

Chapter 1

Introduction and Scope

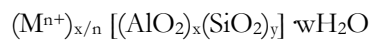
1.1. General introduction to zeolites

A molecular sieve is a material that has selective adsorption properties and can separate components of a mixture by differentiating in molecular size and shape.¹ Molecular sieves include clays, porous glasses, microporous charcoals, active carbons, etc, but one of the most used and studied groups of molecular sieves are zeolites.

Zeolites are crystalline aluminosilicates with fully cross-linked open framework structures made up of corner-sharing SiO_4 and AlO_4 tetrahedra, named primary structural units. The name "zeolite" comes from the Greek words *zeo* (to boil) and *lithos* (stone); and was used for the first time in 1756 by the Swedish mineralogist Cronstedt.²

In inorganic chemistry, aluminosilicates are materials composed of Si^{4+} and Al^{3+} . They are formed when some of the Si^{4+} in silicates are replaced by Al^{3+} . For each Si^{4+} ion replaced by an Al^{3+} , the charge is balanced by other positive ions such as Na^+ , K^+ or Ca^{2+} ions.

The structural formula of a zeolite is based on the crystallographic unit cell, represented by:



where M represents the exchangeable cation of valence n and M is generally a Group I or II cation, although other metal, non-metal and organic cations can also balance the negative charge created by the presence of Al in the structure. The Si/Al ratio of the zeolite is indicated by y/x, and w represents the water contained inside the discrete size cages and/or channels of zeolites.

In addition to Si⁴⁺ and Al³⁺, other elements can also be present in the zeolitic framework. They do not need to be isoelectronic with Si⁴⁺ or Al³⁺, but must be able to occupy framework sites.

Zeolites can be divided into natural zeolites like Chabazite, Faujasite or Mordenite, and synthetic zeolites like zeolite A, X and Y or ZSM-5. Natural zeolites have the advantage of their low economic cost while the second group, although they are more expensive, avoid the problem of impurities and changes in chemical composition, and thus enable their properties to be controlled better.

The structure of zeolites is based on an extensive three-dimensional framework in which the tetrahedral sites are linked by oxygen atoms. The result is a uniform microporous structure, which can be formed of channels and/or cavities.

In the zeolite structure, primary individual structural units are assembled into secondary building units called SBU's (Figure 1), by means of which the topology of all known molecular sieve framework types can be described.³ The final framework structure consists of assemblages of secondary units in space, the union of which gives rise to bigger pentasil (a) or sodalitic (b) like-structural

units (Figure 1). Finally, the expansion of these units in the three space directions generates the different zeolitic structures. Therefore, zeolites can be classified according to the framework symmetry as ZSM, FAU, MFI, etc following the rules described by the International Zeolite Association (IZA).

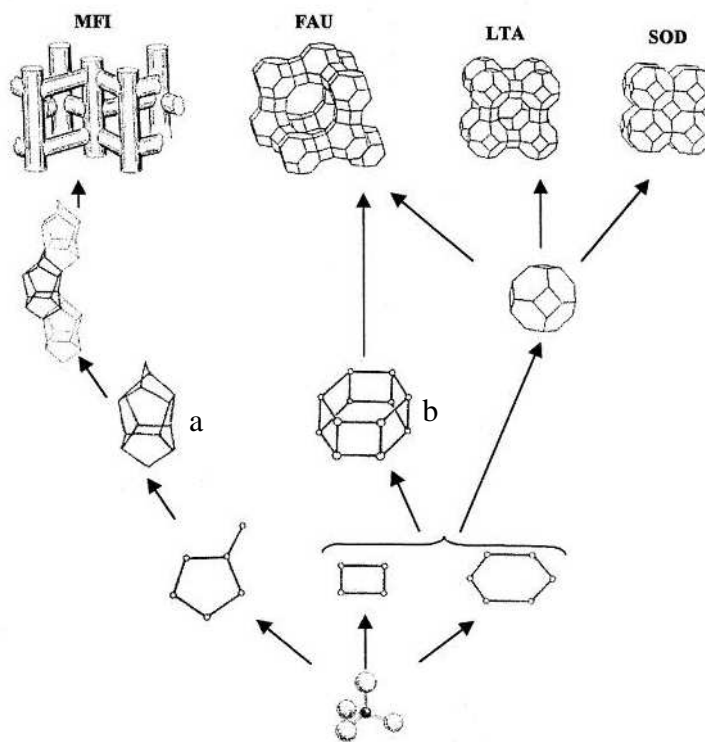


Figure 1. Structural genetics of zeolitic materials based in tetrahedra TO_4 ($T = Si$ or Al).

One of the fundamental characteristics of zeolites is the Si/Al ratio, because several properties such as thermal stability, acidity, and hydrophobic/hydrophilic character are related to it. According to the so-called Loewenstein rule,⁴ Al-O-Al linkages in zeolitic frameworks are forbidden. As a result, all aluminate tetrahedra must be linked to four silicate tetrahedra, but a silicate tetrahedron may have five different possible environments: Si(0Al,4Si), Si(1Al,3Si), Si(2Al,2Si), Si(3Al,1Si) and Si(4Al,0Si).

1.2. Properties and uses of zeolites

The properties of zeolites depend mainly on their cavity and/or channel-based structure, and on their Si/Al ratio. Zeolites with low Si/Al ratios have strongly polar anionic frameworks. Low Si/Al ratios are characteristic of sodalitic-type zeolites, with a hydrophilic character, while high Si/Al ratios are more common in more hydrophobic structures, type pentasil.

The cavities and/or channels that are such a feature of the porous structure of zeolites generate a high internal surface area. In some cases, this surface area can be even higher than one thousand square meters per gram.

Another important property is related to the compensating charge cations. The exchangeable cations, which are necessary to compensate the negative charge of the framework created by the isomorphous substitution of Si⁴⁺ for Al³⁺, originate strong local electrostatic fields. These cations are largely responsible for most of their properties. Thus, protonic exchanged zeolites are considered to be strong acid catalysts^{5,6} while alkali and alkaline earth metal exchanged zeolites can act as basic catalysts.⁷⁻⁹ These cations can also be largely responsible for the

separation of some binary mixtures¹⁰ or resin cation exchange processes for water softening.¹¹

In general, these materials present high thermal stabilities, which depend basically on their Si/Al composition. Thus, the thermal stability increases from about 700°C in low silica zeolites to 1300°C in silica molecular sieves.

Taking into account all these attractive properties, molecular sieves in general, and zeolites in particular, have found widespread industrial applications as highly selective adsorbents, ion exchangers and, most importantly, catalysts of exceptionally high activity and selectivity in a wide range of reactions.¹² Separation processes are another of these applications, one example of which is the separation of N₂ and O₂ from air, by exploiting the different polarities of the two molecules.¹² The amount of adsorbed gas or liquid depends on the pressure, the temperature and the nature of the adsorbate as well as on the kind of molecular sieve, since variations in the chemical composition of the sieve also affect adsorption.

However, in industry, the most important application of zeolites is as acid catalysts. Zeolites combine high acidity with shape selectivity, high surface area and high thermal stability and so they have been used to catalyse a variety of hydrocarbon reactions, such as cracking, hydrocracking, alkylation and isomerisation. In acid catalysis, the activity of zeolites is determined by the Brönsted and Lewis sites, mainly brought about by the presence of aluminium in the zeolite framework.

1.3. The N_2 and O_2 separation process

A separation process can be defined as a process in which a product mixture can be separated into two or more streams that are richer in one of the products.¹³ According to the second law of thermodynamics, this process is not thermodynamically favourable, and consequently, requires an energetic cost.

There are a considerable number of separation processes on both the industrial and the laboratory level.¹³

In the case of gas mixtures, nowadays two industrial processes are applied as a function of the nature of the gas mixture. The first is a cryogenic distillation consisting of liquefaction followed by distillation. The second process is separation by selective adsorption over an adsorbent of one or more components of the mixture in order to give a gas stream that is richer in the lesser adsorbed components.

The first process has the advantages of simplicity and scalability and it also yields high-purity products. But its main drawback is that it is an energy-intensive process. On the other hand, the adsorption processes have the advantages of low energetic cost and the possibility of regenerating the adsorbent but they are less scalable and the purity of the products obtained is lower.

For a long time, distillation played a dominant role in separation technology. However, nowadays both processes are applied in industry and, in general, the choice of whether to use adsorption processes will depend on the nature of the mixture components, on technical considerations and on economic factors.¹⁴

Gas separation by adsorption processes are based on the different strengths of interaction on a given sorbent for the constituents in the mixture.

Table 1 lists some industrial processes based on adsorption and the adsorbents used.

Table 1. Some processes based on adsorption phenomena

<i>Gas separation</i>	<i>Adsorbent used</i>
Normal paraffins/iso-paraffins, aromatics	Zeolite
N ₂ /O ₂	Zeolite
O ₂ /N ₂	Carbon molecular sieves
CO, CH ₄ , CO ₂ , N ₂ , Ar, NH ₃ / H ₂	Zeolites, activated carbon
Acetone/ vent streams	Activated carbon
C ₂ H ₄ / vent streams	Activated carbon
<i>Gas purification</i>	<i>Adsorbent used</i>
H ₂ O/ olefin-containing cracked gas, natural gas, air, synthesis gas, etc.	Silica, alumina, zeolite
CO ₂ /C ₂ H ₄ , natural gas, etc.	Zeolite
Organics/ vent streams	Activated carbon
Sulfur compounds/ natural gas, hydrogen, liquified petroleum gas(LPG), etc.	Zeolite
Solvents/air	Activated carbon
Odors/air	Activated carbon
NO _x /N ₂	Zeolite
SO ₂ /vent streams	Zeolite
Hg/chlor-alkali cell gas effluent	Zeolite

The production of high purity N₂ and O₂ from air components is one of the main separation processes applied in industry nowadays.

N₂ and O₂ separation from an air mixture has been applied since the beginnings of the 20th century using cryogenic distillation.¹⁵ At the end of the 1970s adsorption was first applied to this separation process. Distillation is still dominant in the chemical and petrochemical industries in spite of its higher economic cost, and separation by adsorption processes represents only 20% of the total N₂ and O₂ industrial separation processes at low and medium scale.

Because adsorption methods have developed quickly during the last three decades, various methods have been implemented on the industrial level: Vacuum Swing Adsorption (VSA),¹⁶ Fractionated Vacuum Swing Adsorption (FVSA),¹⁷ Pressure Swing Adsorption (PSA)¹⁸ and Temperature Swing Adsorption (TSA), although the PSA process with carbon molecular sieves as adsorbent is the most frequently used.

Since then, the PSA process has been improved,^{19,20} up to the point that it is now more economic than cryogenic distillation for productions lower than 30 metric tonnes per day.¹⁴ It is expected that new PSA processes using new adsorbents will continue to be developed in the near future. The trends are to use rapid PSA cycles for bulk gas separation and to develop novel adsorbed designs, like radial or rotatory beds.²¹

Throughout the world, oxygen is mainly used for steel making, ethylene oxide production and coal gasification. Substantial quantities of oxygen or oxygen-enriched air are also used to treat municipal waste.

The use of N₂ as an inert gas for blanketing started gaining ground in the 1950s and it was given fresh impetus when it started to be used for purging the tanks and vessels that store hydrocarbons and corrosive liquids in chemical industries. Similarly, in metal industries nitrogen blanketing is used to prevent metal oxidation during smelting. Another growing application for nitrogen is for maintaining dust-free and inert atmospheres in the electronic industry.

Selecting the appropriate sorbent is a key factor in obtaining a good separation. Some of the properties to be considered when choosing an adsorbent are: a) its adsorptive capacity, b) the adsorption selectivity to the desired component c) the heat of adsorption of the molecules on the adsorbent and d) the life of the adsorbent.²² As can be seen in Table 1, zeolites and carbon molecular sieves (CMS) can be used as adsorbents in the N₂ and O₂ separation process. The basis of the separation is different in the two cases.

For CMS, the separation is kinetic, governed by the different diffusion rates of N_2 and O_2 molecules inside the CMS, because O_2 molecules (3.46 \AA) are smaller than N_2 molecules (3.64 \AA).²³

The diffusion time constants expressed for oxygen and nitrogen in carbon molecular sieves, as calculated from sorption uptake, are reported to be $1.7 \cdot 10^{-4} \text{ s}^{-1}$ and $7.6 \cdot 10^{-6} \text{ s}^{-1}$, respectively. This difference explains why the adsorption rate of oxygen is faster (Figure 2) even though both gases have similar adsorption capacities on CMS (Figure 3).

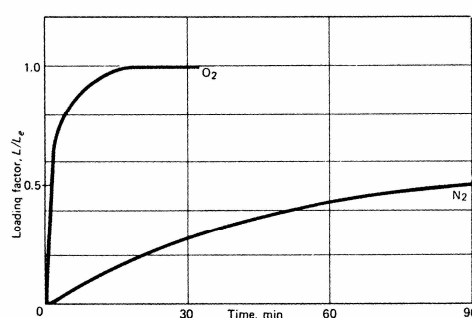


Figure 2. N_2 and O_2 adsorption rate on CMS

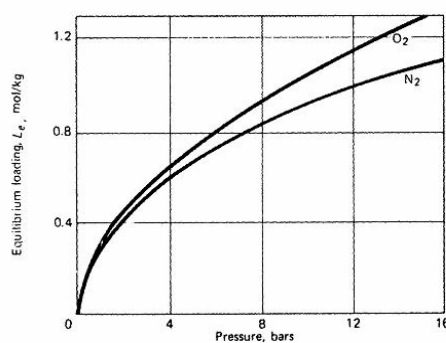


Figure 3. N_2 and O_2 adsorption isotherms on a CMS at room temperature

Several studies have described in detail hydrocarbon deposition in the mouth of sieves, as a step for obtaining a mouth diameter of 5Å . This enables the difference in rate diffusion between nitrogen and oxygen molecules to be increased, thus giving a good selectivity in the entrance of gases into the sieve.²⁴⁻²⁶

On zeolitic adsorbents, however, N_2 and O_2 separation is governed by the different adsorption strengths of the two gas molecules at equilibrium with the adsorbent.

With alkali and alkali earth zeolites, the interaction between the quadrupolar moment of molecules and the extraframework zeolite cations is electrostatic. Considering that the N_2 quadrupole moment (0.31 Å^3) is three times higher than that of O_2 (0.1 Å^3), the electrostatic interaction of N_2 molecules with cations will be stronger than with O_2 molecules.^{27,28}

The first patent was taken out in 1964 when McKee used X zeolite with Si/Al ratios compressed between 1.25 and 1.5 to separate N_2 and O_2 .²⁹ Several studies showed the influence of extraframework cations on the N_2 and O_2 adsorptive properties in zeolite X,^{29,30} and they pointed out the importance of the cation type on the adsorbent-adsorbate interaction (Table 2).

Table 2. Separation factor (α) depending on the cation.

Adsorbent	Exchange degree (%)	Separation factor (α)*
LiX	86	7.6
NaX	100	4.9
KX	100	2.2
RbX	56	3.5
CsX	50	1.5
Mg-X	56	2.4
Ca-X	96	3.5
Sr-X	96	3.6

* $\alpha = ([\text{adsorbed N}_2]/[\text{adsorbed O}_2] \times [\text{O}_2 \text{ gas}]/[\text{N}_2 \text{ gas}])$

Therefore, the authors concluded that in the same periodic group and for a given zeolitic structure, both adsorption selectivity and capacity follow the tendency $\text{Li}^+ \geq \text{Na}^+ \geq \text{K}^+ \geq \text{Rb}^+ \geq \text{Cs}^+$ (i. e. when the radius decreases, the electrostatic interaction between the cation and the gas molecules increases).

Later, Coe et al. in studies also made on zeolite X showed how the exchange degree influenced its N_2 and O_2 adsorption properties, in such a way that the N_2 and O_2 adsorption selectivity increases exponentially when the cation exchange degree increases in the most interacting cation.³¹

Other publications of this period showed the same tendency for other zeolitic structures like chabazite³² and zeolite A.³³

As well as alkali and alkali-earth zeolites, a block of zeolite-based adsorbents that contain silver cations as extraframework cations has emerged more recently. In this case the interaction is a π -complexation bond between the sorbent and the sorbate. Thus, authors such as Yang et al. used the principle that silver-containing zeolites can separate olefins from paraffins to separate N_2 and O_2 , since the electronic properties of this pair are similar to those of the olefin/paraffin pair.^{34,35} This kind of interaction consists of two contributions: a) the usual electron density donation from the antibonding π -orbitals of N_2 and O_2 molecules to the empty s-orbitals of silver cation Ag^+ and b) a backdonation electron density to the antibonding π -orbitals of the molecule to be bonded (N_2 and O_2).

The second contribution basically determines the separation selectivity, since the antibonding π -orbitals of the N_2 molecules are empty whereas they are partially occupied in the O_2 molecules, which does not favour the back-donation interaction.

The total substitution of earth and alkaline earth cations for Ag^+ cations in type X, LSX and Y zeolites leads to higher adsorption selectivities but also to higher

adsorption heats (parabolic isotherms), which are undesirable for the desorption process (Figure 4). Therefore, the introduction of fewer Ag^+ cations equilibrates the adsorption selectivity and the adsorption heat, and means that the adsorption properties are better than those of the corresponding zeolite without silver.^{34,35}

In this kind of silver zeolite adsorbents, a very important factor that must be controlled is the activation temperature, since the formation of Ag_m^{n+} clusters is an autoreduction process that involves framework oxygens and silver cations. The presence of these Ag_m^{n+} clusters modifies the adsorption properties of zeolites, and improves their adsorption properties when they are activated under proper conditions.³⁵ However, when the temperature is increased too much, the size of these clusters also increases, which means that the number of active centres decreases, and the N_2 adsorbed volume and the N_2/O_2 adsorption selectivity also decrease.

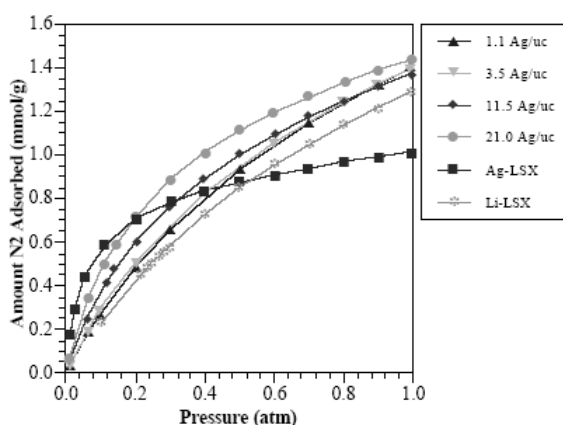


Figure 4. Adsorbed volume depending on the Ag^+ content in LSX zeolite

Parameters other than the nature of the extraframework cations can also influence the N_2 and O_2 adsorption properties: for example, the cation location, the charge on the cation and the presence of water molecules.

As far as the cation location in the zeolite structure is concerned,³⁶ for example, zeolite X has several possible positions, known as sites I, I', II, II' and III (see Figure 5). Thus, for cations with a high charge density, the preferred positions are sites I and I'. These positions are located in the six rings and hinder the access of the gas molecules, while positions II and III are more accessible for N_2 and O_2 . Thus, the N_2 and O_2 adsorption properties will depend on where the cations are located.

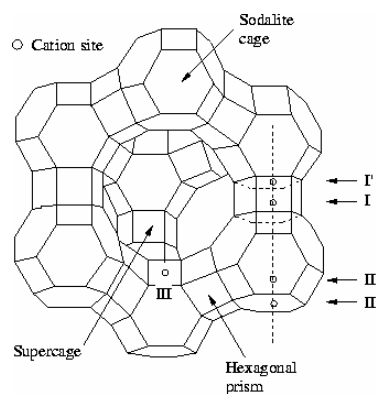


Figure 5. Cation location on an X zeolite

Several FTIR studies of low temperature N_2 adsorption³⁷ and H_2 adsorption³⁸ on alkali zeolites show the different adsorption properties of cations located in different positions on an X zeolite.

Theoretical studies have also been made using DFT (Density Functional Theory) calculations and they reveal the shielding effect that the framework oxygen atoms have on the zeolitic extraframework cations. The results show a decrease in the net cation charge, which therefore disfavours the interaction cation-adsorbate.³⁹⁻⁴¹

The last parameter found in the literature that influences the adsorption properties derives from the fact that zeolites with low Si/Al ratios have high affinity for polar molecules (for example, water molecules). The presence of water molecules inside the zeolite cavities seriously affects the adsorption properties as can be seen in the figure below (Figure 6).⁴²

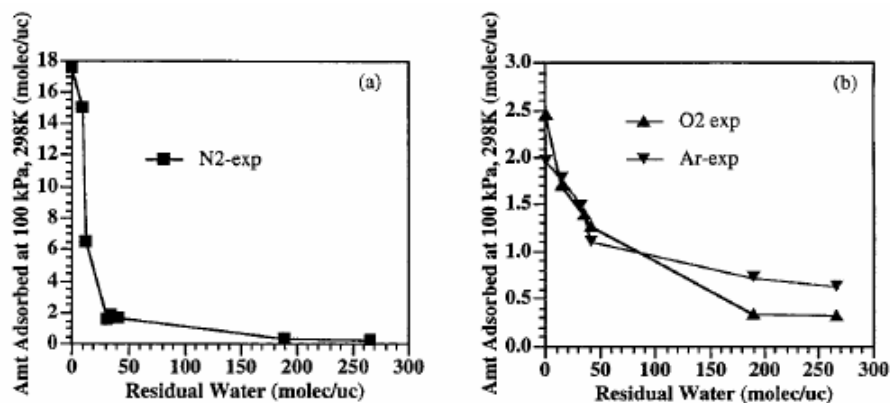
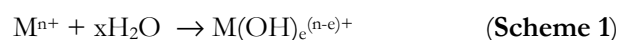


Figure 6. Theoretical and experimental amounts of adsorbed N₂ and O₂ on LiX at 100KPa and 298 K with respect to the amount of residual water

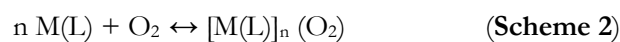
The presence of water is also a drawback in the sense that it favours the hydroxylation of cations (scheme 1), especially those with a higher positive charge.³¹ This hydrolysis quickly deactivates the sites for the adsorption

process because, for example, $\text{Ca}(\text{OH})^+$ species are inactive for nitrogen adsorption.



So far, then, all the examples have shown the use of zeolites as nitrogen adsorbents. However, the literature describes some cases in which zeolites are used as oxygen adsorbents like the CMS adsorbents described above. In some cases, depending on the cations used, zeolites are transformed in size discriminators. Several examples of this are zeolite A with Fe^{2+} cations,⁴³ Na-K-A zeolite,^{44,45} and more recently, Na-Ce-A zeolite.⁴⁶ The separation is based on the different diffusion rates of the adsorbates on the molecular sieve, since the presence of cations in certain positions can convert zeolites into molecular sieves that can discriminate between the N_2 and O_2 size.

Another new, but more unusual, class of oxygen selective adsorbents are those based on inorganic metal complexes, which are able to reversibly bind oxygen in solution or solid state (see scheme 2).^{47,48}



where $n = 1$ or 2

There are several metal complexes of such transition metals as Co^{II} , Fe^{II} , Mn^{II} , Cr^{II} and Cu^{II} , which are able to reversibly bind oxygen. However Co^{II} complexes are the ones that have been investigated most, because they can have an oxidation potential in a range that makes possible to donate some

electrons to oxygen molecules but not to such an extent that the metal is irreversibly oxidised.⁴⁹

The reversible uptake of oxygen by cobalt complexes in solution has been extensively studied.^{50,51} However, the synthesis of these complexes in the porous cavities of microporous solids of a zeolite and their use for air separation is an area of more recent interest.⁵² Therefore, further efforts are needed in order to improve the thermal stability of Co^{II} complexes in a zeolite matrix.

1.4. Acid catalysis

Nowadays acid catalysis is one of the most important fields in catalysis on both the industrial and the laboratory scale. In fact a wide variety of solid-acid catalysts are available.⁵³

Acidity in heterogeneous catalysis can be of two types: Brønsted acidity and Lewis acidity. For aluminosilicates, Brønsted acid sites are generated when the negative charge in the lattice is compensated by a proton. In general terms, a Brønsted acid site is considered to be able to protonate reactant molecules X according to the following scheme:



In aluminosilicates, OH groups can be divided into: a) structural or bridging groups [SiO(H)Al], b) terminal silanol groups [SiOH] and c) aluminium hydroxy groups (AlOH). The first group are considered the strongest Brønsted acid sites, whereas the second group are usually generated on the external surface or by the presence of structural defects, and the last group are basically generated by the presence of an aluminium extraframework phase. The main factors that affect acid strength are the Si/Al ratio and the nature of other M^{3+} species that can be present instead of Al^{3+} . Thus, the acidity increases in the same way as the sequence $Al^{3+} > Ga^{3+} > Fe^{3+} \gg B^{3+}$. There are several methods for achieving stronger acid sites in zeolites or more stable acid zeolites: steam procedures with mineral acids, which can extract M^{3+} atoms from the surface;⁵⁴⁻⁵⁷ the preparation of organic-functionalized zeolites⁵⁸; or the addition of cations such as La^{3+} easily hydrolyzable to form $[La_2(OH)_2]^{4+}$ or $La(OH)^{2+}$.⁵⁹

On the other hand, Lewis acid sites are generated by the presence of cationic species, which are deficient in the number of electrons. In the case of zeolites, the Lewis acidity is associated to the extraframework cations and to the aluminum species dislodged from the framework.

There are many more solid acid catalysts than basic and acid-basic catalysts because they have played an important role in the progress of the petroleum and petrochemical industry in the last 40 years.

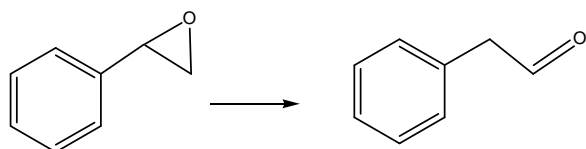
Of the 127 industrial catalytic processes described by Tanabe, 15 are catalogued as industrial isomerization processes.⁶⁰

One of the aims of catalysis nowadays is to find zeolite-based catalysts with very strong acid sites that enable some processes to be carried out at lower reaction temperatures or with smaller catalyst amounts.

1.4.1. Isomerisation of styrene oxide to phenylacetaldehyde

An extremely valuable method for introducing an aldehyde or ketone group into organic fine chemicals is to epoxidize olefins and subsequently to rearrange the oxiranes in the presence of acidic catalysts. Epoxide reactivity has been widely studied, because they are versatile intermediates in organic chemistry.^{61,62} Homogeneous catalysts such as phosphoric acid, BF_3 , FeCl_3 , ZnBr_2 and SnCl_4 , as well as heterogeneous catalysts such as SiO_2 , Al_2O_3 , ZnO , WO_3 , supported metals and various precipitated phosphates have been applied as isomerisation catalysts.

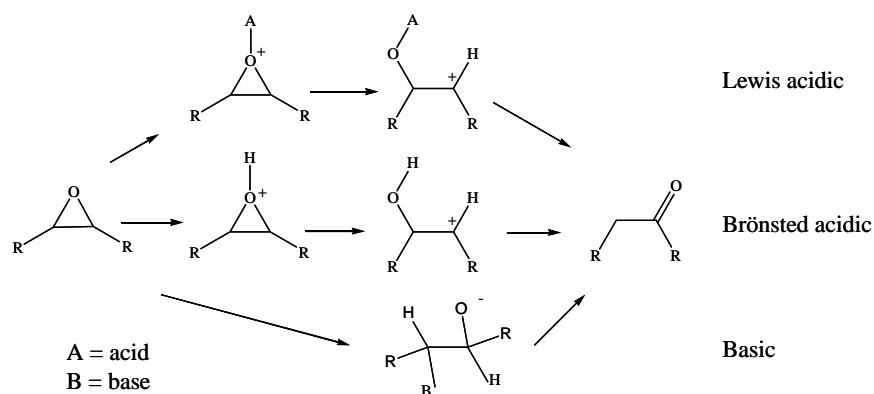
The isomerisation of styrene oxide to β -phenylacetaldehyde (scheme 4) is an acid catalysed reaction, which is used at industrial scale in fine chemistry to produce fragrances (this aldehyde gives a narcissus-like smell in floral perfumes), pharmaceuticals, insecticides, fungicides and herbicides.⁶³ Furthermore, phenylacetaldehyde is a valuable intermediate for producing more stable acetals with a honey aroma (glycolacetate), a sweet leaf odour (diethylacetate) or a tangy aroma (diphenylacetate).⁶⁴



Scheme 4. Isomerisation of styrene oxide to phenylacetaldehyde

Several solid catalysts have been used to study the rearrangement of various styrene oxides under gas and liquid conditions.^{65,66} The main products of the

styrene oxide isomerisation are the corresponding aldehyde and ketone depending on the properties of the catalyst.⁶⁷ This reaction can be catalysed by Brönsted acids (addition of a proton to the epoxide oxygen), by Lewis acids (coordination of the epoxide oxygen to a multivalent cation) and by bases,⁶⁸ although the first are much more active (see scheme 5).⁶⁴ On the whole, increasing the acidity increases the transformation of these oxides and favours the formation of the aldehyde.⁶⁹



Scheme 5. Acid/base catalysed epoxide rearrangement to carbonyl compounds

In the styrene oxide isomerisation reaction to phenylacetaldehyde, conventional catalysts often result in the formation of a mixture of ketones and aldehydes, and also by-products such as aldol condensation products, diols and dioethers. The high-weight molecules formed by aldol condensation are the first step in the formation of 1,3,5-triphenylbenzene and coke, which causes a fast deactivation of the catalysts, and limits their lifetime.⁶⁸

The homogeneous catalysts described above are used in industry although they are not as a rule regenerable, and generate voluminous and often corrosive

waste streams. On the other hand, heterogeneous catalysts like TiO_2 , $\text{P}_2\text{O}_5/\text{SiO}_2$, γ -alumina, $\text{B}_2\text{O}_3/\text{SiO}_2$ and bentonite have been used for this reaction. One of their advantages is that they can be used in gas-phase reactions and therefore continuous processes can be created with relatively little technical effort. However, they do have some drawbacks: incomplete conversion, formation of mixtures of ketones and aldehydes and the formation of aldol condensation products. The formation of these condensation products is the first step in the formation of coke and therefore limits the lifetime of these catalysts. Styrene oxide can also be rearranged in liquid-phase reactions using a titanium-silicalite catalyst (TS-1) with high conversion and high phenylacetaldehyde selectivity.⁷⁰ More recently, zeolites have been used in their H-form for this reaction. This use is of increasing interest because they can stabilize the α -carbocation intermediate and therefore suppress the formation of by-products.⁶⁴ Zeolites favour the selectivity to the aldehyde because of their shape selectivity, and they suppress reactions that form bulkier molecules (e.g. furans or aldol condensation products).⁶² Therefore, zeolites such as ZSM-5 hinder the formation of this aldol condensation because of the steric constraints of the framework. MFI zeolites, which have mild acidity, have also been considered to be good catalysts for this reaction.⁷¹

Nevertheless, these catalytic results depend on the solvent used. Smith et al.⁷² pointed out that, in the liquid-phase, rearranging styrene oxides over zeolites in their H-form gives poor results with protic solvents such as methanol, but yields to phenylacetaldehyde are higher when chlorinated aprotic solvents are used.

Therefore, the efficient suppression of side-products makes the zeolite-based catalytic system environmentally benign and economically superior when the appropriated conditions are used.

1.5. Scope of this thesis

One of the main objectives of this thesis is to design new zeolite-based adsorbents with properties favouring N₂ and O₂ separation. Once we had reviewed the bibliographic section, we saw that for a good separation, adsorbents needed to have a high number of cations, high accessibility to the adsorbates and minimum shielding of the cations. We also saw that in the presence Ag⁺ cations and Ag_mⁿ⁺ clusters, the N₂ and O₂ separation can improve. Therefore, we propose to use systems that allow us to improve the adsorption process from the point of view of the adsorbent. Our proposals are:

- to use Mordenite as the main material to achieve this first objective. Mordenite was chosen because of its high framework robustness, relatively high number of cations (low Si/Al ratio), its apparently high accessibility to the active sites and poor gas diffusion problems. These characteristics mean that it is likely to improve the adsorption properties and therefore lead to a better nitrogen and oxygen separation than the systems found in the literature. Also, other faujasite and sodalite type zeolites have been used through the thesis for comparison.
- to study the adsorption properties of several alkali-cation exchanged mordenites, with such cations as Li⁺ and Na⁺, which have a low q/r ratio.
- to introduce a certain number of fluorine atoms into the mordenite structure framework in order to achieve adsorbent systems in which cations are less shielded.
- to obtain systems with Ag_mⁿ⁺ clusters inside mordenite channels and to study their nitrogen and oxygen adsorption properties.

- to characterize all these materials with appropriate and commonly used characterization techniques, in an attempt to relate the characterization results to their adsorption behaviour, to understand this process better and, therefore, to make improvements.

The second main objective of this thesis is to apply some of these mordenite-based systems as catalysts in acid-catalysed isomerisation reactions. The synthesis and/or modification of zeolites with stronger acid sites is one of the goals of catalysis at the moment.⁷³ Specifically, we propose:

- to test the catalytic activity of NaMOR, HMOR and those mordenites modified with fluorine in an acid catalysed styrene oxide isomerisation reaction, since the presence of highly electronegative atoms, like fluorine atoms, in the structure should favour the obtention of stronger Brönsted acid sites.
- to use microwave heating instead of conventional heating for this reaction. The main advantages of this technique are that reaction rates can be accelerated, yields can be improved, and reaction pathways can be selectively activated or suppressed.

Finally, in order to better understand the behaviour and nature of active sites of our adsorption and/or catalytic systems, we propose to use FTIR spectroscopy through the adsorption/desorption behaviour of several molecules with different electronic properties and sizes (e. g. various nitriles and CO).

1.6. References

- ¹ McBain, J. W. *The Sorption of Gases and Vapors by Solids*, Rutledge and Sons: London, 1932, chapter 5, p. 17.
- ² Cronstedt, A. F. *Rön och beskrifning om en obekant bärg art, som kallas zeolites*. In Kongl. Vetenskaps, Acad. Handl. Stocholm., 1756, Vol. 17, p. 120.
- ³ Smart, L. Zeolites and related structures. In *Solid State Chemistry: An Introduction*, Moore, E. Ed.; Chapman and Hall: London, 1995; p. 238.
- ⁴ Loewenstein, W. *Am. Mineral.* **1954**, 39, 92.
- ⁵ Corma, A. *Chem. Rev.* **1997**, 97, 2373.
- ⁶ Martens, J. A.; Jacobs, P.A. Introduction to Acid Catalysis with Zeolites in Hydrocarbon Reactions. In *Introduction to Zeolite Science and Practice*, Van Bekkum, H.; Flanigen, E. M.; Jacobs, P. A.; Jansen, J. C. Eds., Elsevier: Amsterdam, NL, 2001, chapter 14, p. 633.
- ⁷ Weitkamp, J.; Hunger, M.; Rymsa, U. *Micropor. Mesopor. Mater.* **2001**, 48, 255.
- ⁸ Davis, R. J. *Catal.* **2003**, 216, 396.
- ⁹ Martra, G.; Ocule, R.; Marchese, L.; Centi, G.; Coluccia, S. *Catal. Today* **2002**, 73, 83.
- ¹⁰ Yang, R. T. *Adsorbents: Fundamentals and Applications*, John Wiley and Sons: New Jersey, 2003, chapter 7, p. 157.
- ¹¹ Townsend, R. P.; Coker E. N. Ion exchange in zeolites. In *Introduction to zeolite science and practice*, van Bekkum, H.; Flanigen, E. M.; Jacobs, P. A.; Jansen, J. C. Eds.; Elsevier: Amsterdam, NL, 2001., chapter 11, p. 467.
- ¹² Breck, D. W. *Zeolite Molecular Sieves: Structure, Chemistry and Use*, John Wiley: London, 1974.

- ¹³ King, C. J. *Separation Processes*, Brown, J. V.; Eichberg, M.; Eds., Mc Graw-Hill Chemical Engineering Series: New York, 1981.
- ¹⁴ Yang, R. T. *Gas Separation by Adsorption Processes*, Butterworth: Boston, 1987 reprinted by Imperial College Press, London and World Scientific Publishing Co.: River Edge, N. J., 1997.
- ¹⁵ Isalski, W. H. *Separation of Gases*, Clarendon Pr.: Oxford, 1989.
- ¹⁶ Sicar, S.; Zondlo, J. W. *U.S. Patent* 4012429, 1977.
- ¹⁷ Sicar, S. *U.S. Patent* 5084075, 1992.
- ¹⁸ Knoblauch, K.; Heimbach, H.; Harder, B. *U.S. Patent* 4548799, 1985.
- ¹⁹ Kim, J. N.; Chue, K. T.; Cho, S. H. *Sep. Sci. Technol.* **1995**, 30(3), 347.
- ²⁰ Rege, S. U.; Yang, R. T. *Ind. Eng. Chem. Res.* **1997**, 36, 5358.
- ²¹ Sicar, S. *Adsorpt. Sci. Techn.* **2001**, 19 (5), 347.
- ²² Ruthven, D. M., *Principles of adsorption and adsorption processes*, John Wiley and Sons: New York, 1984, chapter 1, p. 1.
- ²³ Coe, C. G. Structural Effects on the Adsorptive Properties of Molecular Sieves for Air Separation. In *Access in Nanoporous Materials, Proceedings of a Symposium on Access in Nanoporous Materials*. East Lansing, Michigan, 1995, p. 213.
- ²⁴ Cabrera, A. L.; Amor, J. N. *U.S. Patent* 5071450, 1991.
- ²⁵ Gaffey, T. R.; Farris, T. S.; Cabrera, A. L.; Amor, J. N. *U.S. Patent* 5098880, 1992.
- ²⁶ Amor, J. N.; Braymer, T. A.; Farris, T. S.; Gaffey, T. R. *U.S. Patent* 5086033, 1992.
- ²⁷ Drain, L.E. *Trans. Faraday Soc.* **1953**, 49, 650.
- ²⁸ Kington, G. L.; Macleod, A.C. *Trans. Faraday Soc.* **1959**, 55, 1799.

- ²⁹ McKee, D. W.; Buffalo, N.Y. *U.S. Patent 3140932*, 1964.
- ³⁰ McKee, D. W.; Buffalo, N.Y. *U.S. Patent 3140933*, 1964.
- ³¹ Coe, C. G.; Kuznicki, S. M. *U.S. Patent 4481018*, 1984.
- ³² Coe, C.G.; Gaffney, T. R.; Srinivasan, R. S. *U.S. Patent 4925460*, 1990.
- ³³ Chao, C. C.; Sherman, J. D.; Mullhaupt, J. T.; Bolinger, C. M. *U.S. Patent 5174979*, 1992.
- ³⁴ Yang, R. T.; Chen, Y. D.; Peck, J.D.; Chen, N. *Ind. Eng. Chem. Res.* **1996**, 35, 3093.
- ³⁵ Hutson, N. D.; Reisener, B. A.; Yang, R. T.; Toby, B. H. *Chem. Mater.* **2000**, 12, 3020.
- ³⁶ Jasra, R. V.; Choudary, N. V.; Bhat, S. G. T. *Ind. Eng. Chem. Res.* **1996**, 35, 4221.
- ³⁷ Smudde, G. H.; Slager, J. R.; Coe, C. G.; McDougall, J. E.; Weigel, S. J. *Appl. Spectrosc.* **1995**, 49 (12), 1747.
- ³⁸ Kazansky, V. B.; Bülow, M.; Tichomirova, E. *Adsorption* **2001**, 7, 291.
- ³⁹ Pápai, I.; Goursot, A.; Fajula, F.; Plee, D.; Weber, J. *J. Phys. Chem.* **1995**, 99, 12925.
- ⁴⁰ Goursot, A.; Vasilyev, V.; Arbuznikov, A. *J. Phys. Chem. B* **1997**, 101, 6420.
- ⁴¹ Jale, S. R.; Bülow, M.; Fitch, F.R.; Perelman, N.; Shen, D. *J. Phys. Chem. B* **2000**, 104, 5272.
- ⁴² Hutson, N. D.; Zajic, S. C.; Yang, R. T. *Ind. Eng. Chem. Res.* **2000**, 39, 1775.
- ⁴³ Izumi, J. *EP Patent 40935*, 1981.
- ⁴⁴ Oka, N.; Izumi, J.; Suzuki, M. *Adsorption* **2000**, 6, 149.
- ⁴⁵ Izumi, J.; Suzuki, M. *Adsorption* **2001**, 7, 27.

- ⁴⁶ Jayaraman, A.; Yang, R. T.; Cho, S. H.; Bhat, T. S. G.; Choudary, V. N. *Adsorption* **2002**, 8, 271.
- ⁴⁷ Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, 79, 139.
- ⁴⁸ Li, G. Q.; Govind, R. *Ind. Eng. Chem. Res.* **1994**, 33, 755.
- ⁴⁹ Vogt, J. R.; Lester, H.; Faigenbaum, H. M.; Wiberley, S. E. *Chem. Rev.* **1963**, 63, 269.
- ⁵⁰ Howe, R. F.; Lundsford, J. H. *J. Phys Chem.* **1975**, 79, 1836.
- ⁵¹ Taylor, R. J.; Drago, R. S.; George, G. E. *J. Am. Chem. Soc.* **1989**, 111, 6610.
- ⁵² Hutson, N. D.; Yang, R. T. *Ind. Eng. Chem. Res.* **2000**, 39, 2252.
- ⁵³ Campanati, M.; Vaccari, A. Solid-acid Catalysts-General. In *Fine Chemicals through Heterogeneous Catalysis*, Sheldon, R. A.; Van Bekkum, H. Eds.; Wiley-VCH: Germany, 2001, p. 61.
- ⁵⁴ J. Scherzer, ACS Symp Ser. 48, 157, 1984.
- ⁵⁵ Lukyanov, D. B. *Zeolites* **1991**, 11, 325.
- ⁵⁶ Van Bokhoven, J. A.; Tromp, M.; Koningsberger, D. C.; Miller, J. T.; Pieterse, J. A. Z.; Lercher, J. A.; Williams, B. A.; Kung, H. H. *J. Catal.* **2001**, 202, 129.
- ⁵⁷ Peixoto, D. P. B.; Cabral de Menezes, S. M.; Pais da Silva, M. I. *Mater.Lett.* **2003**, 57, 3933.
- ⁵⁸ Jones, C. W.; Tsuji, K.; Davis, M. E. *Nature* **1998** 393, 52.
- ⁵⁹ Carvajal, R.; Chu, P. J.; Lunsford, J. H. *J.Catal.* **1990**, 125, 123.
- ⁶⁰ Tanabe, K.; Hölderich, W. F. *Appl. Catal. A- Gen.* **1999**, 181, 399.
- ⁶¹ Ruiz-Hitzky, E.; Casal, B.; *J. Catal.* **1985**, 92, 291
- ⁶² Neri, C.; Buonomo, F. *US Patent* 4609765, 1986.

- ⁶³ Hölderich, W. H.; Barsnick, U.; Rearrangement of Epoxides. In *Fine Chemicals through Heterogeneous Catalysis*, Sheldon, S. A; Van Bekkum, H.; Eds.; Wiley-VCH: Germany, 2001, p. 217.
- ⁶⁴ Hoelderich, W. F.; Laufer, M. C. Zeolites and "Non Zeolitic" Molecular Sieves in the Synthesis of Fragrances and Flavours. In *Zeolites for Cleaner Technologies*, Guisnet, M.; Gilson, J. P.; Eds.; Imperial College Press: London, Catalytic Science Series, Vol 3, 2002, p. 301.
- ⁶⁵ Hölderich, W.H. *US Patent* 4990684, 1989.
- ⁶⁶ Taramasso, M.; Pergo, G.; Notari, B. *US Patent* 4410501, 1983.
- ⁶⁷ Arata, K.; Tanabe, K. *Catal. Rev. Sci. Eng.* **1983**, 25, 365.
- ⁶⁸ Kochkar, H.; Clacens, J. M.; Figueras, F. *Catal. Lett.* **2002**, 78, 91
- ⁶⁹ Molnár, I. Bucsi, M. Bartók, G. Resofski, G. Gáti, J. *Catal.* **1991**, 129, 303.
- ⁷⁰ Serrano, D. P.; Ugina, M. A.; Ovejero, G.; Grieken, R.V.; Camacho, M. *Micro. Mater.* **1995**, 4, 273.
- ⁷¹ Hölderich, W. F.; Goetz, N.; *Proceedings from the 9th international zeolite conference, Montreal, 1992*; Ballmoos, R. V.; Higgins, J. B.; Treacy, M. M. J. Eds.; Butterworth-Heinemann: USA, 1993, p. 309.
- ⁷² Smith, K.; Al-Shamali, M.; *Proceedings from the 12th International Conference on Zeolites, Baltimore, 1999*; Treacy, M. M. J.; Marcus, B. K.; Bisher M. E.; Higgins, J. B; Eds.; Material Research Society: USA, 1999, vol. 3, p. 228.
- ⁷³ Corma, A. J. *Catal.* **2003**, 216, 298.

