with oxygen at 525 $^{\circ}\text{C}$ for about 2 h was necessary to oxidize the remaining surface carbon impurities. The oxygen was introduced in the segment of the vacuum line where the vessel had been attached after disconnecting this segment from the vacuum pump (Figure III.1). When the zeolite surface whitened again, the vessel was cooled down slowly to room temperature, then re-evacuated, detached from the vacuum line together with the

vacuum stopcock assembly, and the whole set up re-weighed to determine the amount of dehydrated powder. A corresponding quantity of the desired alkali metal was weighed in a small tube (5 mm o.d., 20-25 mm length) and added into the reaction vessel in an argon atmosphere glovebox. The purpose of using these small tubes was to prevent direct contact of the alkali metal with the zeolite powder, in which case prolonged reaction times were necessary, especially for the Na metal. Before loading the tubes, the solid alkali metals (Na, K) were carefully cleaned of solid oxide impurities on the metal surface and cut into small pieces, and the low-melting alkali metals (Rb, Cs) were heated slightly to ease the loading process. After loading with the desired alkali metal, the reaction vessel was re-attached to the vacuum line and re-evacuated. The vessel was then sealed off with a gas torch and placed into a furnace preheated to a specific temperature depending on the alkali metal (100 °C-Cs, 120 °C-Rb, 160 °C-K, 250 °C-Na). The sorption of the alkali metal upon heating soon became apparent by the change in the sample's colour (from white in the starting zeolite to cream in low-loaded samples, brown in highly-loaded samples, and even dark blue for the Cs₂₅/ZSM-5 sample). To ensure the homogeneous distribution of the metal, the samples were periodically shaken and equilibrated at the mentioned temperatures. After the disappearance of the alkali metal (from a few days to weeks depending on the metal and the loading) the sample was slowly cooled down to room temperature. For some samples (i.e. Na₁₀/ZSM-5) a repeated process of cooling down to room temperature followed by re-heating was necessary to speed up the reaction. The product was then transferred into the side arms attached to the

Table III.1 Alkali metal-loaded ZSM-5 samples

Composite, M _x /ZSM-5*	Alkali metal loading			Thermal Treatment	Colour
	Per unit cell	Weight%	Filling factor		
Na ₅ /ZSM-5	4.8	1.9	-	250 °C, ~6 days	Light brown
Na ₁₀ /ZSM-5	12.3	4.7	-	250 °C, ~14 days	brown
K ₅ /ZSM-5	6.4	4.2	-	160 °C, 5 days	light brown
K ₁₀ /ZSM-5	11.2	7.1	-	160 °C, 8 days	brown
Rb ₅ /ZSM-5	5.7	7.7	0.30	120 °C, ~4days	light brown
Rb ₁₀ /ZSM-5	10.6	13.6	0.56	120 °C, ~5days	brown
Rb ₂₅ /ZSM-5	26.2	28.7	1.44	120 °C, ~8days	brickred
Cs ₅ /ZSM-5	5.1	10.4	0.33	100 °C, 5 days	light cream
Cs ₁₀ /ZSM-5	11.1	20.4	0.73	100 °C, 7 days	cream
Cs ₂₅ /ZSM-5	26.3	37.7	1.73	100 °C, ~9 days	dark blue
Cs ₁₀ /Li- ZSM-5	-	-	-	100°C, ~5 days	dark gray

* M = alkali metal, x = number of atoms per unit cell

reaction vessels, which were then sealed off with care to ensure symmetric sealing. When there was a sufficient quantity, the remaining portion of the sample was collected after breaking the access tube to the chamber, then washed several times with distilled water and dried in air. The resulting powders, coloured from white (low loaded samples) to pale yellow (highly loaded samples), were then investigated with PXRD.

Table III.1 lists the alkali metal-loaded ZSM-5 samples, their corresponding colour and the thermal treatment applied (temperature and reaction time).

3.2.2 Experimental Conditions

3.2.2.1 Powder X-Ray Diffraction (PXRD) Measurements

Powder X-ray diffraction patterns for calcined H-ZSM-5 and washed alkali metal-loaded ZSM-5 samples were collected on a Scintag X₂ powder diffractometer ($\text{CuK}\alpha = 1.54056 \text{ \AA}$). Care was taken in preparing the samples for PXRD measurements: the crystals were finely ground, the surface of the sample was carefully leveled, and approximately the same quantity of sample was exposed to X-rays in each experiment (a zero background plate with imposed volume of sample was used). The diffractograms for washed Rb, Na, and K samples and the starting H-ZSM-5 zeolite were recorded with a fast scan rate (1.2 degree per minute), but for washed Cs samples and the starting ZSM-5 zeolite for this series with a slow scan rate (0.048 degree per minute), to minimize the noise. The step size and the range of 2θ were in all cases the same: 0.02° and 5-40 degrees, respectively. A powder pattern search and match was done through the online database of the International Zeolite Association (IZA)³ or the “Collection of Simulated XRD patterns for Zeolites”.⁴

Figure III.2 The Bruker MAS BL 7 mm probe (top); the spinning rotor and a sealed sample (bottom)

3.2.2.2 NMR Experiments

The following NMR experiments were performed: ^1H MAS NMR, ^{29}Si MAS NMR, ^{27}Al MAS NMR, ^7Li MAS NMR, ^{23}Na MAS NMR, ^{87}Rb spin echo NMR, ^{133}Cs static NMR.

The frequency at which the spectra were recorded, the spectrometers and probes used, the type of experiment (MAS or static), the spinning rate of the MAS experiments are listed in Table III.2. Regarding the MAS experiments: (1) highly stabilized spinning frequencies were achieved using a Bruker MAS Remote Control Unit H2620; (2) the experiments were run after an exact magic angle setting (54.7°); (3) 7 mm o.d. zirconia rotors were used (Photos of the BI 7 mm MAS probe used, the rotor and a sealed sample are shown on Figure III.2).

The acquisition parameters (delays, pulse width, sweep width, number of scans) appropriate for each nucleus are also listed in Table III.2. Relaxation delays were chosen to ensure complete relaxation.

Generally, a simple one-pulse sequence was applied for recording the spectra, with the exception of ^{87}Rb NMR for which a spin echo sequence was necessary to minimize the acoustic ringing complicating the single pulse experiment. All experiments were performed at ambient temperature.

The chemical shift reference samples are also listed in Table III.2. The length of the 90° rf pulse for the liquid references (τ_l) was determined via standard procedures and the value for the 90° rf pulse in the solid samples (τ_s) was calculated using the following relation:

Table III.2 Typical conditions of NMR measurements

Isotope	Spectrometer	Resonance frequency, MHz	Acquisition parameters				Reference	Conditions
			Sweep width, kHz	Pulse width p_1 , μ s	Fixed delay d_1 , s	Number of scans		
^1H	DSX 400	400	80	5	3	1k	TMS	MAS 3.5 kHz BL 7 mm
^{29}Si	AMX 300	59.6	15	5	30	1 k	TMS	MAS 3.5 kHz BL 7 mm
^{27}Al	AMX 300	78.2	50	2	0.5	4 k	$\text{Al}(\text{NO}_3)_3 / \text{H}_2\text{O}$	MAS 3.5 kHz BL 7 mm
^7Li	AMX 300	116.6	200	1	1	2 k	0.1 M LiCl / H_2O	MAS 3.5 kHz BL 7 mm
^{23}Na	AMX 300	79.4	75	1.5	0.5	16k	1 M NaCl / H_2O	MAS 3.5 kHz BL 7 mm
^{87}Rb	DSX 400	130.9	700	1.9	0.01	3×10^6	1 M RbNO ₃ / H_2O	Static PM 5 mm
^{133}Cs	AMX 300	39.4	150	2	2	4 k	0.1 M CsCl / H_2O	Static PM 5 mm

$$\tau_s = \frac{\tau_1}{I + 1/2} \quad (3.1)$$

where I is the nuclear spin.

The ^{29}Si MAS and ^{27}Al MAS NMR spectra of hydrated zeolite were recorded with 1 K scans and relaxation delays of 5 s using the same Bruker AMX 300 spectrometer. The fine ZSM-5 powder was carefully packed in a 7 mm zirconia rotor using a press. A Doty 7 mm MAS probe was used and the samples were spun at 3.6 KHz, the spinning speed being adjusted by a Bruker MAS-DB pneumatic air controller.

Baseline correction and spectral deconvolution were performed using Bruker 1D WINNMR 5.0 software.

3.2.2.3 ESR Experiments

ESR spectra of pure zeolite, ion-exchanged and alkali metal-loaded samples were recorded on a Bruker ESP 300 spectrometer operating at X-band frequencies (~9 GHz). The microwave power was provided by an ESP 1600-1048 microwave bridge. All ESR spectra were recorded at 10.1 mW. The microwave frequency was measured with a Systron Donner 6054B frequency counter to an accuracy of +/-10 kHz, and g values were determined through comparison of the resonance field with that of 0.11% coal pitch in KCl at $g = 2.0028$. To provide the maximum accuracy of the ESR measurements all the samples were positioned in the centre of the ESR cavity. For each sample two measurements were run: at narrow (200 Gauss) and broad (1000 Gauss) sweep widths. All spectra were recorded at room temperature.

3.2.2.4 Single-Crystal X-ray Analyses

Rb/ZSM-5 and Cs/ZSM-5 crystals of sufficient size were selected from microcrystalline samples after breaking the seals. The selection was done using a microscope, inside a nitrogen atmosphere glovebox at about 223 K. Then, suitable crystals (about 200 μm) were glued to a thin glass fiber with epoxy resin and immediately mounted on the goniometer of a Siemens SMART⁵ diffractometer equipped with a CCD area detector. Measurements were taken while maintaining the crystal's temperature below 223 K during manipulation and at 125 K during data collection. Initial unit cell parameters were calculated from reflections collected from three sets of 20 frames. Final unit cell parameters were calculated from reflections obtained from the full data collection. Because all crystals were merohedral twins, direct methods failed to produce an adequate solution. Instead, twin refinement was used in all cases with a matrix 010 100 001 and a starting model set of atomic coordinates from the literature.⁶ The amount of the second twin component varied from 25 to 35%. The site occupancy factors of the alkali metals were determined during cycles of refinement with fixed isotropic thermal parameters. The fixed values, in the range of 0.05 - 0.25, are reasonable for complex systems such as the alkali metal-loaded zeolites. The errors in site occupancy were estimated to a maximum deviation of +/-10%.

The structure solution and refinement were conducted using SHELXTL⁷ locally implemented on a Pentium-based IBM compatible computer. Crystallographic manipulations were performed with the aid of RES2INS⁸ and graphical representations were generated using a combination of RES2INS and Atoms.⁹

Figure III.3 ZSM-5 framework: the building unit of eight five-membered ring (a); a chain form by three building units (b); viewed along $[100]$ direction (sinusoidal channel)(c); viewed along $[010]$ direction (straight channels)(d); the channel structure in ZSM-5 (e).

3.3 Results and Discussion

3.3.1 Characterization of the H-ZSM-5 zeolite

3.3.1.1 Structural Consideration

The ZSM-5 zeolite is a MFI type zeolite (pentasil family) according to the IZA³ classification. The framework of ZSM-5 contains a unique configuration of linked tetrahedra shown in Figure III.3 (a), consisting of eight five-membered rings. These ZSM-5 units join through edges to form chains as shown in Figure III.3 (b). The chains can be connected to form sheets and the linking of the sheets lead to a three-dimensional framework structure. The sheets parallel to [100] and [010] are shown in Figure III.3 (c) and (d), respectively. The ZSM-5 framework can be generated by linking the sheets across mirror planes forming four- and six-membered rings. Two types of channels result: sinusoidal channels along the [100] direction (Figure III.3 (c)), and straight channels along the [010] direction (Figure III.3 (d)). The channels are connected to give a three dimensional porous network (Figure III.3 (e)). The cross section of the channels is elliptical, with free sizes of 5.1 x 5.5 Å (straight) and 5.3 x 5.6 Å (sinusoidal). Both channels are defined by 10-ring windows.

3.3.1.2 Optical Microscopy

The ZSM-5 crystal formation was monitored by optical microscopy. Figure III.4 shows an optical microscope image of the as-synthesized crystals. The prismatic crystals with length of about 200 µm are the ZSM-5 crystals, while the hexagonal crystal marked with an arrow is an unknown phase, which completely disappeared after washing the sample with distilled water.

Figure III.4 Optical microscope image of ZSM-5 crystals

Figure III.5 Powder XRD patterns of a polycrystalline H-ZSM-5 zeolite
sample: experimental (a) ; calculated³ (b).

3.3.1.3 PXRD

The PXRD of the calcined H-ZSM-5 zeolite shows almost all the features of the calculated PXRD pattern.^{3,4} As shown in Figure III.5, the sharp, intense and relatively narrow peaks of the PXRD patterns recorded for the ZSM-5 zeolite match well the calculated patterns obtained from data available in the literature. These results confirm high crystallinity and purity of the ZSM-5 zeolite used as the starting material to prepare alkali metal-loaded samples.

3.3.1.4 ²⁷Al NMR

²⁷Al MAS NMR spectrum of the hydrated H-ZSM-5 consists of a very narrow peak (FWHM ~ 500Hz) split into two lines at 54 and 56 ppm as shown in Figure III.6 (b) corresponding to two crystallographically distinct tetrahedral aluminium sites. We note that 6-coordinated aluminum, resonating at about 0 ppm, is absent. Figure III.6 (a) shows the central transition accompanied by sets of multiple spinning side bands (ssb). Observations of the spinning side bands, especially on the left side of the spectrum, point to a ssb envelope with a characteristic shape which passes through a maximum. This feature is typical for spinning side bands originating from the satellite transitions. Both the absence of octahedrally coordinated aluminum and the presence of multiple narrow spinning side bands indicate the high crystallinity of the starting ZSM-5 material. The ²⁷Al MAS NMR spectrum disappears completely in the dehydrated ZSM-5 due to the increased quadrupolar interaction caused by a redistribution of the electric charge and/or conformation change of the [AlO₄] tetrahedra.¹⁰

Figure III.6 ^{27}Al MAS NMR spectra of H-ZSM-5 zeolite: hydrated, wide sweep illustrating multiple spinning side bands (a) ; hydrated, narrow sweep width, central line only (b) .

Note: The chemical shifts are referred to 1 M $\text{Al}(\text{NO}_3)_3$ solution

3.3.1.5 ^{29}Si NMR

The ^{29}Si MAS NMR spectrum of the hydrated ZSM-5 zeolite shown in Figure III.7 (a), displays fairly well resolved spectral patterns characterized by an intense peak at -113 ppm with a shoulder at -116 ppm, lines which have been previously attributed to Si(0Al) units, and a relatively weak signal at about -106 ppm to Si(1Al) units of the ZSM-5 framework.¹⁰ In dehydrated ZSM-5 powder, the ^{29}Si MAS NMR spectrum is broadened as shown in Figure III.7 (b), nevertheless the three components characteristic of the ZSM-5 family are still visible (the main peak at -113 ppm with the shoulder at -115 ppm and the line at -107 ppm).

Figure III.7 ^{29}Si MAS NMR spectra of H-ZSM-5 zeolite: hydrated (a) ;
dehydrated (b) .

All these results (PXRD, optical microscopy, ^{27}Al and ^{29}Si NMR) identify the starting material as ZSM-5 zeolite, and confirm its high crystallinity and purity.

3.3.2 Characterization of the Alkali Metal-Loaded ZSM-5 Samples

3.3.2.1 Monitoring the H-ZSM-5 Framework Survival upon Loading (PXRD, ^{27}Al and ^{29}Si MAS NMR)

The amount of alkali metal adsorbed by the ZSM-5 zeolite from the vapour phase varied with the type of alkali metal. As shown in Table III.1, while large amounts of Rb and Cs were adsorbed by the ZSM-5 zeolite (up to 30% or 40 wt.%, respectively), Na and K were adsorbed in smaller proportion (5 and 7 wt.%, respectively). The properties of the resulting materials would depend on the framework survival upon loading, the loading level, the thermal treatment and the type of the alkali metal atom. The preservation of the framework upon loading was checked using the powder X-ray diffraction technique, ^{27}Al and ^{29}Si MAS NMR. PXRD was applied only to the washed samples, since the X-ray investigation of the intact alkali metal-loaded samples (usually in sealed capillaries) was technically difficult to perform.

3.3.2.1 PXRD

The powder XRD patterns for the washed Cs/ZSM-5, Rb/ZSM-5, and M/ZSM-5 (where M = Na or K) samples are compared with the PXRD patterns of the H-ZSM-5 zeolite in Figures III.8 - III.10. The washed samples, although representing empty templates, are labeled similarly to the original composites. The series of diffractograms for each system are shown in the order of increasing loading. The patterns maintain their

Figure III.8 X-ray powder diffractions patterns for zeolite H-ZSM-5 and washed $\text{Cs}_x/\text{ZSM-5}$ samples ($x = 5, 10, 25$ atoms per unit cell); regular plate, 0.0008 degree/min

respective relative intensities, and where necessary are magnified by the mentioned multiplication factor.

In the Cs/ZSM-5 system, a gradual decrease in intensity of the XRD patterns with increased loading can be seen as shown in Figure III.8. Although less intense, the powder pattern of the washed Cs₅/ZSM-5 sample fairly resembles the one for the calcined ZSM-5 zeolite. The change in relative intensity of the peaks in 6-10 θ and 23-25 θ regions noticed for Cs₅/ZSM-5 is most likely a crystal size effect, since the crystals used to synthesize this sample were slightly larger (the same batch, but different autoclaves). In addition, this change in relative intensity might be also due to different amount and distribution of remaining Cs in the host lattice. The decrease in intensity continues as seen in the diffractogram (8 times magnified) of the washed Cs₁₀/ZSM-5 sample, but the peaks remain narrow and sharp, which proves the retention of the framework crystallinity. However, a dramatic change is observed in the PXRD diffractogram of the washed Cs₂₅/ZSM-5, where only traces of the XRD patterns of the starting ZSM-5 zeolite are observed. In addition, a broad background signal appears in the baseline indicating the presence of an amorphous phase. Both the broadening of the PXRD peaks and the change in the baseline indicate a distortion of the ZSM-5 framework upon the introduction of cesium, with a loss of long-range order (amorphisation), which is not restored after cesium removal.

Figure III.9 X-ray powder diffractions patterns for zeolite H-ZSM-5 and washed Rb_x/ZSM-5 samples (x = 5, 10, 25 atoms per unit cell) (zero - ground plate, 0.01 degree/min)

Figure III.10 X-ray powder diffraction patterns for zeolite H-ZSM-5 and washed $M_x/ZSM-5$ ($M = Na, K$); zero-ground plate, 0.01 degree/min.

Similar to the Cs/ZSM-5 system, an amorphisation process with increased loading is observed for the Rb/ZSM-5 system as shown in Figure III.9. However, compared to the Cs/ZSM-5 system, where for the Cs₂₅/ZSM-5 sample the degree of amorphisation is very high, in the Rb/ZSM-5 system, for the sample loaded with the same number of atoms per unit cell ($x \sim 25$), the effect is obviously milder. Note the intensity multiplication factors, the PXRD of Cs₂₅/ZSM-5 is multiplied 16 times relative to the PXRD of the starting H-ZSM-5 zeolite, while the PXRD of Rb₂₅/ZSM-5 is not magnified.

As shown in Figure III.10, the gradual decrease in intensity of the PXRD patterns observed for Cs and Rb is not repeated for K and Na. The PXRD patterns of the washed K and Na samples retain all of the features of the starting ZSM-5 zeolite.

When the PXRD patterns of the samples with the same loading (for example 10 atoms per unit cell) are compared, it becomes clear, that the framework amorphisation is much more pronounced for heavier and more volatile metals (Rb and Cs) as shown in Figure III.11. In the case of Na and K, retention of the zeolite structure is surprising, since high temperatures (250 °C for Na-loaded samples, and 160 °C for K-loaded samples) and prolonged thermal treatment (depending on loading from 6 to 14 days for Na-loaded samples and from 5 to 8 days for K-loaded samples) were necessary to synthesize these samples. What is more, the brown color of samples with higher Na or K loading indicated the reduction of some of the zeolite's silica. This observation suggests that in case of Na and K the reaction (deposition of the alkali metal) is likely confined to

Figure III.11 X-ray powder diffractions patterns for washed M_{10} /ZSM-5 samples

(M = Na, K, Rb, Cs); zero-ground plate, 0.01 degree/min

the very surface of zeolite crystals: only a small portion of the metal vapor is being adsorbed by the framework, while the major part just “coats” the zeolite surface, “preventing” further reaction. Through washing, the “coating” and the adsorbed metal are removed, leaving empty templates with well-preserved crystallinity similar to that of the starting material.

In conclusion, we can say that, firstly, the templates loaded with low amounts of metals retain their crystallinity, while the highest metal-loaded ones partially lose their long-range order. The “amorphisation” phenomenon is more obvious in the Cs/ZSM-5 system, where at the highest loading levels only traces of the initial XRD patterns were observed. Secondly, the type of alkali metal atoms confined in the zeolite matrix could be another framework distortion factor, the disorder increasing from lighter to heavier alkali metals.

3.3.2.2 ^{27}Al MAS NMR

The introduction of the alkali metal into the ZSM-5 matrix seems to diminish the quadrupolar effects, since the ^{27}Al MAS NMR line reappears in the spectra of loaded samples, yet to a different degree depending on the type of alkali metal and loading. In Figures III.12 and III.13 are shown the ^{27}Al MAS NMR spectra of Rb- and Cs-loaded samples. A significant diminishment of the quadrupolar effects is noticed, since the characteristic ^{27}Al line (similar to that observed in hydrated H-ZSM-5 zeolite) is restored. However, in Na-loaded samples, the ^{27}Al MAS NMR spectra remain broad similar to dehydrated H-ZSM-5, consequently the quadrupolar effects are still dominant (Figure III.14). K-loaded samples show intermediate behavior, with significant quadrupolar

Figure III.12 ^{27}Al MAS NMR spectra of $\text{Rb}_x/\text{ZSM-5}$ samples compared to the ones of dehydrated H-ZSM-5 and Rb-ZSM-5 zeolites

interactions at lower loading and to a lesser extent at higher loading as revealed by the spectra shown in Figure III.14.

The ^{27}Al MAS NMR spectra of $\text{Rb}_x/\text{ZSM-5}$ samples and the two dehydrated zeolites, the protonated form of ZSM-5 and Rb-exchanged ZSM-5, are shown in Figure III.12. As mentioned earlier, in dehydrated H-ZSM-5 the quadrupolar interactions are very strong, so that the ^{27}Al MAS NMR line is broadened beyond detection. However, in dehydrated Rb-exchanged ZSM-5 zeolite, the ^{27}Al MAS NMR line is present, which indicates smaller quadrupolar interactions than in dehydrated H-ZSM-5. The different extent of the quadrupolar interactions in the same aluminosilicate framework, with two different charge-balancing cations (protons versus Rb cations), is likely a dynamic effect. On the one hand, the protons are “fixed” in the H-ZSM-5 framework by strong hydrogen bonds. This leads to a static, very asymmetric environment around Al atoms, and consequently to strong quadrupolar interactions. On the other hand, Rb cations are more mobile than protons, and this increased mobility brings a constant change in the environment around Al atoms, which leads to averaging of the quadrupolar interactions, though not completely (the ^{27}Al MAS NMR spectrum is still asymmetric).

The ^{27}Al MAS NMR spectra of Rb-loaded samples also consist of a line with a chemical shift in the range 50.8 $\pm$ 1 ppm. The introduction of Rb cations into the “rigid” framework of dehydrated H-ZSM-5 seems to have the same effect on the Al atom environment as hydration: an increase in local symmetry around Al atoms as evident from the decrease in the quadrupolar interactions of aluminum. There are indications that water molecules adsorbed at the Bronsted sites in the H-ZSM-5 zeolite form clusters with

Figure III.13 ^{27}Al MAS NMR spectra of $\text{Cs}_x/\text{ZSM-5}$ samples compared to the one of dehydrated H-ZSM-5 zeolites

the acidic proton: $\text{H}^+(\text{H}_2\text{O})_n$ where n is of order 2.^{10,11} Through hydration of the H-ZSM-5 zeolite the position of the H^+ proton is slightly altered and the conformation of, and the charge distribution around, Al-O tetrahedra are changed.¹² As more and more water molecules are added, the environment around Al atoms is continuously changed, change that leads to averaging of the quadrupolar interactions to a higher and higher extent. This effect was observed when monitoring the hydration of Na-ZSM-5 zeolite by ^{27}Al MAS NMR.¹³ With increased water content, the ^{27}Al MAS NMR spectra of hydrated Na-ZSM-5 zeolite shown narrower and more intense lines as the quadrupolar interactions were averaged to a greater degree. This might also be our case, as with increasing Rb-loading a gradual increase in ^{27}Al MAS NMR line intensity and some changes in line width are observed as shown in Figure III.12. These results indicate that the quadrupolar effects in ^{27}Al MAS NMR spectra diminish gradually, attaining a minimum at the highest Rb-loading. The presence of the characteristic ^{27}Al MAS NMR line typical of Al nuclei in symmetric tetrahedral sites, as in zeolite framework, reveals that the symmetry of the Al sites is preserved even at the highest Rb loading, and consequently, the zeolite framework likely remains intact upon loading.

Of all of our samples, it seems that the Rb-loaded ones demonstrated the best framework survival upon loading, and also that for these samples the Rb incorporation can be monitored by ^{27}Al MAS NMR spectroscopy.

In the $\text{Cs}_x/\text{ZSM-5}$ spectral series, the ^{27}Al MAS NMR line appears in the spectrum of the lowest loaded sample (5 atoms per unit cell) at 51.8 ppm, a little shifted when compared to hydrated ZSM-5 (54 ppm and 56 ppm, respectively). This line is narrow

Figure III.14 ^{27}Al MAS NMR spectra of $\text{M}_x/\text{ZSM-5}$ samples compared to the one of dehydrated H-ZSM-5 zeolites ($\text{M} = \text{Na}, \text{K}$)

(FWHM ~ 900 Hz), and asymmetric as shown in Figure III.15. At higher Cs loading (10 atoms per unit cell), the ^{27}Al MAS NMR line increases in intensity, while it remains narrow (FWHM ~ 950 Hz). The asymmetry of the ^{27}Al MAS NMR line observed in all spectra shows the effects of residual quadrupolar interactions, but the increase in intensity and also the narrowness of the line strongly indicate diminishing quadrupolar effects with increasing loading. However, at the highest Cs-loading (25 atoms per unit cell), the line broadens (FWHM ~ 1300 Hz), and its intensity becomes lower than that of the sample with 10 Cs atoms per unit cell. These effects are probably caused by a slightly increased degree of distortion of the aluminum-oxygen tetrahedra upon metal agglomeration inside the zeolite's channels, the empty space available becoming less, especially when filling with bulky Cs cations. As a consequence, the field gradient at aluminum sites increases and the quadrupolar interactions of the aluminum nuclear spins become stronger. In other words, at this high metal loading and taking into account the larger size of the Cs cations, the zeolite framework seems to start falling apart. However, even at the highest Cs loadings, a relatively narrow and intense ^{27}Al NMR spectrum is seen, with the resonance corresponding to Al nuclei in symmetric tetrahedral sites in the zeolite framework.

The ^{27}Al MAS NMR spectra of both $\text{Na}_5/\text{ZSM-5}$ and $\text{Na}_{10}/\text{ZSM-5}$ samples remain broad and almost undetectable as shown in Figure III.14. This might be an indication of the incorporation of only traces of Na metal into the ZSM-5 matrix, or even the absence of reaction. This idea was also indicated by the PXRD results.

In the K_x /ZSM-5 system an increase in ^{27}Al MAS NMR line intensity with loading is observed as shown in Figure III.14. The evolution of the ^{27}Al MAS NMR line for K_x /ZSM-5 samples is somewhere in between the trends mentioned already for the other systems. On the one hand, when compared to Cs- or Rb-loaded samples at the same metal loading, the ^{27}Al MAS NMR lines of K-loaded samples are less intense and broader, but not as much as for Na-loaded samples. These observations show that K is not as easily adsorbed into the zeolite matrix as Cs or Rb, but much easier than Na.

It is interesting to compare the ^{27}Al MAS NMR spectra of samples with similar alkali metal loading (i.e. 10 atoms per unit cell and only for samples which showed ^{27}Al line). Broadening of the ^{27}Al MAS NMR line (FWHM $\sim 950\text{ Hz} < 1050\text{ Hz} < 1450\text{ Hz}$) and a slight up-field shift ($51.8\text{ ppm} > 50.8\text{ ppm} > 49.3\text{ ppm}$) is observed when changing metal from Cs to Rb and K. A cause for the mentioned effects might be the different polarizing power of the cations, which increases ($K > \text{Rb} > \text{Cs}$) with decreasing cation's sizes ($\text{Cs} > \text{Rb} > \text{K}$). The cation with the large polarizing power (K) would cause an increased distortion of the AlO_4 tetrahedra than a cation with a smaller polarizing power (Cs), so that the quadrupolar interactions are diminished to a larger extent when the loaded metal has a smaller polarizing power (i.e. Cs).

To conclude, ^{27}Al NMR spectroscopy was applied to probe the framework survival upon loading with significant amounts of alkali metals. Our results indicate, that for Rb and Cs samples the symmetry of the Al sites is preserved up to the highest metal loadings, and the integrity of the zeolite framework likely remains unchanged. Moreover, ^{27}Al NMR spectroscopy seems to be a good test to follow the deposition of alkali metal.

Figure III.15 ^{29}Si MAS NMR spectra of $\text{Cs}_x/\text{ZSM-5}$ samples ($x = 5, 10, 25$ Cs atoms per unit cell).

In Cs- and especially Rb-loaded samples the gradual decrease in the quadrupolar interactions with loading indicates gradual incorporation of the metal. An exception is the highest Cs loaded sample, where the broadening and decrease in ^{27}Al line intensity is an indication that the framework starts to collapse. In Na-loaded samples the reaction seems to be confined to the surface of zeolite crystals, since the ^{27}Al NMR line remains unchanged compared to that of dehydrated H-ZSM-5. The same thing can be said about low-loaded K samples, but at higher loading the presence of the ^{27}Al NMR line indicates that, at least in part, K deposition indeed took place.

3.3.2.3 ^{29}Si MAS NMR

In Figures III.15- III.17 the ^{29}Si MAS NMR spectra for each alkali metal loaded-ZSM-5 system are compared with the ^{29}Si MAS NMR spectrum of dehydrated ZSM-5. As a general observation, the behavior of samples with Cs and Rb is different from samples with Na and K.

On the one hand, the spectral series of the Cs/ZSM-5 and Rb/ZSM-5 systems (Figures III.15 and III.16) are very similar, each showing a gradual decrease in the ^{29}Si signal amplitude and broadening of the NMR lines with introduction of the alkali metal. At the highest loading (25 Cs or Rb atoms per unit cell) the ^{29}Si MAS NMR spectrum is still observable, but is severely broadened with large experimental error, most of the signal not being detected.

On the other hand, the spectral series for K/ZSM-5 and Na/ZSM-5 systems are also similar one to the other as shown in Figure III.17, but they do not follow the same trend as observed for the Cs/ZSM-5 and Rb/ZSM-5 systems. We do see a dramatic decrease in

Figure III.16 ^{29}Si MAS NMR spectra of $\text{Rb}_x/\text{ZSM-5}$ samples ($x = 5, 10, 25$ Rb atoms per unit cell).

^{29}Si NMR signal amplitude in K/ZSM-5 and Na/ZSM-5 systems with the introduction of the first portion of the alkali metal (in the samples with 5 atoms per unit cell), but further decrease in ^{29}Si NMR signal amplitude with increasing loading is not that significant, as seen for samples with 10 atoms per unit cell loading (Figure III.17).

The decrease in the ^{29}Si signal amplitude and broadening of the NMR lines with introduction of the first portions of alkali metals (5 atoms per unit cell), which was noted for all spectral series, is likely caused by the strong interaction between silicon nuclei (adjacent to the channels) and the electrons, resulting through the ionization of the alkali metal. Similar results were reported for cesium loaded ITQ-4 and beta zeolites.¹⁴ The decrease in the ^{29}Si signal amplitude and broadening of the NMR lines with increasing loading for Cs/ZSM-5 and Rb/ZSM-5 systems indicates a continuous delocalization of the electron density throughout the zeolite framework. Nevertheless, the NMR spectrum is still observable even at the highest alkali metal loading (25 atoms per unit cell). At such loadings (1 metal atom per 4 Si atoms) additional broadening of the ^{29}Si NMR lines may be caused by “amorphisation” of the zeolite framework as detected in PXRD discussed earlier. Extent of the “amorphisation” is likely to depend on the type of alkali metal. Comparing the ^{29}Si MAS NMR spectra of $\text{Cs}_{25}/\text{ZSM-5}$ and $\text{Rb}_{25}/\text{ZSM-5}$ samples it is clear that the line broadening is more severe in the former case. This is likely to be the result of the larger size of Cs atoms as compared to Rb atoms.

Unlike the case of Rb and Cs, in the ^{29}Si MAS NMR spectra of Na- and K-loaded samples there was little or no change when the metal loading was doubled from 5 to 10 atoms per unit cell (Figure III.17). This very important observation supports the earlier

Figure III.17 ^{29}Si MAS NMR spectra of $\text{M}_x/\text{ZSM-5}$ ($\text{M}=\text{Na}, \text{K}$ and $x = 5, 10$) samples.

indication that for these two metals the deposition is likely confined to the very surface of zeolite crystals. When more metal is added, it builds up at the surface, not penetrating deeply into the crystals. This would produce very inhomogeneous metal deposition throughout the crystals, when the outer shell of crystals is heavily loaded and the inner core remains practically intact. This type of inhomogeneity can explain other “anomalies” noted in the behavior of these samples, such as the unexpected retention of framework crystallinity detected with PXRD. When the ^{29}Si MAS NMR spectra of $\text{Na}_{10}/\text{ZSM-5}$ and $\text{K}_{10}/\text{ZSM-5}$ samples are compared (Figure III.17), the spectrum for the Na-loaded sample is less intense and broader, likely due to more damage to the framework, since deposition was performed at higher temperature and for a longer period of time.

Overall, the ^{29}Si MAS NMR results indicate that the zeolite framework retains its integrity, at least with short-range order, with introduction of the alkali metals. With the first portions of alkali metal added, the ^{29}Si NMR spectra become broader and less intense due to delocalization of electrons produced via ionization of incoming alkali metal atoms. For highly volatile alkali metals (Rb and Cs) the level of such delocalization will gradually increase with loading, leading to concurrent gradual broadening and loss in intensity of the ^{29}Si NMR spectra. For less volatile metals (K and Na) these effects seem to be less “predictable” most likely because of the apparent inhomogeneity of deposition and, possibly, stronger (chemical) interaction between the host framework and the guest alkali metal which could result in partial silica reduction. The latter is especially expected for Na-loaded samples, since deposition was performed at elevated temperatures.

Monitoring Deposition of Alkali Metals in H-ZSM-5 Zeolite.

The host ZSM-5 zeolite for alkali metal deposition was chosen as protonic (H-ZSM-5) rather than any other cationic form (M-ZSM-5) to avoid unnecessary complications when characterizing the resulting composites. Using the H-form of zeolite, we were expecting that the first portions of alkali metal vapor would interact with protons, thus releasing molecular hydrogen and forming alkali metals cations (M-form of zeolite ZSM-5). At loadings higher than the proton content (3.7 per unit cell), the alkali metal vapour would start to interact with M-ZSM-5 zeolite leading to variety of alkali metal species/clusters within the zeolite's pores.

The reaction of alkali metal with H-ZSM-5 zeolite was followed by ^1H MAS NMR, ^{27}Al MAS NMR, and ^{29}Si MAS NMR spectroscopy and powder X-ray diffraction (PXRD). The formation of the alkali metal-containing species was monitored by alkali metal NMR spectroscopy and ESR spectroscopy. When the quality of the metal-loaded ZSM-5 crystal permitted (Rb and Cs), single crystal X-ray diffraction was applied for crystal structure determination.

3.3.2.4 ^1H MAS NMR

The ^1H MAS NMR spectra recorded for the alkali metal loaded-samples were grouped in spectral series depending on the metal and loading level, and compared with the spectrum of dehydrated H-ZSM-5 zeolite.

As shown in Figure III.18, the ^1H MAS NMR spectrum of dehydrated H-ZSM-5 exhibits two narrow lines at 1.8 ppm and 3.9 ppm (all other lines in the spectrum are

Figure III.18 ^1H MAS NMR spectra of $\text{Cs}_x/\text{ZSM-5}$ samples; MAS spinning speed was 3.5 kHz in all cases. Spinning sidebands are marked (with asterisks) only on the first spectrum.

spinning sidebands and are marked with asterisks). These two lines are attributed to two distinct types of protons in the zeolite structure: (i) non-acidic, terminal SiOH groups on the surface of zeolite crystallites and at crystal defects sites (1.8 ppm); (ii) acidic, bridging hydroxyl groups of the zeolite framework, Si(OH)Al (3.9 ppm).⁸ This ¹H MAS NMR spectrum will change upon deposition of alkali metals depending on the type and amount of alkali metal loaded.

In the ¹H MAS NMR spectra of the Cs-loaded samples (Figure III.18), a gradual decrease in intensity and broadening of both ¹H NMR lines, from terminal and bridging hydroxyl groups, is observed with increasing cesium content. At the same time, with introduction of cesium a new line at around 4.9 ppm appears in the spectrum. At the highest Cs-loading (25 atoms per unit cell), this line is the most intense, while the line at 3.9 ppm disappears completely, and the line at 1.8 ppm is still present although somewhat broadened.

Indeed, these changes in the Cs spectral series are the result of the interaction of cesium vapour with hydroxyl groups of the zeolite. At loadings lower than the proton content (3.7 per unit cell), Cs-ZSM-5 zeolite is expected to form, and at higher loadings, as more and more Cs is added, subsequent cluster formation might start, as illustrated by the following reactions:

Figure III.19 ^1H MAS NMR spectra of $\text{Rb}_x/\text{ZSM-5}$ samples; MAS spinning speed was 3.5 kHz in all cases. Spinning sidebands are marked (with asterisks) only on the first spectrum.

Although the reactions suggest formation of molecular hydrogen, this seems not to be the case: molecular H_2 when adsorbed in dehydrated H-ZSM-5 zeolite gives a very characteristic 1H NMR line at 4.4 ppm without spinning sidebands (Figure III.18, upper spectrum). The spinning sidebands visible in the spectrum of H_2 /ZSM5 sample originate not from the most intense signal at 4.4 ppm, but from the underlying, much less intense line at 3.9 ppm as in dehydrated zeolite. Note, that this spectrum is presented not with the same vertical scale as all other spectra. The presence of the line at 4.9 ppm indicates the retention of hydrogen in the system, but not in its free molecular form.

In the 1H MAS NMR spectra recorded for Rb-loaded samples, a gradual decrease of the 1H NMR line intensities at 1.8 ppm and 3.9 ppm is also observed as shown in Figure III.19. Similar to the Cs case, a new line also appears but now at 4.5 ppm. This line increases in intensity with rubidium loading. And it is the only line observed in the spectrum of the Rb_{25} /ZSM-5 sample.

The 1H MAS NMR spectra for Na- and K-loaded ZSM-5 samples are shown in Figure III.20. As was mentioned earlier, the low-melting alkali metals (K and Na) require higher temperatures (160 $^{\circ}C$ and 250 $^{\circ}C$ respectively) and longer thermal treatment for the deposition reaction to complete, since even under these extreme conditions the partial vapour pressures of both metals remains very low. This is well illustrated by 1H MAS NMR spectra of K-loaded ZSM-5 samples, where only minor changes were found with loading. Nevertheless, a new low-intensity signal at 4.6 ppm was observed, indicating some diffusion of K vapour into zeolite pores. At the same time there were practically no changes in the spectra of Na_x /ZSM-5, other than some broadening and, possibly, intensity

Figure III.20 ^1H MAS NMR spectra of $\text{M}_x/\text{ZSM-5}$ samples ($\text{M} = \text{Na}, \text{K}$)

MAS spinning speed was 3.5 kHz in all cases; spinning

sidebands are marked (with asterisks) only on the first spectrum

loss. Of all alkali metals, Na has the lowest vapour pressure (see Table III.3). To reach a vapour pressure sufficient for noticeable Na diffusion into the channels the reaction should be carried out at or above 250 °C. At these temperatures, Na vapour reacts readily with the surface of the zeolite powder, reducing it and not penetrating deep inside the pores. As a result the reaction stops at the surface of zeolite.

¹H MAS NMR spectroscopy can be used successfully to follow deposition of alkali metals into the zeolite host matrix by monitoring the state of the terminal and bridging zeolite's hydroxyl groups. The deposition seems to proceed more readily for low-melting alkali metals like cesium and rubidium. For sodium and potassium, however, the reaction should be carried out at elevated temperatures. Even then, there were no signs of sodium vapour interacting with internal hydroxyl groups, indicating that the reaction was most likely confined to the surface of zeolite crystals. When the deposition did occur, the disappearance of both the terminal and bridging zeolite's hydroxyl groups was evident, and this was most prominent in the case of Rb₂₅/ZSM-5 and, to a lesser extent for the Cs₂₅/ZSM-5 sample. It was found, that hydrogen released due to interaction of the hydroxyl groups with hot alkali vapour did not immediately leave the system. Instead it remained there as a sort of species of unknown nature, most likely associated with the incoming alkali metal. The latter was supported by the fact, that the chemical shift of the corresponding line in ¹H MAS NMR spectra was different for each alkali metal: 4.9 ppm for Cs, 4.5 ppm for Rb and about 4.6 ppm for K. It is well known, that hydrogen dissolves easily in melted alkali metals forming a variety of alkali metal hydrides.¹⁵ We

may suggest that similar hydrides may form during deposition of alkali metals in H-ZSM-5 zeolites, although this suggestion is yet to be confirmed.

3.3.2.5 Alkali Metal NMR (^{133}Cs , ^{87}Rb , and ^{23}Na)

^{133}Cs NMR

As suggested previously, with the first portion of Cs vapours introduced in the H-ZSM-5 zeolite, protons are substituted by the Cs^+ cations, which might further act as anchor points for incoming atoms as loading increases. We might expect the formation of Cs-clusters with low nuclearity at low Cs-loading, and high nuclearity as Cs-loading increases. This process can be followed by ^{133}Cs NMR spectroscopy, as shown in Figure III.22 where the ^{133}Cs static NMR spectra for cesium-loaded ZSM-5 samples are compared with that of Cs-exchanged ZSM-5 (Cs-ZSM-5). The latter spectrum originates from framework charge-balancing Cs^+ cations in ZSM-5 zeolite and shows a maximum at about -160 ppm. The deconvolution of this spectrum reveals that it consists of two overlapping lines: a broader one (~ 2.7 KHz) at -143 ppm and a narrower one (1.1 KHz) at -161 ppm (see inset in Figure III.22). Olson et. al.¹³ in their study on the structure of dehydrated Cs-ZSM-5, found three crystallographic sites for Cs cations: the first, Cs1, located in the channel intersection near the sinusoidal channel, the second, Cs2, is in the straight channel and the third, Cs3 is located close to Cs1 in the sinusoidal channel as shown in Figure III.21.

They found that about 60% of the Cs sites are in or near the sinusoidal channel (Cs1 and Cs3), and only about 40% in the straight channel (Cs2). Using these results, and

Figure III.21 The location of the three different Cs ion positions in the channel structure of dehydrated Cs-ZSM-5 ¹¹

based on their relative integral intensity, we can make a tentative assignment of the two lines observed in the ^{133}Cs NMR spectrum of Cs-ZSM-5: the broader line probably corresponds to the sites Cs1 and Cs3, which have similar oxygen environments, and are possibly in exchange, while the narrower line is from Cs2 cations. An exchange between sites Cs2 and (Cs1&Cs3) is unlikely, since it will involve a cation leaving the straight channel and entering the sinusoidal one.

A similar, relatively narrow line, with the intensity decreasing as the Cs loading increases can be seen in the ^{133}Cs NMR spectra of the low-loaded Cs/ZSM-5 samples as shown in Figure III.22. It belongs to Cs^+ cations formed via reaction of Cs vapour with protons:

Figure III.22 ^{133}Cs NMR spectra of dehydrated Cs-ZSM-5 zeolite (shown with deconvolution) and Cs-loaded ZSM-5 samples

and occupying the regular crystallographic sites in ZSM-5 framework.

The second line observed for Cs-loaded samples is very broad. Its chemical shift changes with loading from -28 ppm to 116 ppm, but the linewidth remains almost the same (~14kHz). This line is likely due to another type of cationic Cs species not at regular crystallographic sites. The intensity of this line increases with cesium loading, but not additively. Assuming that each sample tube contained the same amount of sample (a reasonable assumption keeping into account that the sealed NMR tubes have roughly the same volume), we expected a ratio of absolute integral intensities in the overall spectrum of 5:11:26 in the Cs/ZSM-5 series. However, the ratio was found to be 5:11.7:18.5. For two low-loaded samples (Cs5 and Cs10) the values found are in good agreement with the real cesium loading, i.e. ca. 100% of the introduced cesium being NMR-detectable, while for the highest loaded sample (Cs25) the value found indicates that ca. 30% of cesium is NMR “invisible”. It should be mentioned that we found no other lines in the ^{133}Cs NMR spectra of the Cs/ZSM-5 samples, including possible lines in the Knight Shift region at 14,900 ppm from metallic species. However, it is well established that in similar systems (alkali metal loaded, but not overloaded, zeolites samples) lines with Knight Shifts were never observed.

The disappearance of the ^{133}Cs NMR signal at the highest Cs-loading might be due to several reasons, including: (i) oscillation of electronic density in small particles; (ii) strong paramagnetic broadening due to unpaired electrons; (iii) distribution of the chemical shift; (iv) quadrupolar interactions.

If introduced Cs did form clusters of varying nuclearity, then their nanometer sizes (dimensions are limited by the zeolite channel's diameter) can be associated with severe NMR line broadening, even beyond detection. Small metal particles have a high surface-to-volume ratio. It is known that at the surface the periodic potential felt by the conduction electrons is interrupted. This results in electron density oscillations near the surface (Bardeen-Friedel oscillations),¹⁶ and the role these play increases with decreasing in the particle size. From the NMR point of view, the oscillations of the electron density lead to oscillation of the Knight Shift, since the latter is proportional to the electronic spin density. These oscillations lead to much broader NMR lines in small particles with respect to the bulk.¹⁶

If the Cs-containing clusters have unpaired electrons (even or odd in number), such clusters will also be out of detection range with NMR, much as Cs in the atomic state. The chemical shift distribution might also contribute to the disappearance of the ¹³³Cs NMR line, since the clusters that might form have different nuclearity, each type with a corresponding chemical shift.

Finally, the disappearance of the ¹³³Cs signal can be due to quadrupolar broadening, yet to a smaller extent. As mentioned in chapter II, the ¹³³Cs nucleus has the smallest linewidth factor ($I = 1.2 \times 10^{-6} \times 10^{56} \text{ m}^4$) of any quadrupolar nuclide, and as a result Cs line widths are relatively narrow in common inorganic compounds.

All of the mentioned reasons for a diminishing ^{133}Cs NMR line intensity at high Cs-loading provide arguments for cluster formation. In general, two kinds of metal clusters can be formed when alkali metal vapours react with zeolite: ionic clusters (M_n^{m+} , i.e. Na_4^{3+} , Na_6^{5+} , K_3^{2+} , or K_4^{3+}) and alkali metal particles (M_n).¹⁷⁻¹⁹ The formation of alkali metal-cluster and their type are determined by the zeolite structure, the charge balancing framework cation, or the size of the introduced alkali metal atoms. Since H-ZSM-5 is a channel zeolite with diameters of the channels at 5.1x5.5 Å (straight) and 5.3x5.6 Å (sinusoidal), and Cs is a bulky atom with a diameter of 5.3 Å, a tight Cs confinement is expected. As a possibility, Cs within the pores can form both ionic and metallic clusters, but also “isolated” Cs^+ cations or Cs^0 atoms. In addition, as suggested by the ^1H NMR results smaller amounts of cesium hydrides might form.

Besides ^{133}Cs NMR and ^1H MAS NMR, which both indicate, more or less directly the formation of Cs cations inside the ZSM-5 channels, additional insights come from simple estimates. For example, in the highest Cs-loaded sample ($\text{Cs}_{25}/\text{ZSM-5}$) the calculated volume of added Cs metal (bulk density 1.9 g/cm³) exceeds the available pore volume (the pore volume of ZSM-5 zeolite is 0.19 cm³/g) by almost a factor of two (filling factor ~1.7) (Table III.1). It is obvious that to fit the available pore volume, at least 40% of the added cesium should be in the cationic form, since Cs^+ cations are smaller (3.4 Å). Cs cations in the zeolite pores can occupy regular crystallographic sites as mentioned previously, or can be part of the Cs_n^{m+} clusters.

To conclude, in low-loaded samples, the ^{133}Cs lines attributed to Cs^+ cations in regular crystallographic sites indicate that the Cs1/Cs2/Cs3 sites are being occupied.

These “fixed” cations are likely to be the anchoring points for the incoming Cs atoms as more metal is added. The result is the formation of Cs-clusters, with low nuclearity at low Cs-loading, and with high nuclearity as loading increases. This assumption is mainly based on the fact that at higher loading more and more Cs becomes “NMR invisible” due to the formation of large clusters (either paramagnetic or metallic in nature). This “clustering” is controlled by the size and connectivity of the ZSM-5 channels: a single-file arrangement of Cs species is possible, and as loading increases, this arrangement would elongate through the zeolite structure for long distances as well.

⁸⁷Rb NMR

Due to the larger quadrupolar moment of ⁸⁷Rb ($0.12 \times 10^{-28} \text{ Q/m}^2$) its NMR spectra are less well resolved and broader than for ¹³³Cs. In addition, the long delay times required for spin-echo measurements made it difficult to obtain noise-free spectra, even after carrying out a large number of scans ($2\text{--}3 \times 10^6$). In order to optimize the conditions for obtaining fairly well resolved spectra, different spin echo pulse sequences were applied with fixed delays $d_6 = d_7$ of 30, 50, 100 and 200 μs . A good compromise of sensitivity versus experimental time were the spectra recorded after applying 3×10^6 scans with pulse sequence $d_6 = d_7 = 100 \mu\text{s}$. The ⁸⁷Rb spin echo NMR spectra of Rb-loaded ZSM-5 zeolite and Rb-ZSM-5 zeolite are shown in Figure III.23, all spectra being recorded under the same conditions.

Figure III.23 ^{87}Rb spin echo NMR spectra of dehydrated Rb-ZSM-5

zeolite and Rb-loaded ZSM-5 samples

Unlike the ^{133}Cs spectrum of Cs-exchanged ZSM-5 zeolite, which shows at least two lines, in the ^{87}Rb spin echo NMR spectrum of Rb-exchanged ZSM-5 zeolite, only a single broad line ($\Delta\nu_{1/2} = 43$ kHz) can be seen with a maximum at -56 ppm. The position of this line suggests that the rubidium species are cationic (the known chemical shift range for Rb^+ is between +328 ppm and -56 ppm),^{20,21} but no further information regarding their type or positions inside ZSM-5 channels can be obtained from the ^{87}Rb NMR spectrum.

The ^{87}Rb NMR spectra of Rb-loaded ZSM-5 samples are also very broad and featureless, with the line width increasing with loading, from 56 kHz ($\text{Rb}_5/\text{ZSM-5}$), 59 kHz ($\text{Rb}_{10}/\text{ZSM-5}$) to 77 kHz ($\text{Rb}_{25}/\text{ZSM-5}$). At the same time, the intensities of the spectra increase with loading, and their maxima shift slightly to higher frequency (from -37 to 48 ppm), indicating the possible influence of Rb-paramagnetic species. Any quantitative comparison of integral intensities (as was done for ^{133}Cs NMR spectra of Cs/ZSM-5 samples) are not relevant in the Rb/ZSM-5 system, since not all Rb are NMR-detectable even in the reference sample of dehydrated Rb-ZSM-5 zeolite due to the large quadrupolar interactions of the ^{87}Rb nucleus. However, taking into account the similarities of the previous NMR spectroscopic results for Cs/ZSM-5 and Rb/ZSM-5 samples, we may suggest the same scenario for rubidium deposition as for cesium: the first portions of Rb vapour may react with H-ZSM-5 to form Rb-ZSM-5 zeolite. At metal loadings higher than the proton content (3.7 atoms per u.c.), the rubidium vapour interacts with the Rb-ZSM-5 zeolite, with any excess electrons transferred to the framework, and Rb clusters formed. This scenario is also supported by the SC-XRD

results, which indicate Rb confinement. The SC-XRD results will be described in a further section.

²³Na MAS NMR

The ²³Na MAS NMR spectra of Na-loaded ZSM-5 samples compared with the spectrum of dehydrated Na-ZSM-5 are shown in Figure III.24. The latter spectrum consists of at least two overlapping lines from two non-equivalent sodium cations at -25 ppm and -30 ppm. In comparison with ¹³³Cs NMR spectrum of Cs-ZSM-5, the ²³Na NMR spectrum of Na-ZSM-5 is less resolved due to the larger quadrupolar moment of ²³Na nucleus ($0.12 \times 10^{-28} \text{ Q/m}^2$), as was the case of the ⁸⁷Rb nucleus. Similar ²³Na spectra were reported previously for Na-ZSM-5 zeolites.²² We note, however, that the number of lines in the ²³Na NMR spectra of Na-ZSM-5 zeolites, and the relative integral intensities of these components, may vary depending on Si/Al ratio and Na-exchange level.^{23,24}

For the lowest loaded sample (Na₅/ZSM-5), the interaction of the zeolite powder with hot sodium vapour is revealed by the appearance of a new broad line at around 0 ppm that may be attributed to Na cations at the zeolite's surface. Similar lines were observed in ²³Na static NMR spectra of Na-loaded controlled pore glasses.²⁵ The signals from cations occupying regular crystallographic sites (at ca. -20 -30 ppm) appear only at the highest Na loadings (Na₁₀/ZSM-5 sample). This confirms earlier ¹H NMR observation that sodium vapour would first interact with the external surface of the zeolite powder, very slowly penetrating inside.

Briefly, it seems that for Cs and Rb samples, metal confinement in the zeolite's

Figure III.24 ^{23}Na MAS NMR spectra of dehydrated Na-ZSM-5

zeolite and Na-loaded ZSM-5 samples.

pores is more likely to take place than for Na samples where most of the metal remains at the surface and only traces are deposited inside the zeolite channels. The NMR-detected species are cationic, although there are indications that paramagnetic species can also be present.

3.3.2.6 Electron Spin Resonance (ESR)

Interaction of alkali metal vapour with some zeolites leads to formation of variety of paramagnetic clusters such as Na_4^{3+} , Na_5^{4+} , and Na_6^{5+} , or K_4^{3+} and K_3^{2+} , which suggests that other similar species may form within the zeolite's void spaces.^{17,19,26-28} For example, Rb_4^{3+} clusters may also form, but they are likely to be unstable, since the stability of the ionic clusters appears to decrease with increasing atomic number.¹⁷ Such paramagnetic centers have only been observed in zeolites containing sodalite cages in their structure (zeolites X, Y, and A), which suggests that they reside within these structural units. The first cluster identified, Na_4^{3+} , was obtained by Kasai²⁹ four decades ago upon irradiation (under vacuum) of dehydrated Na-Y zeolite with γ and X-rays. The ESR spectrum of this cluster is very characteristic and consists of 13 lines due to hyperfine splitting, which is in agreement with expectation for a system of four equivalent ^{23}Na nuclei ($I=3/2$): $2nI + 1$ lines. The hyperfine-split ESR spectra are observed only at low concentrations of the added metal. At higher concentrations, dark solids are produced with single-line ESR spectra, which were attributed to metallic clusters within the zeolite.¹⁷ It was also suggested that the coupling between adjacent centers at metal loading above a critical stage might lead to the loss of the observed ESR

Table III.3 ESR parameters of ion-exchange ZSM-5 zeolites and alkali metal-loaded samples

Sample	Frequency (GHz) (± 0.00007)	Magnetic field B(Gauss)	Peak-to-peak linewidth ΔH_{pp} (Gauss)	g-factor
Li-ZSM-5	9.77584	3487.408	1.5 (± 0.1)	2.0028 (± 0.0001)
Na-ZSM-5 ⁽¹⁾	9.77380	No signal detected		
Rb-ZSM-5	9.76460	3484.222	1.5 (± 0.1)	2.0023 (± 0.0001)
Cs-ZSM-5	9.77110	3486.511	5.7(± 0.1)	2.0024 (± 0.0001)
H-ZSM-5 ⁽¹⁾	9.77003	No signal detected		
Na ₅ /ZSM-5 ⁽²⁾	9.77557	3485.168	7.1 (± 0.2)	2.0040 (± 0.0002)
Na ₁₀ /ZSM-5 ⁽³⁾	9.76647	3484.168	2.0 (± 0.1)	2.0028 (± 0.0001)
K ₅ /ZSM-5 ⁽⁴⁾	9.77570	3483.755	11.4 (± 0.2)	2.0049 (± 0.0002)
K ₁₀ /ZSM-5 ⁽⁴⁾	9.77211	3486.613	1.2 (± 0.1)	2.0025 (± 0.0001)
Rb ₅ /ZSM-5	9.77115	3483.184	14.9 (± 0.2)	2.0045 (± 0.0002)
Rb ₁₀ /ZSM-5 ⁽⁵⁾	9.77122	3486.515	28.6 (± 0.2)	2.0030 (± 0.0002)
Rb ₂₅ /ZSM-5	9.76705	3480.8	17.1 (± 0.3)	2.0060 (± 0.0005)
Cs ₅ /ZSM-5 ⁽²⁾	9.77401	3495.187	4.2 (± 0.2)	1.9980 (± 0.0002)
Cs ₁₁ /ZSM-5	9.77115	3483.755	13.7 (± 0.3)	2.0039 (± 0.0002)

⁽¹⁾- the samples were treated with oxygen after dehydration, then re-evacuated; this treatment was also applied to all loaded samples;

⁽²⁾- the spectra show super-hyperfine splitting; for Na₅/ZSM-5 two overlapped resonances are possible;

⁽³⁾- a second resonance is possible;

⁽⁴⁾- at least two overlapped lines for K₅/ZSM-5 and K₁₀/ZSM-5 are possible;

⁽⁵⁾ – possible super hyperfine splitting

Figure III.25 ESR spectra of dehydrated M-ZSM-5 zeolites (M = Li, Na, Rb, Cs); (narrow sweep of the central region); (*) possible impurity; Samples HZSM-5 and Na-ZSM-5 were treated in oxygen after dehydration and then re-evacuated.

hyperfine structure.³⁰ It is expected that at high metal loadings there would be enhanced electron-electron interactions and the possibility of an insulator-metal transition.³¹ Other species, some unusual, identified within the zeolite frameworks: neutral alkali atoms³², or alkalide species as Na⁻ in the K/Na-A³³ and Rb/Na-A systems²¹, cannot be observed with ESR.

From the NMR experiments performed in this study using alkali metal-loaded ZSM-5 samples, certain indications were obtained that paramagnetic centers may exist within the ZSM-5 zeolite. Therefore, we have used ESR spectroscopy to further confirm their presence, and to possibly identify them.

One important observation made during the ESR experiments was link to the handling/treatment of zeolite powders prior to loading with alkali metals: zeolite samples, which were not treated with oxygen after dehydration (Li-, Rb- or Cs-ZSM-5 samples) produced strong and sharp ESR signals with a g-factor characteristic of free electrons (Table III.3, Figure III.25). On the other hand, the samples, which were treated with oxygen after dehydration and then re-evacuated at room temperature (Na- and H-ZSM-5 zeolites), did not give any significant ESR signals as shown in Figure III.25. [We note that zeolite H-ZSM-5 used to synthesized Cs-ZSM-5 sample was of commercial origin, which can explain the larger linewidth ($\Delta H_{pp} = 5.7$ G) of the main ESR signal when compared with the other samples ($\Delta H_{pp} = 1.5$ G), and the presence of a second weak resonance on the right side of the spectrum as the result of the presence of some impurities.]

Figure III.26 Electron spin resonance spectra of $\text{Cs}_x/\text{ZSM-5}$ samples

($x = 5, 10$ atoms per unit cell) and dehydrated H-ZSM-5 zeolite at room temperature; (narrow sweep of the central region);

Note: The ESR spectrum for $\text{Cs}_{25}/\text{ZSM-5}$ could not be recorded due to apparent high conductivity of the sample.

Figure III.27 Electron spin resonance spectra of $\text{Cs}_x/\text{ZSM-5}$ samples
($x = 5, 10$ atoms per unit cell) and dehydrated H-ZSM-5 zeolite
at room temperature (wide sweep of the central region)

The sharp ESR signal observed in dehydrated Li-, Rb- or Cs-ZSM-5 could arise from surface defects or impurities, or, most likely, from unpaired electrons resulting from partial framework reduction due to oxygen depletion (the dehydration was carried out in vacuum at 450 °C, see the Experimental part), via the following reaction:

Treatment with oxygen immediately after dehydration restores the diamagnetic character of the framework. Keeping this in mind, prior to loading with alkali metal all zeolites were treated with oxygen.

ESR spectra (narrow and broad sweeps over the central region) recorded for alkali metal-loaded ZSM-5 samples are shown in Figures III.26 - III.31. These spectra have one common feature – an ESR line with a g-factor close to that of free electrons. However, since all of the samples were treated with oxygen prior to loading, the above mentioned oxygen depletion of the zeolite framework, which gave rise to the ESR signal, is unlikely in the loaded samples (possible contamination of the samples during loading, should still be considered, since ESR is very sensitive to even smallest amounts of paramagnetic impurities). In some cases, the splitting of the main resonance or additional ESR lines are also observed. For example, in the ESR spectra of the low loaded Cs and Na samples, a super-hyperfine splitting (see below) is clearly seen, while in the ESR spectra of K-loaded samples at least one more resonance is visible. These results reveal the presence of paramagnetic species formed in zeolites upon introduction of alkali metals, yet

Figure III.28 Electron spin resonance spectra of $\text{Rb}_x/\text{ZSM-5}$ samples
($x = 5, 10, 25$ atoms per unit cell) and dehydrated H-ZSM-5 zeolite
at room temperature (narrow sweep of the central region)

Figure III.29 Electron spin resonance spectra of $\text{Rb}_x/\text{ZSM-5}$ samples
($x = 5, 10, 25$ atoms per unit cell) and dehydrated H-ZSM-5 zeolite
at room temperature (wide sweep of the central region)

unambiguous identification of these species is not possible at this time due to apparent complexity of the system. The following paragraphs present only a preliminary interpretation of our ESR experiments, emphasizing that more experiments are needed.

The super-hyperfine structures observed in the ESR of the low-loaded Na/ZSM-5 (~19 lines, a hyperfine splitting constant, $A = 2.1$ G) and Cs/ZSM-5 (~12 lines, $A = 1.4$ G) samples are most likely induced by lattice Al^{3+} ions ($I = 5/2$). Similar super-hyperfine structures were previously reported for samples containing Cr(V) and V(IV) in cationic sites of H-ZSM-5 zeolite.^{34,35} This splitting demonstrates the interaction between the unpaired electron of paramagnetic species and the nuclear spin of lattice Al^{3+} ions. Another example of such a splitting induced by lattice Al^{3+} ions was found in the ESR spectra of Mo/ZSM-5 catalysts, where four signals were detected: two from Mo species located at the catalysts surface, and two from Mo species migrating into the channels of the zeolite.³⁶ Intra-channel Mo species had shown ESR signals with super-hyperfine structures (both with 12 lines; the first: $g = 1.982$, $A = 9.0$ G, and the second: $g = 1.953$, $A = 7.6$ G), which were attributed to the interaction between Mo species and lattice Al^{3+} ions.³⁶ In our $\text{Na}_5/\text{ZSM-5}$ sample, the large number of ESR lines (19) could arise from at least three overlapping resonances, since three sub patterns spaced at a larger distance (6.3 G) can be resolved as shown in Figure III.30. The observed complex resonance could also be caused in part by the partial reduction of the framework silicon, since the reaction was carried out at elevated temperatures (above 250 °C). We may also consider the formation of a Na_6^{5+} cluster within ZSM-5 channels, which would give rise to 19 ESR lines. Such a cluster, if it exists, would most probably form at the intersection of the

channels. It is clear that more experiments are necessary to further elucidate whether or not cluster formation is the cause of the complex ESR pattern observed for this sample.

Another important point to be mentioned is the disappearance of the super-hyperfine splitting in the ESR lines at high metal loadings, with both Cs₁₀/ZSM-5 and Na₁₀/ZSM-5 samples showing a smooth ESR envelope. This seems to be typical for all ESR spectra recorded for highly loaded zeolites. As mentioned before, the featureless signal is likely caused by delocalization of the electrons throughout the zeolite structure, a process also found in ²⁹Si MAS NMR spectra. The possibility of an insulator-metal transition as observed in other alkali metal-doped zeolites³⁰ may be applicable to our samples too, since there were indications that the highest Cs-loaded ZSM-5 sample was highly conductive and possibly metallic. This suggestion is based on its specific behavior (inability to tune the ESR spectrometer while attempting to record its spectrum) and the almost black colour of the sample, which is an indication of narrow band-gap semiconductors and metals. Further study of the electrical conductivities is needed to confirm this.

The ESR parameters (peak-to-peak linewidth, ΔH_{pp} , g-factor) calculated from the frequency and the magnetic field data for alkali metal-loaded ZSM-5 samples are summarized in Table III.3. The ESR data are only approximate when the spectra had super-hyperfine splitting (Cs₅ and Na₅/ZSM-5 samples), or where there were possible additional and/or very broad lines. In general, the obtained ESR values do not fully correlate with the limited amount of data reported in literature, with the exception of the super-hyperfine splitting observed in the ESR spectra of low loaded Cs and Na samples.

Figure III.30 Electron spin resonance spectra of $M_x/ZSM-5$ samples

($M = Na, K$; $x = 5, 10$ atoms per unit cell) at room temperature;

(narrow sweep of the central region)

Figure III.31 Electron spin resonance spectra of $M_x/ZSM-5$ samples

($M = Na, K$; $x = 5, 10$ atoms per unit cell) at room temperature;

(broad sweep of the central region).

However, there are similarities in g-factors and linewidths found for alkali metal particles in alkali metal cation exchange X zeolites.¹⁸ There the g values were found to decrease as a function of the type of alkali metal in the series: Na > K > Rb > Cs. Although for our sample this trend was not followed exactly, there are some similarities: the g values for the extreme in the series are also decreasing (i.e. for Na/ZSM-5 $g = 2.0040$ compared with Na/Li-X $g = 2.0016$, and Cs/ZSM-5 $g = 1.9980$ compared with Cs/Li-X $g = 1.9640$), and the linewidths are comparable as well: i.e. between 2.0 G (± 0.1) and 28.6 G (± 0.2) for our samples compared with 4.3 G (± 0.2) and 33.0 G (± 1) for M/Na-X system.

To conclude, several paramagnetic species were detected by ESR spectroscopy in alkali metal-loaded zeolite ZSM-5. In the low loaded samples (see examples of Cs₅/ZSM-5 and Na₅/ZSM-5) the paramagnetic sites are located close to the lattice Al³⁺ ions, which is clearly indicated by the super-hyperfine splitting observed in the corresponding ESR spectra. At higher loadings (Cs₁₀/ZSM-5, Rb₂₅/ZSM-5), the smooth ESR envelopes suggest the presence of electron delocalization and strong coupling between isolated paramagnetic clusters. These electron coupling effects will eventually lead to development of metallic properties in such typical non-metallic system as zeolite ZSM-5 (insulator-metal transition). This transition has most likely occurred in the Cs₂₅/ZSM-5 sample as indicated by its specific behavior and the almost black color. Further study of the electrical conductivities in these samples is needed to support this idea.

3.3.2.7 Single Crystal X-ray Diffraction (SCXRD)

Since ESR is sensitive only to alkali-metal species/clusters with unpaired electrons, all the diamagnetic species, if present in the same samples will avoid detection with ESR. On the other hand, NMR spectroscopy has its own limitations and is applicable only to the magnetically active nuclei as was mentioned in the previous sections. Some of these limitations can be overcome by using single-crystal X-ray measurements. With this technique a number of alkali metal clusters have already been identified and located within zeolite structures.³⁷⁻³⁹ However the use of SC X-ray diffraction is restricted by the quality and size of the available metal-loaded crystals.

Using optical microscopy we were able to select a few Rb- and Cs- loaded ZSM-5 crystals suitable for SC XRD analysis. Full-matrix least-squares refinement was initiated using framework coordinates obtained from Olson's determination of the structure of dehydrated Cs-ZSM-5 (Rietveld powder diffraction data).⁶ A summary of the data collection and refinements for both Rb- and Cs- loaded ZSM-5 crystals is presented in Table III.4.

In Cs₂₅/ZSM-5 sample there were 16 unique Cs crystallographic sites found with occupancies varying from 19 % to 4 %. In Figure III.32 the first three most populated Cs sites with occupancy factors between 19 and 14 % are marked as Cs1, Cs2 and Cs3. These sites are shown as dark violet spheres, and their distances from the framework (Cs-O) are shown at the bottom of the same figure. Cs1 and Cs2 are located in the straight channel, while Cs3 is located in the sinusoidal channel. Cs1's shortest distance, 3.61 Å, is

Table III.4 Parameters for the metal (Cs and Rb) loaded ZSM-5 zeolite. Single X-ray structure refinement

Chemical formula	Cs _{11.68} Al _{3.7} Si _{92.3} O ₁₉₂	Rb _{6.36} Al _{3.7} Si _{92.3} O ₁₉₂
Unit cell dimensions		
• a, Å	19.984(3)	19.894(8)
• b, Å	19.866(3)	19.657(8)
• c, Å	13.390(2)	13.434(5)
Cell volume, Å ³	5316(1)	5254(4)
Cell density, mg/m ³	2.298	2.264
Space group symmetry	Orthorhombic, Pnma	
Number of reflections		
• total	24266	67277
• unique	4144	8066
• with I>2σ	1082	4452
2θ _{Max} , degree	56.2	56.2
Residual electron density, eÅ ⁻³		
• max	1.86	1.05
• min	-1.45	-0.73
Residual indices (I>2σ(I))		
• R ₁	0.25	0.099
• wR ₂	0.50	0.25
GooF (goodness of fit) on F ²	1.071	0.997

Occupancy of different Cs sites is colour-encoded as shown. The most intensive violet coloured spheres indicate the Cs sites with the highest occupancy in decreasing order (Cs1, Cs2, Cs3).

with oxygen atoms O19. The shortest Cs2-O distance, to O7 is 3.4 Å, and the shortest Cs3-O distance, to O8 is 3.03 Å. All other Cs sites are grouped in order of decreasing percentage of occupancy in three other categories (13-11 %, 10-8 %, and 6-4 %) as shown in Figure III.32 as spheres of different shades of violet. Most of these sites are located in the sinusoidal channel and at the intersection of the channels, with very few in the straight channel in a close proximity to Cs1 and Cs2. The framework positions of these sites are very close to each other; often the difference is less than 1 Å.

Our findings bear certain similarities with the earlier reported PXRD data for dehydrated Cs-ZSM-5 zeolite prepared via ion exchange.¹¹ We note, that the differences are not surprising, taking into account that we followed a different synthetic method for our Cs/ZSM-5 crystals (chemical vapour deposition), different Si/Al ratio (25), and Cs loading (~25 Cs atoms per unit cell). The Cs/ZSM-5 crystal studied by Olson was obtained by an ion exchange method, and the Al content of the starting ZSM-5 zeolite was significantly higher. The distances between the Cs atoms and framework oxygen found in our study varied between 3.0 and 3.96 Å, with the shortest Cs-O distance of 3.03 Å for the group of sites with the highest occupancy (Cs1-Cs3), while in the cited reference the shortest Cs-O distance reported for the highest occupied site was 3.31 Å, and the longest Cs-O distance found for the least occupied site was 3.63 Å. Shorter Cs-O distances, matching better with our values have been reported for CsNaY zeolite.⁴⁰ For this system, a Cs-O distance of 3.04 Å, close to the sum of the ionic radii, 3.09 Å, was reported for SII Cs ions in the six-member ring windows.

Figure III.33 Schematic representation of Rb sites within the ZSM-5 zeolite.

Occupancy of different Rb sites is colour-encoded as shown. The most intensive blue coloured spheres indicate the Rb sites with the highest occupancy in decreasing order (Rb1, Rb2, Rb3).

Using the same starting model, the structure of Rb-loaded ZSM-5 crystal was also refined successfully. The shortest Rb-O distance found was 3.4 Å, the longer 3.8 Å. The site occupancies varied from 14% to 4 %, and the locations of the Rb cations into the ZSM-5 lattice closely match the model for Cs/ZSM-5. The first three most occupied sites marked as Rb1, Rb2, and Rb3 (site occupancy between 14 and 12 %) are marked as dark blue spheres as shown in Figure III.33. At the bottom of the figure are shown the corresponding distances to the specified oxygen atoms. Rb1 and Rb3 are located in the straight channel, and close to each other (2.19 - 3.6 Å), while Rb2 is located at the intersection of the channels. All the other less occupied Rb sites (7 sites) are grouped in order of decreasing site occupancy in three categories: 10-11 %, 6-7 %, and 4 %, each of it represented by a sphere of different shade of blue as shown in the Figure III.33. These sites are located almost exclusively in the sinusoidal channel close to the intersection with the straight channel. These sites are also very close to each other (less than 1 Å), as was the case for Cs sites.

The chemical formulas determined from SC X-ray data for Cs/ZSM-5 and Rb/ZSM-5 crystals were found as $\text{Cs}_{11.68}\text{Al}_{3.7}\text{Si}_{92.3}\text{O}_{192}$ and $\text{Rb}_{6.36}\text{Al}_{3.7}\text{Si}_{92.3}\text{O}_{192}$ as compared with the unit cell compositions estimated according to the metal loading $\text{Cs}_{26.3}\text{Al}_{3.7}\text{Si}_{92.3}\text{O}_{192}$ and $\text{Rb}_{10.6}\text{Al}_{3.7}\text{Si}_{92.3}\text{O}_{192}$. The difference is most likely due to the inhomogeneity in metal deposition, especially at high metal loadings (~26 atoms per unit cell for Cs/ZSM-5). Thus, the analyzed crystals are probably not representative of the bulk samples. In the Figure III.34 the microscopic images of Cs/ZSM-5 and Rb/ZSM-5 crystals immediately after air exposure are shown. The inhomogeneous metal distribution in Rb/ZSM-5

crystals can be seen as different shades of brown colour. Another important observation from the Figure III.34 is that the contours of the crystals are well preserved, the edges being still sharp, which is remarkable taking into account very high alkali metal loadings in these samples.

Figure III.34 Optical microscope images of the Cs/ZSM-5 (left) and Rb/ZSM-5 (right) crystals immediately after air exposure; the sizes of the crystals are indicated below the images.

To conclude, the crystal structures of two Cs- and Rb- loaded ZSM-5 samples have been determined by SC X-ray analysis. Cs was found with partial occupancy in 16 different positions. The first two most populated Cs sites (Cs1 and Cs2) are located in the straight channels, and the third (Cs3) is located in the sinusoidal channels. Rb was found with partial occupancy in 10 different positions, the first three most populated are located as follow: Rb1 and Rb3 in the 10-ring windows of the straight channel, and Rb2 is at the channel intersection. All other least occupied sites are located almost exclusively in the

sinusoidal channels, close to the channel intersections. The ranges of Cs-O and Rb-O distances found are 3.03 - 3.91 Å, and 3.14 - 4.12 Å, respectively.

3.3.3 The Influence of Charge-balancing Cations on ZSM-5 Framework Stability

It was reported that Li^+ cations in lithium-exchanged zeolites were more resistant to reduction than protons and heavier alkali metal cations in the corresponding exchanged zeolites. For example, when the Li-X zeolite was exposed to Cs vapors, only cesium-containing clusters have been obtained, but when Na-X was exposed to Cs vapors, sodium clusters have also been formed. This fact was attributed to the stronger lattice interactions for smaller Li^+ cations, which in turn can stabilize the zeolite framework.¹⁸ Another study indicated that the reduction of zeolites with both high lithium and low sodium content (i.e. $\text{Li}_{44}\text{Na}_{12}\text{-Y}$, $\text{Li}_{50}\text{Na}_6\text{-Y}$, $\text{Li}_{82}\text{Na}_5\text{-X}$, or $\text{Li}_{50}\text{Na}_6\text{-Y}$) had resulted in the formation of sodium-containing clusters only (either Na_4^{3+} or Na_3^{2+}).⁴¹ Quantum mechanical calculations showed that the residual charge on a lithium ion in a dehydrated Y zeolite is less than one sixth of that on a sodium ion in a similar site which may explain lithium inertness.⁴² This apparent inertness of lithium, together with its possible stabilizing effect on a zeolite framework led us to prepare a Cs-loaded Li-ZSM-5 sample (10 Cs atoms per unit cell). For this sample, the Li^+ cations in the Li-ZSM-5 zeolite were expected to have a similar stabilizing effect as in the cited examples, meaning that compared to the H-ZSM-5 zeolite, the Li-ZSM-5 lattice would be more resistant toward

Figure III.35 ^{27}Al MAS NMR spectra of Cs_{10} -loaded H-ZSM-5 (a) and Li-ZSM-5 zeolites (b)

Figure III.36 ^{29}Si MAS NMR spectra of Cs_{10} -loaded H-ZSM-5 (a) and Li-ZSM-5 zeolites (b).

reduction upon reaction with cesium vapour. In addition, the reaction of Cs vapor with the Li-ZSM-5 zeolite was anticipated to result in the formation of cesium-containing species only.

The integrity of the Li-ZSM-5 framework upon Cs-loading was checked with ^{27}Al MAS NMR and ^{29}Si MAS NMR spectroscopies, the Cs deposition was followed with ^1H MAS NMR spectroscopy, and the Cs-containing species were monitored with ^{133}Cs NMR spectroscopy. ^7Li MAS NMR spectroscopy was used to probe the change in lithium environment in the Li-ZSM-5 zeolite upon loading with Cs.

3.3.3.1 ^{27}Al MAS NMR and ^{29}Si MAS NMR

Figure III.35 shows the ^{27}Al MAS NMR spectrum of the cesium-loaded lithium-exchanged Li-ZSM-5 sample ($\text{Cs}_{10}/\text{Li-ZSM-5}$) compared to the cesium-loaded H-ZSM-5 sample ($\text{Cs}_{10}/\text{H-ZSM-5}$). The former spectrum shows the same characteristic signal at about 51.8 ppm assigned to tetrahedrally-coordinated aluminum,⁸ and the fact that this is the only signal observed indicates that the $\text{Cs}_{10}/\text{Li-ZSM-5}$ sample does not contain extra-framework (octahedral) aluminum. The ^{27}Al MAS NMR spectrum of the $\text{Cs}_{10}/\text{Li-ZSM-5}$ sample is also asymmetric and as broad as that of the $\text{Cs}_{10}/\text{H-ZSM-5}$ sample, which indicates residual quadrupolar interactions in both. It is not clear why the intensity of this spectrum is noticeably diminished comparing with $\text{Cs}_{10}/\text{H-ZSM-5}$ sample. Perhaps, this effect can be attributed to stronger paramagnetic effects, more significant in the $\text{Cs}_{10}/\text{Li-ZSM-5}$ sample (see below). Nevertheless, the observation of the ^{27}Al line attributed to Al in tetrahedral coordination proves the preservation of the Li-ZSM-5 framework integrity upon loading with Cs, as was the case for the H-ZSM-5 zeolite.

Figure III.36 shows the ^{29}Si MAS NMR spectra of the $\text{Cs}_{10}/\text{Li-ZSM-5}$ and $\text{Cs}_{10}/\text{H-ZSM-5}$ samples. As a result of the “inertness” of the Li-ZSM-5 framework mentioned previously, it was expected that the electron delocalization would be stronger in the Li-ZSM-5 lattice than in the H-ZSM-5 lattice. The latter suggestion is also supported by the difference in colour of the two samples: the $\text{Cs}_{10}/\text{Li-ZSM-5}$ sample is gray, while the $\text{Cs}_{10}/\text{H-ZSM-5}$ sample is cream (both starting Li-ZSM-5 and H-ZSM-5 zeolites are white powders). The different colours show that the energy band gap in the samples are different, narrower for $\text{Cs}_{10}/\text{Li-ZSM-5}$ than for $\text{Cs}_{10}/\text{H-ZSM-5}$, as a consequence of different degree of filling with electrons of the host material band gaps (more electrons for $\text{Cs}_{10}/\text{Li-ZSM-5}$). This effect is most likely the cause of the somewhat stronger broadening of the ^{29}Si MAS NMR spectrum of the $\text{Cs}_{10}/\text{Li-ZSM-5}$ sample as compared with the $\text{Cs}_{10}/\text{H-ZSM-5}$ (Figure III.36). It is also noticeable that the overall ^{29}Si spectra intensity is not affected by the charge balancing framework cations (Li^+ versus H^+), both ^{29}Si MAS spectra for $\text{Cs}_{10}/\text{Li-ZSM-5}$ and $\text{Cs}_{10}/\text{H-ZSM-5}$ having similar ^{29}Si integral intensities.

3.3.3.2 ^1H MAS NMR and ^{133}Cs NMR

Figure III.37 shows a comparison between the two ^1H MAS NMR spectra of $\text{Cs}_{10}/\text{Li-ZSM-5}$ and $\text{Cs}_{10}/\text{H-ZSM-5}$. Similar to the ^1H MAS NMR spectra of $\text{Cs}/\text{H-ZSM-5}$ samples, the spectrum for $\text{Cs}_{10}/\text{Li-ZSM-5}$ shows a new line at 4.9 ppm, but somewhat broader. The line associated with the surface Si-OH defects is also seen at 1.9 ppm. It seems that the new line attributed to Cs associated with hydrogen forms regardless of the type of cation exchanged ZSM-5 zeolite. Moreover, this new line originates from either

Figure III.37 ^1H MAS NMR spectra of Cs_{10} -loaded H-ZSM-5 (a) and Li-ZSM-5 zeolites (b); MAS spinning speed was 3.5 kHz in both cases; spinning sidebands are marked (with asterisks) only on the first spectrum

Figure III.38 ^{133}Cs NMR spectra of Cs_{10} -loaded H-ZSM-5 (a) and Li-ZSM-5 zeolites (b).

the bridging proton line or the defect center line, or both. The larger line width of this new line observed in the ^1H MAS NMR spectrum of the $\text{Cs}_{10}/\text{Li-ZSM-5}$ sample is probably due to residual heteronuclear dipole-dipole interactions of the protons with the quadrupolar $^{6,7}\text{Li}$ nuclei. This is in addition to other factors which might affect the line width in the ^1H MAS NMR spectrum of the $\text{Cs}_{10}/\text{H-ZSM-5}$ sample, such as residual heteronuclear dipole-dipole interactions of the protons with the quadrupolar ^{27}Al and ^{133}Cs nuclei, the effect of zeolite dehydration, or paramagnetic broadening.

The ^{133}Cs spectrum of the $\text{Cs}_{10}/\text{Li-ZSM-5}$ sample is similar to, but broader than, that of the $\text{Cs}_{10}/\text{H-ZSM-5}$ sample as shown in Figure III.38. The similarity is seen in the presence of two ^{133}Cs lines, one relatively narrow and of low intensity at about -160 ppm, which is attributed to Cs cations in regular crystallographic sites as mentioned previously, and the other very broad line with a chemical shift at about 95 ppm, which can be attributed to Cs species, also cationic but not in regular crystallographic sites. The presence of the line at -160 ppm in the ^{133}Cs spectrum of the $\text{Cs}_{10}/\text{Li-ZSM-5}$ sample is not surprising since the Cs^+ and Li^+ cations can occupy different sites in the ZSM-5 framework: the larger Cs^+ cations occupy the ten-member ring of the ZSM-5 channels,⁴ while the smaller Li^+ cations preferably occupy the sites on top of the six member rings of the channels wall.⁴³ The first Cs^+ cations formed inside the Li-ZSM-5 channels would occupy the regular crystallographic Cs sites, and as the reaction proceeds, Cs^+ might associate and form different Cs-containing species as discussed for Cs/H-ZSM-5 system.

The broadening of the ^{133}Cs lines observed in the ^{133}Cs spectrum of the $\text{Cs}_{10}/\text{Li-ZSM-5}$ when compared to the $\text{Cs}_{10}/\text{H-ZSM-5}$ one may be attributed to strong paramagnetic

broadening, since the Cs₁₀/Li-ZSM-5 sample should contain more unpaired electrons than the Cs₁₀/H-ZSM-5 sample, where some of Cs metal would interact with zeolite protons. To some extent the ¹³³Cs spectrum of Cs₁₀/Li-ZSM-5 sample is similar to the spectrum of the Cs₂₅/H-ZSM-5 sample (similar linewidths ~ 14.3 kHz and ~14.4 kHz, respectively).

3.3.3.3 ⁷Li MAS NMR

The ⁷Li MAS spectra of the Cs₁₀/Li-ZSM-5 sample and the dehydrated Li-ZSM-5 zeolite are compared In Figure III.39. In the latter spectrum, one sharp resonance is observed at -0.9 ppm. This peak is asymmetric with a shoulder at the high frequency side of the spectrum. Since in the asymmetric unit of ZSM-5 there are 12 crystallographically independent tetrahedral (T) atoms, it is expected that aluminum will be distributed with equal probability among them,⁴⁴ and so presumably there can be up to 12 distinct coordination sites for lithium. However, lithium has a narrow chemical shift range, so that would be difficult to resolve individual lines, thus resulting in strong overlap. Yet, it seems that not all these sites are equally populated. For example, by using ⁷Li MAS NMR to test the accessibility of lithium cations to oxygen, Accardi et al ⁴⁵ found three different types of lithium sites. In another study, by combining FTIR spectroscopic and microcalorimetric measurements on adsorbed CO, only two lithium sites were found.⁴⁸ Our NMR results indicate that in Li-ZSM-5 there are at least two distinct Li sites as indicated by deconvolution of the ⁷Li MAS NMR spectrum (inset, Figure III.39 (a)). The results of deconvolution (position of the lines, line widths, and the integral intensities) are presented in Table III.5. The line at about -0.91 ppm is sharp (38

Figure III.39 ${}^7\text{Li}$ MAS NMR spectra of dehydrated Li-ZSM-5 zeolite (a) and Cs₁₀/Li-ZSM-5 sample (b). Corresponding deconvoluted spectra are shown as insets (black— experimental spectrum, blue – simulated spectrum, red, yellow and green – components of the simulated spectrum).

Hz), the other at about -0.69 ppm is broader (85 Hz), and less intense, and can be actually a superposition of two lines.

Table III.5 The results of the deconvolution of ^7Li MAS spectra of Li-ZSM-5 and $\text{Cs}_{10}/\text{Li-ZSM-5}$ samples

Component	Position [ppm]	Width [Hz]	Line shape Gauss/Lorentz	Integral intensity [%]
1	-0.69	86	0.7	65.8
2	-0.91	36	0.4	34.2
1	1.63	542	0.5	28.3
2	0.11	192	1.0	25.7
3	-0.87	100	0.4	46.0

The introduction of Cs in the Li-ZSM-5 zeolite resulted in the third ^7Li line, seen on the left side of the ^7Li MAS NMR spectrum of $\text{Cs}_{10}/\text{Li-ZSM-5}$ sample (Figure III.29 (b)). All three components of this spectrum when compared to Li-ZSM-5 are shifted to higher frequency (-0.87 ppm, -0.11 ppm, 1.63 ppm) and are broader (100 Hz, 192 Hz, 542 Hz) which is positively due to paramagnetic effects caused by the presence of Cs paramagnetic species in zeolite channels. Similar paramagnetic shifts were observed in ^7Li MAS NMR spectra when oxygen was adsorbed in ZSM-5 zeolite.⁴⁵

To conclude, it seems that the Li-ZSM-5 framework behaves upon loading with cesium similarly to the H-ZSM-5 (^{27}Al and ^{29}Si NMR data). In addition, the Cs-species which can form inside both Li-ZSM-5 and H-ZSM-5 zeolites are likely similar. The advantage of preparing Cs-clusters using a Li-ZSM-5 matrix instead of H-ZSM-5 is the larger extent of electron delocalization observed for the former, and also the increased

Figure III.40 The alkali metal-loaded ZSM-5 samples prepared ($x = 5, 10, 25$ alkali metal atoms per unit cell)

number of Cs atoms (Cs^+ / electron pairs) available for cluster formation. This may lead to a larger amount of more uniform Cs-clusters per the same Cs loading.

The ^7Li MAS NMR results indicate the presence of Cs-species inside zeolite's channels, which although of unknown structure are clearly paramagnetic. This can be considered as an important finding of the current work, proving alkali metal cluster formation inside ZSM-5 zeolite.

3.3.4 The Colour of the Alkali Metal-Loaded ZSM-5 Samples.

In Figure III.40, the photographic images of the prepared alkali metal-loaded ZSM-5 samples are shown. In each image, the samples are presented in order of increasing loading, starting with H-ZSM-5 zeolite. As the loading increases, the colour changes from white as in ZSM-5 zeolite to cream or light brown in the samples with low loading to dark brown in $\text{Rb}_{25}/\text{ZSM-5}$ or dark blue in $\text{Cs}_{25}/\text{ZSM-5}$.

A qualitative explanation of the observed variations in colour relies upon a short introduction to band theory using an elementary quantum mechanical approach. According to quantum theory, the energy of an electron in the crystal must fall within well-defined bands. The energies of valence orbitals, which form bonds between atoms, represent such a band of states or "the valence band". The next higher band is the conduction band, which is separated from the valence band by the energy gap (bandgap) of width E_g . The band configuration in an insulator or semiconductor is shown in Figure III.41 (a). The energy level of the highest-energy electrons, marked E_f , is called the Fermi energy or Fermi level.⁵⁰ Materials with wide bandgaps do not absorb light in the visible spectrum and, as a result, are colorless. The change in colour indicates a narrowing of the

Figure III.41 Band configuration in an insulator or semiconductor (a); the variation of the colour with the size of the band gap (b).⁵⁰

Figure III.42 The band structure of the lowly doped (left) and highly doped (right) K/Na-A system; E_f is the Fermi energy.⁴⁹

bandgap, as the more narrow the band gap, the darker the colour of the material will be (as shown in Figure III.41 (b)).

It is known that zeolites, and many other aluminosilicates, have very wide electronic bandgaps (~ 10 - 11 eV), which makes these materials optically transparent and excellent electrical insulators. Doping with alkali metals results in mixing of the zeolite bands with orbitals of incoming metal. This leads to apparent narrowing of the bandgap with the optical-absorption threshold showing the quantum confinement blue shift. Such effects have been previously observed for Na clusters in sodalite⁴⁷ or K clusters in zeolite A and X.³⁸

There are methods to calculate the band structure of doped systems, and, for example, such calculations were done for K doped Na-A zeolite.⁴⁸ In Figure III.42, the band structure of low and highly doped K/Na-A systems are shown. For the lowly doped system, a direct band gap of 2.3 eV was obtained, in agreement with this sample being an insulator and light coloured. For the highly doped system, the Fermi level is shifted upward into the conduction band since the number of doping electrons has increased. The sample shows dark colour and metallic behavior.

This situation is most likely valid for our Cs loaded samples too, since similar changes in colour with Cs loading have been observed (from light cream to dark blue) and the highest loaded sample is possibly conductive as was previously discussed. Of all the alkali metals the Cs/ZSM-5 system seem to be the closest to demonstrating an insulator-metal transition. The reddish colour of the Rb loaded samples may also indicate

the narrowing of the original zeolite's bandgap, but at current loadings not far enough to cross the “metallic barrier”.

In the case of the Na- and K- loaded ZSM-5 samples, the light colour of the samples at low loadings is more likely due to the low degree of metal incorporation in zeolite lattice. The same can be said about Na₁₀/ZSM-5 sample, which shows a golden colour, while for K₁₀/ZSM-5 its brown colour may be an additional indication that for this sample a higher degree of metal incorporation was attained than for Na₁₀/ZSM-5 sample.

3.6 Conclusions

We have demonstrated that zeolite H-ZSM-5 can adsorb considerable amounts of alkali metals via vapour deposition. For highly volatile alkali metals (Cs and Rb) such deposition can be performed even at room or slightly elevated temperature, while for less volatile alkali metals (Na and K) more intense heating is needed. The first portions of alkali metal vapour would interact with charge-balancing protons of H-ZSM-5 to give corresponding cations. These cations can serve as centers of subsequent cluster formation as more and more alkali metal is introduced. The channel pore structure of ZSM-5 zeolite would naturally induce a one-dimensional motif for such clusters and, when clusters merge, nanowires. Such nanowires can be of particular interest for both pure and applied nanotechnology.

We have used a range of modern characterization techniques including multinuclear solid-state magnetic resonance spectroscopy (NMR), electron spin resonance (ESR), powder and single-crystal X-ray diffraction to study the formation and properties of these nanoparticles. The metal deposition within the ZSM-5 zeolite host was more pronounced

for more volatile metals Rb and Cs (^{27}Al NMR, ^1H NMR, ^{29}Si NMR). This was also supported by the darker colour of these samples characteristic of narrow bandgap semiconductors and metals. Sodium and potassium metals were deposited to a lesser extent, with most of the metal remaining at the surface of the zeolite (^{27}Al NMR, ^1H NMR, ^{29}Si NMR, PXRD), and only small portions entering the channels (^{23}Na NMR). At higher loadings Cs metal causes strong distortion of the zeolite framework, most likely due to the larger size of Cs atoms. These effects were less prominent for Rb, which, combined with its high volatility, makes this metal an ideal choice for deposition in zeolites of ZSM type.

In ZSM-5 zeolite the introduced alkali metal forms paramagnetic and diamagnetic clusters of different nuclearity. The diamagnetic species were detected in NMR spectra of corresponding metals (^{87}Rb , ^{133}Cs). The presence of paramagnetic species in Cs-loaded Li-ZSM-5 zeolite was confirmed by ^7Li NMR. Additional information was also brought by ESR spectroscopy, which has indicated the presence of several types of paramagnetic species.

The most direct information on the arrangement of intrapore alkali metal species in Rb and Cs loaded ZSM-5 zeolite was obtained via refinement of the single-crystal XRD data. These results clearly indicated a high degree of disorder of the metal centres inside the zeolite channels. These centres likely act as starting points in cluster formation.

3.7 Future Work

The samples highly loaded with alkali metals are dark or almost black in colour implying their possible narrow-bandgap semiconductor or metallic properties. To confirm this further, electrical conductivity measurements are needed. It would also be interesting to determine exact degree of loadings for different alkali metal required for “insulator-metal” transition to occur. The change in bandgap energy with loading should be followed with optical spectroscopy in UV-visible range.

More detailed analysis of the ESR spectra is required to determine exact nature and concentrations of different types of paramagnetic species in alkali metal loaded zeolite samples.

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Chapter IV

Nano-sized Cs particles in Mesoporous Templates

4.1 Introduction

As was discussed in the previous section, Cs metal is the most convenient alkali metal to work with for two main reasons: (i) the metal deposition into the porous templates can be carried out at low temperature, allowing one to avoid chemical interaction with the host material; (ii) ^{133}Cs nucleus is more easy detectable by NMR than any other alkali metal nuclei (i.e. ^{23}Na , ^{39}K , ^{87}Rb). In addition, by applying ^{133}Cs NMR to Cs-loaded ZSM-5 zeolite, only signals from cationic Cs^+ species were detected, one of the limiting factors being the pore size of the template (micropores). It is logical to extend the search into the mesopore range in order to detect larger Cs species, including nano-sized metal particles. The main objective of the present study was to prepare and to NMR-detect metallic confined Cs species with a chemical shift in the Knight Shift region ($\sim 14,900$ ppm). The first steps would be to find a proper template for the limiting pore size and to organize the Cs-loading. Further, modifying the pore sizes in the chosen template and varying the Cs-loading would allow the study of the quantum size effect in such systems.

Three types of silica-based mesoporous materials were used as potential templates in our study. One of them belongs to the M41S family of materials, namely MCM-41, and the other to the SBA family of materials, SBA-15. The two materials are similar and often referred to as ordered mesoporous silica (OMS) materials. The similarity is seen in their pores structures, both materials displaying an ordered structure with uniform mesopores arranged in a hexagonal ($P6mm$), honeycomb-like lattice.

The main differences between the two materials are in the thickness of the pore walls (thicker walls for SBA-15) and in the fact that SBA-15 contains both mesopores and micropores (30 % of volume), whereas MCM-41 contains only mesopores. The third template, controlled-pore glass Vycor was a commercial sample, already tested previously as a support for small metal particles (Pt, Pd).¹

4.2 Experimental Section

4.2.1 Samples Preparation

4.2.1.1 Synthesis of OMS's materials

Mesoporous silica SBA-15 was synthesized using Pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, $M_{\text{av}} = 5800$, Aldrich) and tetraethylorthosilicate (TEOS, 98 %, Aldrich), under acidic conditions.² In a typical preparation, 2 g of P123 was dissolved under stirring in 53 g of water and 63 g of HCl (1.9 M) aqueous solution at room temperature. The solution was heated to 35 °C before adding TEOS, and was allowed to prehydrolyse for 1 h. The resulting solution was stirred for 22 h at 35 °C, and then the mixture was aged at 100 °C for 48 h under static conditions. The solid product was recovered by filtration and air-dried at room temperature overnight.

The synthesis of MCM-41 was carried out as follow³: Cab-O-Sil silica (3.6 g) was mixed with water (6 g) and 25 wt-% Tetramethylammonium Hydroxide (TMAOH, 6.16 g). A mixture of 3.65 g Cetyltrimethylammonium Bromide (CTAB), 6.16 g water, and 1.17 g 30 wt-% NH_4OH was added under vigorous stirring. After 30 min, the gel was transferred into polypropylene bottles, and then heated at 343 K for 3 days. Both as-

synthesized SBA-15 and MCM-41 materials were calcined in air at 550 °C for 8 h with a 4 h dwell drying period at 120 °C (heating rate 1 °C/min).

4.2.1.2 Vycor Glass Treatment

Porous Vycor glass (Corning glass #7930) was supplied in a tubular form of 6.7 mm diameter. Before activation, the Vycor glass was cleaned according to the supplier's instructions: the Vycor tube was heated in concentrated HNO₃ solution containing a few KClO₃ crystals, then washed with distilled water, dried at 140 °C for 4 h, and stored in a dessicator. Before dehydration, the Vycor tube was finely ground. One experiment on Cs loading was performed with an intact piece of Vycor tube (c.a. 1 cm in length) cleaned as described.

4.2.1.3 Preparation of the Cesium-Loaded Mesoporous Materials

The preparation procedure was similar to the synthesis of the cesium loaded-ZSM-5 zeolite. The dehydration of the OMS templates was done in vacuum at 120 - 200 °C for 24 - 48 h. After dehydration, additional oxygen treatment was applied at 200 - 300 °C in order to oxidize the residual carbon impurities. After approximately two hours of oxygen treatment the samples were re-evacuated. The dehydration and the oxygen treatment for Vycor glass were done under the same conditions as for ZSM-5 zeolite. The Cesium deposition was carried out at 75 - 100 °C, under vacuum. The samples were periodically shaken and equilibrated in order to get homogeneous metal deposition. The reactions were considered complete when no metal film remained on the vessel's walls and on the surface of the material. The Cs-loaded mesoporous samples prepared are listed in Table IV.1. The quantities of the starting materials and the metal loadings are also shown. All

the samples were sealed in 5 mm o.d. tubes containing approximately the same amount of sample.

Table IV.1 Cesium loaded-Mesoporous Materials samples

	Sample	$m_{\text{MCM or Vycor, g}}$ (± 0.0002)	$m_{\text{Cs, g}}$ (± 0.0002)	Cs loading		Colour
				Weight %	Filling factor	
1	Cs/SBA-15	0.2721	0.1332	32.5	0.24	Cream
2	Cs/SBA-15	0.2413	0.3514	59.3	0.73	Brown
3	Cs/SBA-15	0.2734	0.5712	68.0	1.07	Dark brown
4	Cs/SBA-15	0.2225	0.6824	75.6	1.55	Black
5	Cs/MCM-41	0.3422	0.0936	21.0	0.40	Cream
6	Cs/MCM-41	0.4021	0.1811	31.0	0.60	Cream
7	Cs/Vycor	0.5532	0.2721	33.0	0.83	Dark blue
8	Cs/Vycor ⁽¹⁾	0.5319	0.0448	7.5	0.13	Blue

(1) Vycor in tubular form (6.7 mm diameter)

Table IV.2 Morphology of OMS (SBA-15, MCM-41) and Vycor glass

Ordered Mesoporous Material (OMS)	BET surface area (m^2/g)	Pore size ⁽¹⁾ ($\text{\AA}$)	Pore volume ⁽²⁾ (cm^3/g)
SBA-15	835.5506 (± 1.4683)	60 (± 9)	1.11 (± 0.01)
MCM-41	1086.9921 (± 0.6511)	26 (± 3)	1.09 (± 0.03)
Vycor	233.2292 (± 0.3464)	44 (± 6)	0.26 (± 0.01)

⁽¹⁾ The pore size was calculated from the desorption branch data by BJH method

⁽²⁾ The pore volume was determined from the desorption branch data by BJH method.

4.2.2 Experimental Condition

4.2.2.1 Powder X-Ray Diffraction (PXRD) Measurements

Powder X-ray diffraction patterns for as-synthesis and calcined SBA-15 and MCM-41 were collected on a Scintag X₂ powder diffractometer ($\text{CuK}\alpha = 1.54056 \text{ nm}$). The diffractograms were recorded after instrument alignment for low angle measurements. The conditions for powder X-ray measurements were as follow: the step size of 0.02 degree, the scan rate of 0.24 degree/minute and the range of 2θ between 0.6 and 7 degrees for SBA-15, and between 1.5 and 7 degrees for MCM-41.

4.2.2.2 Porosimetry

The adsorption/desorption isotherms of nitrogen were measured at 77 K using a Micromeritics ASAP 2010 instrument. Each sample was outgassed at 200 °C (calcined OMS materials, and Vycor powder) until a stable static vacuum of 3×10^{-3} Torr was reached (approximately 12 hours). The mesopore diameter was calculated from the desorption branch of nitrogen isotherms by the Brunauer-Jura-Harkins (BJH) method, which has been shown to provide reliable results for the OMS materials.⁴ The pore volume was determined from desorption branches of the N₂ isotherm by using the same method.

4.2.2.3 NMR Experiments (²⁹Si MAS NMR, ¹³³Cs NMR)

²⁹Si MAS NMR

The ²⁹Si MAS spectra of non-calcined and calcined OMS samples (SBA-15 and MCM-41) were recorded with 300 scans, and relaxation delays of 180 s using a Bruker DSX 400 spectrometer (the corresponding resonance frequency for ²⁹Si is 79.48 MHz). A

simple one-pulse sequence was applied for recording the spectra (the 90° rf pulse, $p_1 = 8 \mu\text{s}$). The chemical shifts were referenced to TMS solution. The OMS powders were carefully packed in a 7 mm zirconia rotor under moderate pressure. A Doty 7 mm MAS probe was used and the samples were spun at 5.5 KHz, the spinning speed was controlled by a Bruker MAS-DB pneumatic air control unit.

^{133}Cs NMR

The ^{133}Cs NMR spectra of Cs-loaded mesoporous materials were recorded with 4 k scans and relaxation delays of 2 s using a Bruker AMX 300 spectrometer (the corresponding resonance frequency for ^{133}Cs is 39.36 MHz). The length of the 90° rf pulse was 2 μs . The chemical shifts were referenced to 0.1 M CsNO_3 solution. A 5 mm horizontal static probe was used.

4.3 Results and Discussion

4.3.1 Characterization of the Mesoporous Materials

4.3.1.1 PXRD

Because of the geometry of their lattices, both SBA-15 and MCM-41 can be indexed with a hexagonal unit cell (space group $P6mm$), with $a = b$ and $c = \infty$ (a , b , and c the unit cell parameters). By introducing the h , k , l indices and d spacing in the equation (2.26) the following parameters can be found: $a = b \sim 11.4 \text{ nm}$ and $c = \infty$ for SBA-15, and $a = b \sim 4.2 \text{ nm}$ for MCM-41. Since the parameters a and b are on the order of nanometers instead of tenths of nanometers, as usually encountered in crystals, in OMS materials the X-rays are diffracted over small angles only. Thus, the diffractograms of SBA-15 and MCM-41

Figure IV.1 X-ray powder diffractions patterns for SBA-15 mesoporous material

Figure IV.2 X-ray powder diffractions patterns for MCM-41 mesoporous material

consist of a limited number of reflection peaks, all at the low angle as shown in Figures IV.1 and IV.2. In both figures three well-resolved reflections are present: one very intense, (100), and two much weaker peaks, (110), and (200). For SBA-15 all the reflections appear at lower angles than for MCM-41, since the pore sizes are larger for the former. According to the PXRD, both materials had well-defined ordered structures.

4.3.1.2 Porosimetry

The isotherm plots for the tested materials, SBA-15, MCM-41 and Vycor glass, are of the type IV according to IUPAC classification,⁵ which is characteristic of mesoporous materials. All isotherms show a hysteresis loop, but with different shapes and arising at different relative pressures. Table IV.2 summarizes the results of the nitrogen adsorption analysis, including data regarding the available void spaces.

For all the isotherms, four similar regions can be distinguished (Figures IV.3 (a) - IV.5 (a)): (i) monolayer-multilayer adsorption (region I-II), (ii) capillary condensation (region III), and (iii) multilayer adsorption on the outer particle surfaces (region IV). At a very low relative pressure (p/p_0) a large amount of nitrogen becomes physisorbed (region I). Nitrogen physisorption at these low pressures is usually assigned to condensation of N_2 in micropores. The assignment is valid for SBA-15, since this material contains micropores,⁶ but for MCM-41 and Vycor, the process is likely a monolayer adsorption of nitrogen on the surface (both on the external surface and inside the mesopores). The monolayer adsorption for Vycor glass and SBA-15 occurs at a slightly higher relative pressure than in MCM-41, since the pores of these materials are larger. Following monolayer adsorption, multilayers of N_2 start to develop on the external surface and in

Figure IV.3 Nitrogen adsorption-desorption isotherm plot for calcined SBA-15

mesoporous silica (a). Pore size distribution plots calculated from adsorption branch

(b) and desorption branch (c) by BJH method.

the mesopores (region II). At a relative N_2 pressure of about 0.3 for MCM-41, 0.45 for Vycor glass and 0.65 for SBA-15 a sudden steep increase of the amount of adsorbed N_2 is observed. This steep increase is caused by the capillary condensation of N_2 inside the mesopores. The occurrence of capillary condensation is shifted to higher p/p_0 with increasing pore size. The sharp step is accompanied by a narrow hysteresis loop with parallel adsorption and desorption branches for SBA-15 material (H1 type according to IUPAC recommendations⁵), or a broad triangular hysteresis loop with a steep desorption branch for Vycor glass (H2 type), but does not show hysteresis loop for MCM-41. For OMS materials with 2D hexagonal structure of the pores, the occurrence and the shape of the hysteresis loop depend on the pore size of the material.⁸ Materials with cylindrical pores < 4 nm do not show a hysteresis loop,⁹ as is the case of the MCM-41 material (36 Å). The narrow hysteresis loop for SBA-15 indicates a highly ordered material with cylindrical pore geometry, and a high degree of pore size uniformity.^{10,11} After the mesopores are completely filled with N_2 only the external surface of the material remains accessible for nitrogen adsorption, and so the region IV is associated with multilayer adsorption of N_2 on the external surface of the material. This region is almost flat and extended for the case of MCM-41, since the surface area of this material is high. At a relative pressure close to 1, the N_2 uptake by the sample increases again, and a small hysteresis loop evolves upon subsequent desorption, but only for MCM-41 (region V). This feature can be assigned to condensation of N_2 within the voids between MCM-41 particles.¹²

Figure IV.4 Nitrogen adsorption-desorption isotherm plot for calcined **MCM-41** mesoporous silica (a). Pore size distribution plots calculated from adsorption branch (b) and desorption branch (c) by BJH method.

The calculated pore size distribution plots for OMS materials accompany corresponding isotherms (Figures IV.3 – IV.5). A very narrow distribution, centered at ~ 28 Å is obtained for MCM-41. Almost the same results are obtained for adsorption and desorption data. A similar narrow distribution centered at ~ 78 Å (adsorption branch) and ~ 66 Å (desorption branch) is obtained for SBA-15. For Vycor glass a broad distribution with a maximum at ~ 62 Å is obtained from the adsorption branch, and a very narrow distribution centered at ~ 42 Å is obtained from the desorption branch. The Vycor case is typical for ink-bottle pores, when the distribution calculated from the desorption branch is artificially narrow.

The pore sizes used in this work were calculated from the desorption branches of the isotherms using the Barrett-Joyner-Halenda (BJH) method. It is well established that this theory is valid only for materials with pores > 4 nm and underestimates the diameter of smaller mesopores by approximately 1 nm.¹³ Since by the BET method the pore size calculated for MCM-41 gave a value (35.6 Å) close to those from the BJH method, the latter method was applied in all cases. The total pore volume was also calculated by applying the same method. The data are summarized in Table IV.2.

4.3.1.3 ^{29}Si MAS NMR

Figure IV.6 shows the ^{29}Si MAS NMR spectra of MCM-41 before and after calcination, and of calcined SBA-15. The ^{29}Si MAS spectrum of uncalcined MCM-41 reveals two distinct resonances at -109 ppm assigned as Q^4 , and at about -100 ppm assigned as Q^3 , with a weak resonance at about -89 ppm attributed to Q^2 . During

Figure IV.4 Nitrogen adsorption-desorption isotherm plot for **Vycor glass** (a).

Pore size distribution plots calculated from adsorption branch (b) and desorption branch (c) by BJH method.

Q^4 environments are formed at the expense of Q^3 and Q^2 , as shown in Figure IV.6. Both calcined MCM-41 and SBA-15 exhibit broad resonances (~ 1.35 kHz), much broader than those in the ^{29}Si MAS NMR spectrum of calcined ZSM-5 zeolite (~ 0.3 kHz). This is due to the fact that OMS are not crystalline molecular sieves as zeolites, and in terms of the local structure and bonding, OMS resemble amorphous rather than crystalline materials.¹²

To conclude, the hexagonal symmetry of the mesopores' arrays (space group $P6mm$) and the high degree of order in the synthesized OMS materials was confirmed by X-ray diffraction. The ^{29}Si MAS NMR revealed spectra characteristic of this type of materials. The pore structures in three materials have been characterized by the nitrogen adsorption technique. The commercial Vycor glass has a relatively small total pore volume comparing with the two other templates.

4.3.2 Characterization of the Cesium-Loaded Mesoporous Materials

Regarding Cs-loading of all prepared samples, the SBA-15 template needed the shortest synthesis time (from few days to a week), and the amount of adsorbed Cs vapour was very high (i.e. a filling factor of 1.55 was obtained for the highest Cs-loaded sample). This is not surprising, since SBA-15 has large pores with a narrow pore size distribution (type H1 hysteresis loop). The metal deposition inside the MCM-41 template was slow (several days for relatively low loadings - filling factor 0.4-0.6) and for this reason only two samples were prepared. The slow rate of metal deposition for MCM-41 can be explained by the presence of smaller pores of this material, and perhaps, by blocked pores with dense packing of the particles which are usually small. As a comparison, the absorption of the metal vapour on the surface of SBA-15 and Vycor templates was very

Figure IV.6 ^{29}Si MAS NMR spectra of SBA-15 and MCM-41 mesoporous silica materials

fast, complete only after a few hours as indicated by the blue coloration of the surface, yet for MCM-41 this coloration was observed only after waiting 24 h or even longer. As a result, the temperature for cesium deposition in SBA-15 was only 75 °C while for the other templates it was chosen to be 100 °C. For the Vycor template, the cesium deposition rate was faster than for MCM-41, but slower than for the SBA-15. The colour of the Cs-loaded mesoporous materials depended on the metal loading, the low-loaded samples were cream coloured and the highest loaded samples were dark blue (Cs/Vycor) or black (the highest loaded Cs/SBA-15 sample). The darker colour of the samples with the highest Cs-loadings is an indication of their possible metallic nature, similar to the highest loaded Cs/ZSM-5 sample.

As was mentioned in the Experimental section, porous Vycor glass was supplied in a tubular form. For most of the Cs-loading experiments this Vycor tube was ground into a fine powder. We were able, however, to prepare Cs-loaded samples using whole intact pieces of the Vycor tube (ca. 1 cm in length) (Table IV.1). When necessary precautions were taken, the tube kept its shape after Cs-loading. Such Cs-loaded Vycor tubes had very deep blue/dark blue colour, with the most intensive coloration at the surface of the tube declining towards the tube interior. The coloration pattern most likely reflects Cs diffusion gradients into the tube.

4.3.2.1 PXRD

The PXRD patterns of air exposed Cs/MCM-41 samples were less intense than for the starting materials and showed only the (100) reflection shifted to a higher diffraction angle as shown in Figure IV.7. In addition, they indicate some decrease in the unit cell

parameter caused by metal deposition, the unit cell parameter in the Cs-loaded MCM-41 sample being lower than in the starting material ($a = 3.7$ nm). The mentioned changes may suggest some loss of long-range order in the template upon Cs-loading. However, the presence of the main reflection suggests that the pore structure of MCM-41 material is likely preserved.

Figure IV.7 X-ray powder diffractions patterns for starting MCM-41 material and Cs-loaded MCM-41 sample immediately after air exposure

4.3.2.2 ^{133}Cs NMR

The ^{133}Cs NMR spectra recorded for all Cs-loaded mesoporous templates exhibit very broad and featureless signals in the diamagnetic region of the spectrum (at about 100-240 ppm) as shown in Figure IV.8 – IV.9. Similar types of resonances were observed in the ^{133}Cs spectra of Cs-loaded ZSM-5 samples. As in the latter case, for Cs-loaded mesoporous templates we can attribute these broad signals to Cs cations. When spectra are compared in the same spectral series (i.e. Cs-loaded SBA-15 samples, Figure IV.8) the increase and the broadening of the ^{133}Cs NMR signal with loading is noticeable (from about 11 kHz in the lowest loaded sample to about 19 kHz in the highest loaded one). At the same time, a shifting of the ^{133}Cs resonance from ~123 ppm to ~238 ppm is also observed. Despite our efforts to optimize the NMR conditions (i.e. different NMR probe used, varying the NMR parameters, applying spin-echo sequences etc.), not any other lines were found in the ^{133}Cs NMR spectra of the Cs-loaded mesoporous samples, including any possible lines in the Knight Shift region at 14,900 ppm from metallic species. The ^{133}Cs NMR spectrum taken with a broad sweep width (sweep width = 1.5 MHz) of Cs/Vycor sample is shown in Figure IV.9 (b). Only a single ^{133}Cs resonance can be seen at ~102 ppm, with the chemical shift which is characteristic for Cs^+ cations. Similar spectra over broad sweeps were recorded for all other Cs-loaded samples.

We may conclude, therefore, that NMR-detected cesium in our samples is only in cationic form; still we could not rule out the possible presence of Cs species other than diamagnetic, for example paramagnetic could also be present. It is also likely that the broadening of the ^{133}Cs lines with decreasing Cs particle sizes makes its impossible to

Figure IV.8 ^{133}Cs NMR spectra of Cs/SBA-15 samples.

Corresponding Cs filling factors are shown in brackets.

*The spectrum was recorded with shorter delay ($d1 = 0.5$ s)

Figure IV.9 ^{133}Cs NMR spectra of Cs-loaded: MCM-41 (a, narrow sweep width) and Vycor samples (b, wide sweep width).

detect NMR spectra below a critical Cs particle size. This critical value remains unknown, and more work should be done in order to find out the answer to this problem.

3.4 Conclusions and Future Work

Of all the templates used in our experiments, the SBA-15 material has reacted more readily and adsorbed the largest volume of Cs vapour. The dark blue and black colours of Cs-loaded Vycor and the highest Cs-loaded SBA-15 samples, respectively, are indications that possible insulator to metal transitions have occurred there upon Cs-loading. ^{133}Cs NMR spectroscopy was applied, and the only NMR-detected Cs-species were diamagnetic.

Future conductivity measurements would be useful in probing the metallic character of the highest Cs-loaded SBA-15 and Vycor samples. For all Cs-loaded SBA-15 and Vycor glass samples it would also be useful to measure the optical spectra in UV-visible range in order to find the bandgap energy for these materials.

We have demonstrated that the porous templates for alkali metal loading can be used not only as fine powders, but also as bigger pieces of any prefabricated shape, for example tubular, as for Vycor glass. Availability of such samples can be very useful when studying conductivity in these systems, or in possible future applications as "ready-to-use" parts of the electronic devices.

3.5 References

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