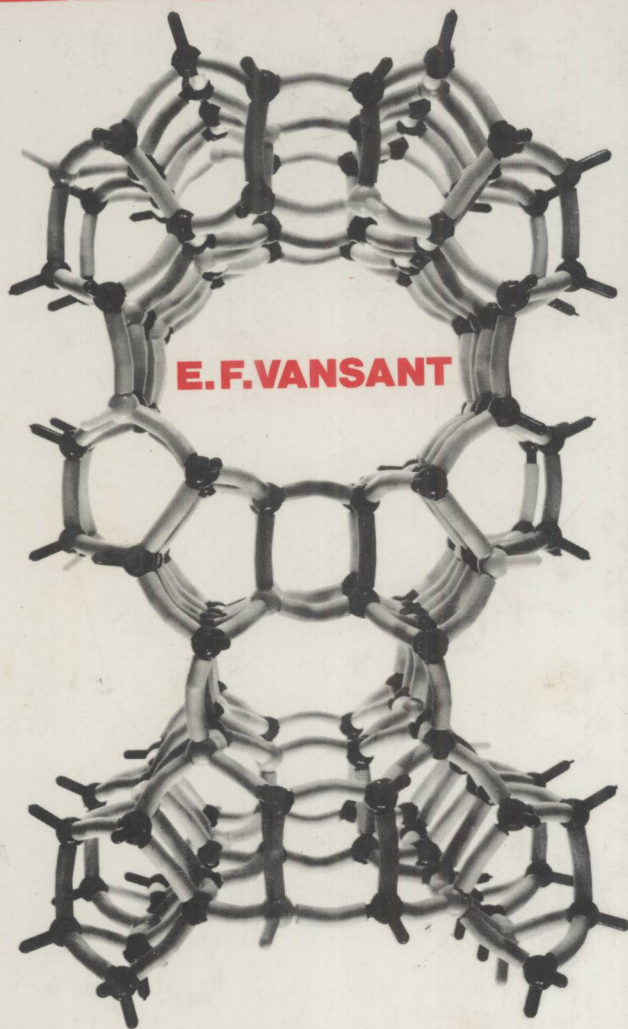


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PORE SIZE ENGINEERING IN **ZEOLITES**



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PORE SIZE ENGINEERING IN ZEOLITES



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PREFACE

Zeolite science and technology continue to develop in a rapid way. The use of zeolites has been explored in many scientific disciplines: modern inorganic and organic chemistry, physical chemistry, mineralogy, etc. and in all types of chemical engineering process technology. The wide variety of applications includes separation and recovery of gases, liquids and ions, catalysis (isomerization, alkylation, hydrogenation, cracking, etc. reactions) and ion exchange.

The main purpose of this book is to give a review of the different modification techniques that can be applied to vary in a controlled way the porosity of zeolites and related materials.

As D.E.W. Vaughan stated in *Zeolites: Facts, Figures, Future, Part A*, the pores in zeolites range from 0.22 nm for the silica polymorphs tridymite and cristobalite to about 1 nm for VPI-5, in terms of molecular accessibility from He to triethylbenzene. Crystallographically, the diffusion pathways increase in discrete steps from 6-rings to 8-rings, 10-rings, 12-rings, 12-rings and 18-rings. However, an important influence can be observed from the configuration of the rings, the localization and number of exchangeable cations and the increasing vibrational amplitudes of the structures with temperature or the chemical modification of the zeolite framework, so that the effective ring diameters can be changed in a continuous way from <0.2 nm to 1.5 nm.

In order to tune the zeolitic pore system in a controlled way, various modification techniques will be discussed, such as: (a) a modification by a cation exchange process; (b) a modification by a preadsorption of polar molecules, and (c) a modification of the zeolitic framework. Depending on the modification method, both the molecular sieving and selectivity of zeolites can be altered in a controlled way, which is an important tool in the separation, encapsulation and catalyst technology.

In the last decade, pore size engineering in zeolites and related materials (sepiolite, montmorillonite, silica, alumina, etc.) was extensively studied in the Laboratory of Inorganic Chemistry at the University of Antwerp (U.I.A.) in order to tune the sorbent specificities of various zeolites and to increase the shape and product selectivity of zeolitic catalysts. Therefore, the author wishes to thank his research team, namely Dr G. Peeters, Dr A. Thys, Dr J. Philippaerts, Dr Y. Yan, Dr P. De Hulsters

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E.F. Vansant

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CONTENTS



PREFACE	ix
ACKNOWLEDGEMENT	xi
Chapter 1 INTRODUCTION	1
1.1 Generalities	1
1.2 Zeolitic architecture	2
Chapter 2 PORE SIZE ENGINEERING IN ZEOLITES	5
2.1 Modification by a cation exchange process	5
2.2 Modification by preadsorption of polar molecules	8
2.3 Modification of the zeolitic framework	9
2.3.1 Pore size modification by crystallographic changes	11
2.3.2 Internal and external modification of the zeolite structure	11
2.3.2.1 Silanation	11
2.3.2.2 Disilanation	20
2.3.2.3 Boranation	60
2.3.2.4 Implantation of boron-nitrogen compounds	74
2.3.2.5 Modification by inorganic acids and their salts	86
2.3.3 External surface modification of the zeolite crystals	99

Chapter 3 APPLICATIONS	102
3.2 Encapsulation of gases in zeolites	102
3.2 Separation of gases by modified zeolites	113
3.2.1 Pore size engineering by modifying the mordenite pore system	114
3.2.2 Separation of gas-mixtures on a modified H-mordenite	120
CONCLUDING REMARKS	128
APPENDIX: Description of the equipment	129
A.1 On laboratory scale	129
A.2 On pre-pilot scale	132
REFERENCES	138
INDEX	141

Chapter 1

INTRODUCTION

Zeolites, which have a cage-like structure of precise geometry with pores of uniform shape throughout the entire crystal, are molecular sieves that can be used for separating gas mixtures by molecular sieving effects or selective adsorption and for shape-selective catalytic reactions.

1.1. Generalities

The zeolites constitute a particular group of tectosilicates, which are formed in nature by hydrothermal reactions and are often combined in their paragenesis with postmagmatic minerals. They are discovered and named in 1756 by Baron Cronstedt, a Swedish mineralogist. In 1840, Damour observed that the zeolite crystals were reversibly dehydrated without any change in the external crystal form (1). However, the ability of these materials to selectively adsorb molecules other than water was not reported until 1932. McBain (2) was the first who used the term 'molecular sieves' for the zeolite minerals, to explain the structural properties of these minerals by which they admit or reject adsorbates on the basis of the molecular size. By the early 1930s X-ray diffraction studies were revealing the zeolites to be crystalline materials having within each crystal a system of precisely arrayed cavities and pores.

Following the discovery of these natural zeolites, Barrer was the first to synthesize identical synthetic forms (3). By 1953, more than 30 distinct pure zeolite species had been prepared. The discovery of synthetic zeolites resulted in a wide variety of scientific and industrial investigations. Since their development and introduction to industry in 1954 by the Union Carbide

Corporation, these unique adsorbents have been used commercially in many systems for drying and purifying liquids and gases. In addition, zeolites have made possible the development of large-scale separation processes used to recover normal paraffins from branched-chain and cyclic hydrocarbons. When properly modified, zeolites also have catalytic properties which in commercial applications are producing significant process improvements over conventional catalyst systems (4).

Generally, a zeolite can be defined as a crystalline aluminosilicate, with a tetrahedral framework structure, enclosing cavities occupied by cations and water molecules, both of which have enough freedom of movement to permit cation exchange and reversible dehydration.

1.2. Zeolitic architecture

The growing drive to new zeolite-like materials reflects the importance of improving the performance of zeolites as molecular sieves or catalysts. The structural architecture is the source of the ability of zeolites to separate mixtures of molecules, in both gas and liquid phases, on the basis of their effective sizes (5). Moreover, zeolites have very special practical advantages over the traditional catalysts because they will admit only certain reactant molecules and this can be potentially tailored to produce selected products (shape-selective catalysts). A matching of size, shape and orientation of the reactant and product molecules to the geometry of the zeolitic network controls the catalysed reaction.

At present some 50 naturally occurring zeolite species have been recorded and their structures determined. In addition, more than 120 synthetic species with no known natural counterparts have been reported in literature.

In order to improve the performance of zeolites as molecular sieves or catalysts, several modification techniques were developed to vary in a

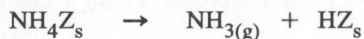
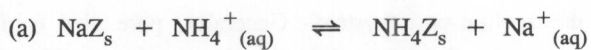
controlled way the zeolitic pore system. Generally, pore size engineering in zeolites can be the result of: (a) a modification by a cation exchange process, (b) a modification by a preadsorption of polar molecules or (c) a modification of the zeolitic framework.

The zeolitic pore size can be altered, in a controlled way, by changing the exchangeable cations so that the cation population and/or a resiting of cations, which are normally located near the pore openings, are responsible for a variation in the zeolitic pore structure. Another method for changing the molecular sieving effect of a zeolite is by preadsorption of polar molecules because of a change in the diffusion by clustering the polar molecules around the exchangeable cations in the zeolite channels. Furthermore, pore size engineering in zeolites can be achieved by a modification of the zeolitic framework. Indeed, (a) crystallographic changes by a thermal treatment, (b) an internal and external structural modification by implantation of additional atom groups, or (c) an external surface modification of the zeolite crystal (coating process) can produce important changes in the molecular sieve behaviour of zeolites.

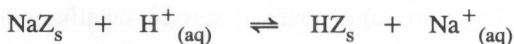
Using these modification methods, both the molecular sieving and the adsorption selectivity of zeolites can be altered in a controlled way, which is an important tool in separation and encapsulation technology.

The internal and external structural modification in zeolites by the implantation of additional atom groups is the result of a chemical reaction of the modifying agents with structural hydroxyl groups or hydration water. This means that the activity of the zeolite for these modifications is based upon the creation of zeolitic hydroxyls or the presence of water molecules in the zeolite pore structure.

The structural hydroxyls are usually formed either by (a) an ammonium procedure or (b) a polyvalent cation exchange followed by a calcination step (6).



Also, the protonated zeolites can be made by a direct exchange with mineral acids.



Furthermore, adsorbed water molecules can act as active centres for the modifying agents, resulting in the formation of amorphous phases in the zeolitic channels or cavities.

Depending on the geometry of the zeolitic framework, number of active reaction sites, type and concentration of the modifying agent and reaction conditions (temperature, time, procedure, etc.) the zeolitic pore system can be altered in a controlled way.

Chapter 2

PORE SIZE ENGINEERING IN ZEOLITES

Pore size engineering in zeolites can be the result of a

- modification by cation exchange process
- modification by a preadsorption of polar molecules
- modification of the zeolitic framework.

2.1 Modification by a cation exchange process (7-8)

Changing the exchangeable cations in a zeolite may effectively enlarge the pore openings by diminishing the cation diameter, population and/or a resiting of cations which are normally located near these openings. In the zeolite A, divalent ion exchange opens the aperture to full diameter, whereas exchange with a larger univalent ion diminishes the aperture size. Figure 1a shows the effect of the potassium exchange for sodium on the sieving properties of zeolite A. The pore size reduction does not occur gradually with increasing extent of exchange but rather suddenly at a level of about 25% potassium exchange. Also, an increase in the adsorption can be observed by a calcium exchange in NaA and again it does not occur in a linear fashion but rather abruptly (Figure 1b). Similar effects are exhibited by the zeolites mordenite, chabazite, zeolite X and offretite.

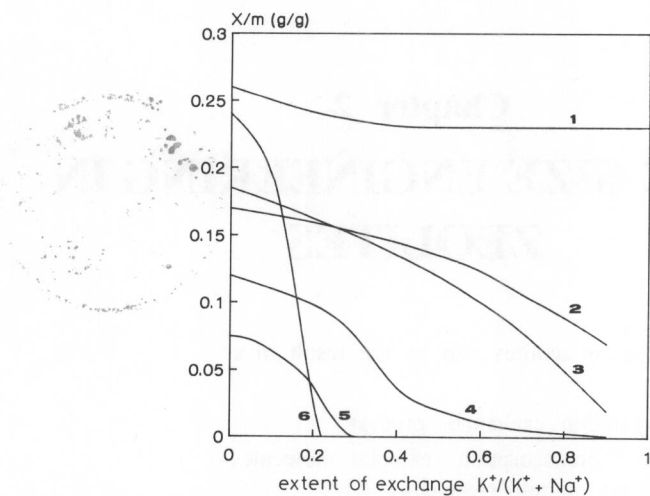


Figure 1a Effect of potassium exchange for sodium on the sieving properties of zeolite A: (1) water at 600 Pa, 298 K; (2) methanol at 533 Pa, 298 K; (3) carbon dioxide at 93.31 kPa, 298 K; (4) ethylene at 93.31 kPa, 298 K; (5) ethane at 93.31 kPa, 298 K; (6) oxygen at 93.31 kPa, 90 K

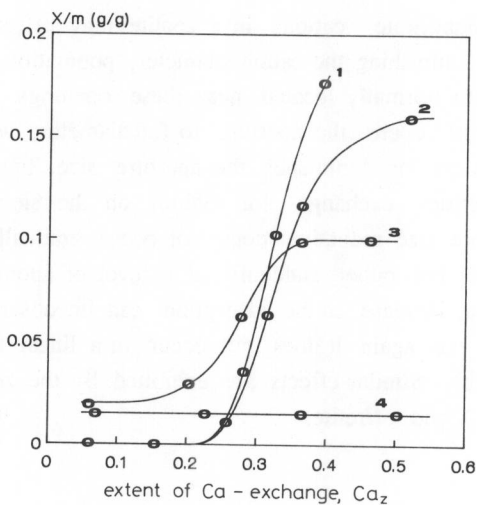


Figure 1b Effect of calcium exchange for sodium on the sieving properties of zeolite A: (1) nitrogen, 2 kPa, 77 K; (2) n-heptane, 6 kPa, 298 K; (3) propane, 33.33 kPa, 298 K; (4) isobutane, 53.32 kPa, 298 K

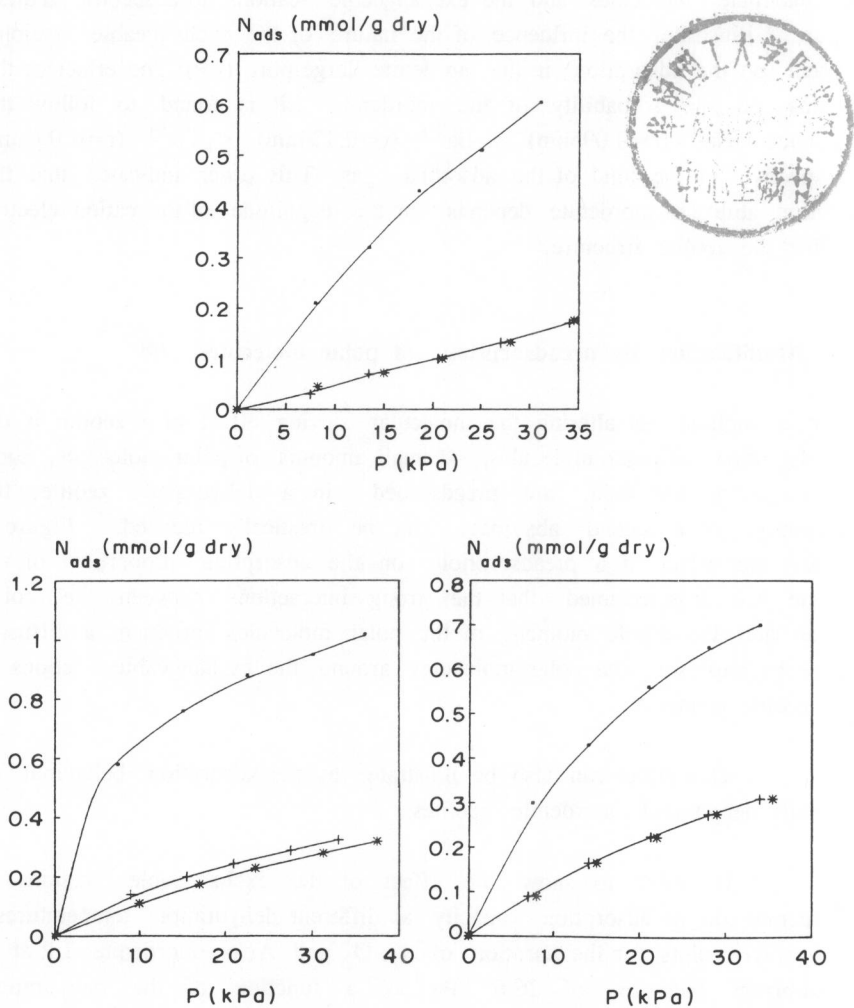


Figure 2 Adsorption isotherms of N_2 , O_2 and Ar at 273 K on dehydrated (723 K) Na-mordenite LP (a), Ca-mordenite LP (b) and Ba-mordenite LP (c) (N_2 , o; O_2 , +; Ar, *)

Besides the molecular sieving effects, the adsorption behaviour is also controlled by the adsorption selectivity, caused by the interaction between the adsorbate molecules and the exchangeable cations in a specific zeolite. Figure 2 illustrates the influence of the nature of the exchangeable cations present on the adsorption in the mordenite large-pore (LP). The effect of the cations on the sorbability of the mordenite LP is found to follow the sequence Na^+ ($r=0.095\text{nm}$) $<$ Ba^{2+} ($r=0.124\text{nm}$) $<$ Ca^{2+} ($r=0.092\text{nm}$) irrespective of the kind of the adsorbed gas. This order indicates that the sorption ability of mordenite depends on the magnitude of the cation electric field in the zeolite structure.

2.2 Modification by preadsorption of polar molecules (9)

Another method for altering the molecular sieving effect of a zeolite is the preadsorption of polar molecules. If small amounts of polar molecules, such as water or ammonia, are preadsorbed in a dehydrated zeolite, the adsorption of a second adsorbate can be drastically reduced. Figure 3 shows the effect of a preadsorption on the adsorptive properties of the zeolite A. It is assumed that the strong interactions between the zeolite cation and the dipole moment of the polar molecules produce a diffusion block by clustering the polar molecules around the exchangeable cations in the zeolite channels.

This effect can also be illustrated by the adsorption behaviour on partially dehydrated mordenite zeolites.

In order to show the effect of the exchangeable cations in mordenite on its adsorption capacity at different dehydration temperatures, comparative plots for the sorption of N_2 , O_2 and Ar on mordenite LP at an equilibrium pressure of 26.6 kPa as a function of the dehydration temperature are shown in Figure 4. These figures reveal that the adsorption capacity of the mordenites is largely dependent on both the dehydration temperature and the nature of exchangeable cation. Generally, in partially dehydrated mordenites (323-548 K) the adsorption capacity of the mordenite

for N_2 , O_2 and Ar decreases on changing the exchangeable cation according to the sequence $Na^+ > Ba^{2+} > Ca^{2+}$.

This behaviour can be explained by the interactions between the exchangeable cations and water molecules, influenced by the nature of the cations and the resulting electrical field in the mordenite framework.

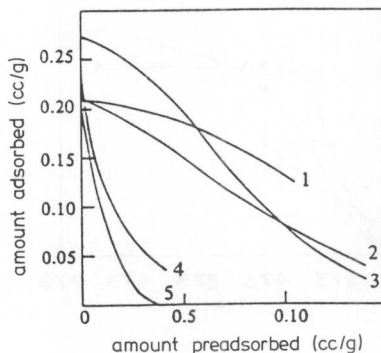


Figure 3 Effect of preadsorption on the adsorptive properties of zeolite A at 298 K: (1) *n*-butane on CaA with preadsorbed water; (2) *n*-butane on CaA with preadsorbed CH_3NH_2 ; (3) N_2 on CaA with preadsorbed CH_3NH_2 ; (4) O_2 on NaA with preadsorbed water; (5) O_2 on NaA with preadsorbed ammonia

2.3 Modification of the zeolitic framework

Pore size engineering in zeolites can also be achieved by a modification of the zeolitic framework resulting from:

- (1) crystallographic changes by a thermal treatment
- (2) internal and external structural modification by implantation of additional atom groups
- (3) external surface modification of the zeolite crystal (coating process).