

The pH-value and its importance for the crystallization of zeolites

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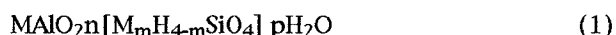
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1. Introduction

The alkalinity in a synthesis batch is one of the most important parameters for the control of the crystallization of zeolites. It determines their composition and is to a great extent responsible for the type of the crystallizing product. [1-13]

Generally, the crystallization proceeds via the solution phase so that the species of silicate, aluminate, and aluminosilicate in the solution are important for the crystallization mechanism. The pH-value of the solution is determined by the total alkali content and complicated buffering equilibria of the mentioned species. [14, 15] Zeolites are usually synthesized in the presence of an amorphous gel phase. The solubility of this gel phase also depends on the alkalinity. It assures the supersaturation for nucleation and growth processes.

The composition of synthesis batches can be described by the formula:



The "excess alkalinity" (m) in this formula is the difference between total alkalinity (MOH) and the alkali aluminate (MAIO_2) per mol of SiO_2 .

$$m = (\text{MOH} - \text{MAIO}_2)/\text{SiO}_2 \quad (2)$$

In systematic studies of the influence of the alkalinity on the product Si/Al-ratio, m is generally used as a critical parameter. [1-4]

A detailed discussion of the formation of zeolites has been given recently by Jansen [5] and by Feijen, et al. [6] In [7-12] thorough studies of the Si/Al ratio and the rate constant of linear growth in their dependence on m and n have been carried out for a series of zeolites.

The pH-value has been discussed in only a few papers in connection with the parameters of the crystallization. Generally, the different zeolite types crystallize within rather narrow ranges of pH. For faujasites, values between 12.3 and about 13.8 are observed. Robson has discussed procedures of a synthesis of NaY with Si/Al = 5 at pH = 11. [12] Between 11.3 and 12.7 mordenite usually crystallizes; at lower values ZSM-5 is obtained. [1,12] Donahoe and Liou have found a linear dependence of the Si/Al ratio of phillipsite and merlinoite in the pH range 13.3-13.7 in crystallization experiments from clear solutions of systems with an extremely high silica content. [13] In a series of papers, single values of the pH or pH changes before and after crystallization are reported. These differences are usually 1-2 units on the pH-scale.

Much work has been done in the analysis of the species in silicate and silico-aluminate solutions. Important results have been obtained from NMR. [14-16] A summary of this and other work can be found in the book of Engelhardt and Michel [16]. A thermodynamic analysis of these species has been undertaken by Guth, et al. [17, 18]

Generally, it was found that in the pH range of the crystallization of zeolites, the silicate is most probably present as $[\text{SiO}_2(\text{OH})_2]^{2-}$ or $[\text{SiO}(\text{OH})_3]^-$. Only comparatively low concentrations of higher condensed species are present at pH values above about 12.0. At lower pH the concentration of dimers and four-membered ring species increases. This range can be roughly identified with the crystallization region of the more siliceous zeolites with five-membered rings in their structure.

The aluminate is generally present in very low concentrations and is often described to be present as $[\text{Al}(\text{OH})_3\text{OSi}(\text{OH})_3]^-$. [16,18] A general survey of the pH-dependency of the hydrolysis

equilibria of cations has been given by Livage. [19] These data are important for syntheses with other anions present beside aluminate and silicate or aluminate and phosphate. [20]

For a more detailed investigation of the pH in zeolite synthesis, we have done thorough experiments on the connection of the pH with m and n and the Si/Al ratio of faujasites within a broad range of compositions.

2. Remarks on the Measurement of pH

Direct control of the pH during the crystallization would be desirable especially for industrial processes. However, this is difficult because zeolites crystallize at rather high pH-values. For a measurement of these values the PtH₂-electrode or the glass-electrode can be used.

With the PtH₂-electrode, in principle, very exact results can be obtained as has been shown by Lagerström [21] and Ingri [22] in very careful studies of the pH-dependency of the hydrolysis equilibria in silicate solutions. However, the PtH₂-electrode is not applicable for routine measurements for automatic control of a crystallizing batch in an industrial reactor.

For measurements with the glass electrode, it must be taken into account that this electrode responds to the concentration of the alkali ions as well as the H₃O⁺ present in the solution. This so-called "alkaline error" becomes important at pH > 11.0, depending on the sensitivity of the electrode material. Data for different electrode materials are demonstrated in [23]. The alkaline error increases with temperature. It is advisable to follow the suggestions of the manufacturer of the electrode carefully. At high pH the properties of the glass membrane of the electrode may change with time. An obvious alternative is to take samples from the crystallizing batch and to carry out the measurement of the pH at ambient temperature. This procedure is thoroughly described in the literature.

3. Preparation of the Reaction Mixtures and pH-Measurements

Generally, the batches for zeolite crystallization were prepared by mixing a silicate source and aluminate source and adjusting the excess alkalinity m with a suitable quantity of alkali hydroxide. For the present study the following sources were used:

Alumina source: 2.5 mole Al(OH)₃ (Merck, reinst) and 5 mole NaOH (Merck, reinst) in 1000 g solution.

Silica source: Water glass [Merck, sp. gr. = 1.37) or Silicic acid (Fällungskiesel säure, Merck) and NaOH to give 273.5 g SiO₂ in 1000 g solution.

The solutions were mixed at ambient temperature adding the silicate to the aluminate and the additional NaOH. Most of the experiments ($p = 400$) were carried out with a concentration of 50 g (AlO₂⁻ + n SiO₂) / 1000 g H₂O.

Regarding the general batch composition, MA₂O₂ n (M_mH_{4+m}SiO₄)pH₂O, the concentrations were adjusted to values of $n = 2.0 - 14.0$, $m = 0.3 - 2.5$ and $p = 400$. Some of the batches had lower water contents of $p = 195$ and $p = 260$.

After 2 hours homogenization an appropriate amount of nucleation gel was added to assure the crystallization of Y-zeolite, again stirred for half an hour and then the pH measured. The nucleation gel had a composition of NaAlO₂ 7.5 (Na_{2.0}H_{2.0}SiO₄) : 155 H₂O. [11] The batch was then heated to the crystallization temperature of 88°C.

After crystallization the samples were recovered and characterized as described in [7-11]. The Si/Al-ratios of the products were determined by the EDAX method in a Phillips SEM 515 and the EXAX-Analyzer PV 9900. The reaction mixtures had pH values between 12.4 and 14.1. From all mixtures faujasite crystallized. The pH measurements were done with WTW512 and a pH electrode belonging to this apparatus.

Reproducible results could be obtained according to the following procedure:

- Calibrate at pH = 7.0 using a commercial buffer solution (Riedel de Häen).
- Calibrate at pH = 13.0 using a commercial buffer solution (Riedel de Häen) and adjust the slope of

the instrument.

- Read the pH of the sample. Usually a time of about 5 minutes was sufficient to obtain a constant reading.

Between the different steps the electrode was cleaned with distilled water.

4. Discussion

In Fig. 1 the correlation of m and the measured pH values is demonstrated for the different Si/Al ratios n in the batch. The relation of both quantities can be fitted by a logarithmic relation which is equivalent to a titration curve of a weak acid with a strong base at the alkaline end. For $n < 5$, the curves for the different n are fairly close together. For higher n , deviations are observed which are not demonstrated in Fig. 1. These n are often applied for crystallization of NaY

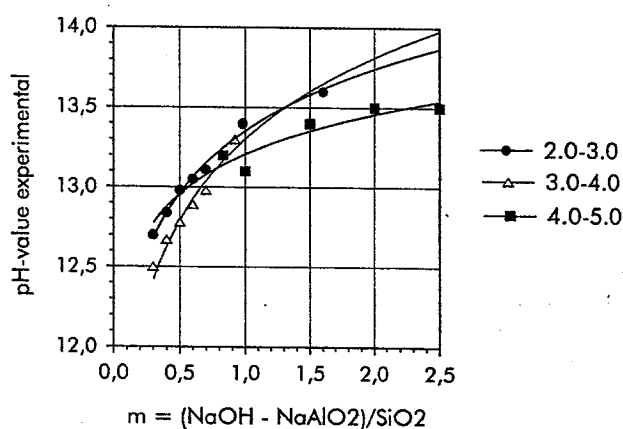


Figure 1: pH-value in the solution phase of batches with different Si/Al-ratios n in dependency of the excess alkalinity m . The data have been fitted to the function $\text{pH} = a + b \log (cm)$

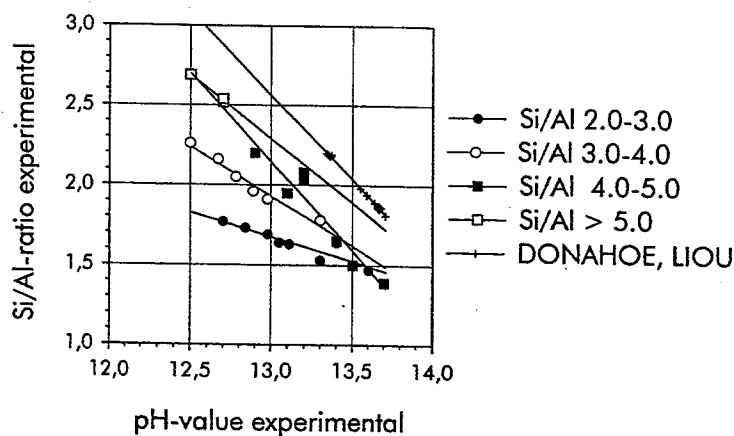


Figure 2: The Si/Al-ratio of the products in dependency of the pH - value in the solution phase for different Si/Al - ratios n in the batch

with high Si/Al ratios and also for crystallization of the more siliceous zeolites as, e.g., mordenite or ZSM-5. *m* is a more sensitive measure for the alkalinity than the pH value, apart from the advantage that it is given directly by the batch composition.

Fig. 2 shows the dependency of the Si/Al ratio of the products on the measured pH for different *n* in the batches. The crosses demonstrate results of crystallization experiment leading to phillipsite and merlinoite carried out by Donahue and Liou. [12]

The product Si/Al ratio decreases almost linearly with the pH if *n* is held constant. For increasing *n* the slope of these straight lines increases. The values for *n* = 6.0, 7.5 and 8.0 lie near the curve for *n* = 5.0. Formally, the curves for different *n* meet at Si/Al = 1.5 and about pH = 13.5.

Extrapolating the curve of *n* = 5 and 6.0, 7.5 and 8.0 in Fig. 2 to pH = 11.0 as it was suggested for the faujasite synthesis, a Si/Al ratio of about 4.0 can be obtained. [12]

Summarizing, Fig. 2 shows that for fixed *n* the Si/Al ratio of faujasites is a unique function of the pH value in the solution phase. However, for a prediction of the Si/Al ratio, the pH is not very suitable because exact pH values in the batches can be expected only after a time-consuming aging procedure.

Therefore, we have tried to find a direct relation between the parameters *n* and *m* of the batch composition and the final Si/Al ratio. [11] From extensive experiments, including studies of the concentrations of OH⁻ ions and the silicate in the solution phase [7-10], a simple relation could be derived which holds with great accuracy

$$\text{Si/Al} = 1 + b \frac{[\text{SiO}_2]_{\text{sol}}}{[\text{OH}^-]_{\text{sol}}} \quad (3)$$

using *b* = 2. Eq. 3 can be explained by a simple model of the formation of zeolites. [24]

Like the pH values, the concentrations are not very suitable for practical use in the prediction of the Si/Al ratios from the initial composition of the gel. With some obvious assumptions, Eq. 3 has been changed to an empirical relation containing only *n* and *m* as parameter with the constant *b* = 2.

$$\text{Si/Al} = \frac{(b + m)n}{(b + mn)} \quad (4)$$

In Fig. 3 a large number Si/Al product ratios from batches for different *m* with 1.4 < *n* < 14.0 are compared with values which have been calculated using Eq. 4.

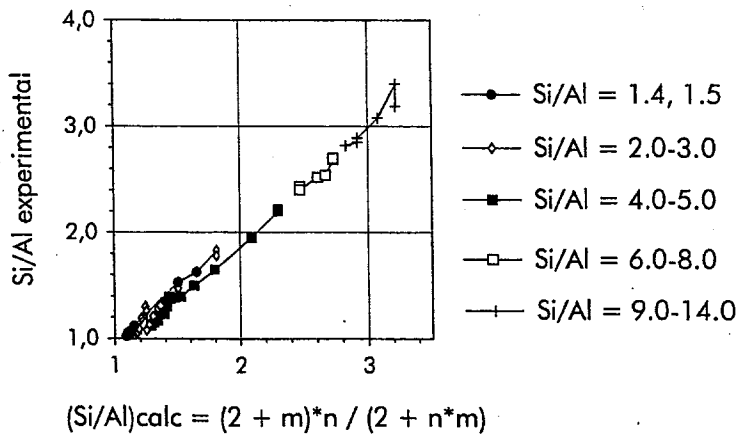


Figure 3. Si/Al - ratio of the product in dependency of $(2 + m)n / (2 + nm)$

It can be seen that the Si/Al ratio of the crystallizing product can be predicted by Eq. 4 over the whole range of n much more reliably than from the pH values of the solution phase.

From extensive studies of literature data, especially from [1-4] and the first edition of "Verified Syntheses," it could be seen that Eq. 4 can be used successfully for all zeolites with four- and six-membered rings in their structure. [24] As examples, ZSM-3, LTL, Rho and offretite shall be mentioned. Data for high silica zeolites like mordenite, ZSM-5 and Beta can be described by Eq. 4 using larger values of b . [25]

Systematic arguments for a choice of b for a special zeolite are, however, missing until now. Therefore, Eq. 4 must be regarded as an empirical relationship at the present stage of discussion.

The general role of the OH^- ion as a mineralizer can be partially replaced by fluoride leading to a variety of new syntheses at lower pH values. These syntheses are usually called "low alkaline syntheses" or "fluoride route." Most probably the F^- increases the solubility of the aluminate as could be shown, for example, in kinetic experiments of the crystallization of Y zeolites. [26]

5. Conclusions

The composition and the ranges of stability of the zeolitic products depend on the pH value, the alkalinity and the Si/Al ratio present in the batch. For practical use in the planning of syntheses, the pH value is rather complicated to handle. The empirical Eq. 4 proved to be suitable for a prediction of the product Si/Al ratio from the batch composition with the restrictions discussed for high silica zeolites. Eq. 4 includes the influence of the alkalinity m as well as the Si/Al ration n of the batch.

Predictions of the kind of the crystallizing zeolite and also of the effect of templates have not been possible thus far and remain a matter of experience.

6. References

- [1] R. M. Barrer, Hydrothermal Chemistry of Zeolites, Acad. Press, London, 1981
- [2] D. W. Breck, Zeolite Molecular Sieves, John Wiley & Sons, New York, London, Sydney, Toronto, 1974
- [3] Zeolite Synthesis, ACS Symposium Series 398, M. L. Occelli, H. Robson (eds.), Amer. Chem. Soc., Washington DC, 1989
- [4] Molecular Sieves, Vol. 1, M. L. Occelli, H. Robson (eds.), Van Nostrand Reinhold, New York, 1992
- [5] J. C. Jansen, in Introduction to Zeolite Science and Practice, H. van Bekkum, E. M. Flanigen, J. C. Jansen (eds.), Elsevier, Amsterdam, 1989, p. 77
- [6] E. J. P. Feijen, J. A. Martens, P. A. Jacobs, in Stud. Surf. Sci. Catal. 84A, J. Weitkamp, H. G. Karge, H. Pfeifer, W. Hölderich (eds.), Elsevier, Amsterdam, 1994, p. 3
- [7] H. Kacirek, H. Lechert, J. Phys. Chem. 79 (1975) 1589
- [8] H. Kacirek, H. Lechert, J. Phys. Chem. 79 (1975) 1291
- [9] H. Lechert, H. Kacirek, Zeolites 11 (1991) 720
- [10] H. Lechert, H. Kacirek, H. Weyda, in Molecular Sieves, M. L. Occelli, H. Robson, (eds.), Van Nostrand Reinhold, New York, 1992, p. 494
- [11] H. Lechert, P. Staelin, Ch. Kuntz, Zeolites 16 (1996) 149
- [12] H. E. Robson, in Zeolite Synthesis, ACS Symposium Series 398 M. L. Occelli, H. Robson (eds.), Amer. Chem. Soc., Washington DC, 1989, p. 436
- [13] R. J. Donahoe, J. G. Liou, Geochim. Cosmochim. Acta, 49 (1985) 2349
- [14] G. Harvey, L. S. Dent Glasser, in Zeolite Synthesis, ACS Symposium Series 398, M. L. Occelli, H. Robson (eds.), Amer. Chem. Soc., Washington DC, 1989, p. 49
- [15] A. T. Bell in Zeolite Synthesis, ACS Symposium Series 398 M. L. Occelli, H. Robson (eds.), Amer. Chem. Soc., Washington DC, 1989, p. 66
- [16] G. Engelhardt, D. Michel, High Resolution Solid State NMR of Zeolites, Wiley Sci. Publ., Chichester (1987)

- [17] J. L. Guth, P. Caullet, A. Seive, J. Patarin, F. Delprato, in *Guidelines for Mastering the Properties of Molecular Sieves*, D. Barthomeuf, et al (eds.), Plenum Press, New York, 1990, p. 69
- [18] P. Caullet, J. L. Guth, *Zeolite Synthesis*, ACS Symposium Series 398, M. L. Occelli, H. Robson (eds.), Amer. Chem. Soc., Washington DC, 1989, p. 83
- [19] J. Livage, in *Stud. Surf. Sci. Catal.* 85, J. C. Jansen, et al. (eds.), Elsevier, Amsterdam, 1994, p. 1
- [20] J. L. Guth, H. Kessler, R. Wey, in *New Development in Zeolite Science and Technology*, Y. Murakami, A. Lima, J. W. Ward (eds.), Kodansha, Elsevier, Amsterdam, 1986, p. 121
- [21] G. Lagerström. *Acta Chim. Scand.* 13 (1959) 722
- [22] N. Ingri, *Acta Chim. Scand.* 13 (1959) 775
- [23] D. A. Skoog, J. J. Leary, *Principles of Instrumental Analysis*, Saunders College Publishing, Harcourt Brace College Publishers (1992) 498
- [24] H. E. Robson, *Verified Syntheses of Zeolitic Materials*, Micropor. Mesopor. Materials 22, H. Robson (ed.), Elsevier, Amsterdam, 1998, p. 495
- [25] H. Lechert, *Micropor. Mesopor. Mat.*, submitted for publication
- [26] T. Lindner, H. Lechert, *Zeolites* 14 (1994) 582

Microwave technology in zeolite synthesis

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Microwaves have a wavelength between 1 millimeter and 1 meter which corresponds to frequencies of 300 GHz and 300 MHz. These frequencies are indicated in the electromagnetic wave spectrum in Fig. 1.

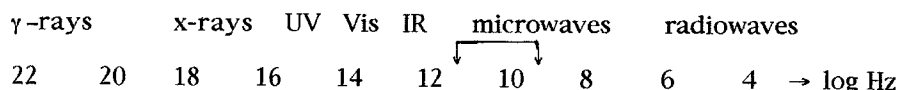


Fig. 1. Electromagnetic spectrum including microwave frequencies between infrared and radio frequencies.

As radar and telecommunication also use the microwave frequency band, only 4 specific frequencies are available for microwave heating. One of them, actually 2.45 GHz, is applied in household microwave ovens.

A microwave has an electric and a magnetic component which are in phase and perpendicular to each other in amplitude. Both wave components are perpendicular to the direction of travel. The heating effect in all types of materials that can interact with microwaves is mainly caused by the electric component. The total polarization (α_t) of the material based on the displacement of electrons, nuclei, permanent dipoles and quadrupoles and charges at interfaces is the sum of the following parameters:

$$\alpha_t = \alpha_e + \alpha_a + \alpha_d + \alpha_i : \text{in which}$$

α_e is the electronic polarization, displacement of electrons

α_a the atomic polarization, polarization of nuclei

α_d the dipolar polarization, polarization of permanent dipoles and quadrupoles

α_i is the interfacial polarization, polarization of charges at the interface

As both the electronic and atomic polarization operate at time scales that are smaller than required for microwave frequency field oscillations, these polarizations do not result in conversion of microwave into heat energy. The time-scale of the orientation of permanent dipoles is, however, comparable to the time scale of microwave oscillations. Thus when the amplitude of the electric field increases, the dipoles align themselves accordingly. Next, as the field amplitude decreases to zero intensity, the dipoles return to their random orientation. The change in orientation in both operations results in an energy conversion from electric into thermal energy. The interfacial polarization contributes to dielectric heating when conducting particles are suspended in a non-conducting phase. This effect is not substantial at microwave frequencies and thus results in a modest contribution to the heating. Conduction effects can also contribute to the dielectric heating. Since ions are charged, they accelerate in an electric field. Herein, the electromagnetic energy is converted in kinetic energy which is transferred to neighboring molecules resulting in unordered kinetic energy, actually heat.

The way the above mentioned materials react on microwaves is determined by their dielectric constants. The complex dielectric constant ϵ can be expressed as:

$$\epsilon = \epsilon' - i\epsilon'' ; \text{in which:}$$

ϵ' is the real component

ϵ'' is the imaginary component and

i is $\sqrt{-1}$, indicating a 90° phase shift between ϵ' and ϵ''

The real part, or relative permittivity, represents the degree to which an electric field may build up inside a material when exposed to an electric field. The imaginary part, or dielectric loss, is a measure of how much of that field will be converted into heat. The loss angle δ is the phase difference between the electric field and the polarization of the material. The loss angle as formulated below is referred to as the dissipation factor.

$$\tan \delta = \epsilon'' / \epsilon'$$

The dissipation factor, or $\tan \delta$ is a measure for the material's ability to transform electromagnetic energy into heat. The higher the dissipation factor, the better the transformation of microwave energy into heat. In Table 1, dissipation factors are given for relevant materials.

It is clear from Table 1 that water, and particularly water with a high Z-value, has a high ability to transform microwave energy into heat. Materials that are not heated by microwaves are, for example, glass and Teflon.

The dielectric constants of the materials also determine the penetration depth, which is defined as the depth into the material where the power is reduced to about 1/3rd of the original intensity.

The penetration depth is formulated as:

$$D_p \propto \lambda \sqrt{(\epsilon' / \epsilon'')}, \text{ in which:}$$

λ_o is the wavelength. Thus a material with a higher dissipation factor will have a lower penetration depth. The wavelength and hence the frequency also greatly influences the penetration depth. From the above it is clear that the sample size, the penetration depth and heating rate are coupled and can result in a homogeneous or heterogeneous heating of the material.

Thus in case a fast homogeneous heating is preferred, the material, for example a zeolite synthesis mixture, must have a relatively high dissipation factor, a high external surface and small volume. In the case of water this phase must have the form of a thin disk. At the same time one should take into account the microwave frequency applied. Higher frequencies will give smaller penetration depths. In case of extremely fast heating of zeolite syntheses mixtures, boiling point retardation might occur which results in small, but uncontrollable, explosions.

Table 1. Dissipation factors of relevant materials for zeolite synthesis

Material	$\tan \delta \times 10^4$	microwave frequency (GHz)	
		2.45	3.00
Teflon	2.1×10^{-4}	+	
Glass	4.0×10^{-4}	+	
Benzene	14×10^{-4}	+	
Ice	9.0×10^{-4}	+	
Water	0.157		+
0.1 M NaCl	0.240		+
0.5 M NaCl	0.625		+
methanol	0.640		+
ethanol	0.250		+
ethylene glycol	1.000		+

In general it is concluded that microwave effects, particularly for zeolite syntheses, are mainly recognized as converting microwave energy into heat. There are still many contributions in literature stating that microwaves do influence the reaction rate and product distribution on a molecular scale. However, microwave photons that have intrinsically a power not much larger than $\sim 10^{-5}$ eV at 2.45 GHz are too small and not applicable for molecular activation as compared to those encountered, for example, in UV photochemistry.

In zeolite syntheses heated with microwaves [1], the inexpensive set-up ($\sim \$1,500$), compared to commercially available ovens including autoclave equipment ($\sim \$30,000$), comprises of [2]:

- * An ordinary household microwave oven, one of the larger types to avoid local hot spots, with a controllable temperature setting in steps of 100 W up to 1000 W.
- * An autoclave, with walls of 1 cm in thickness, of Teflon, very low dissipation factor and thus transparent for microwaves (see Table 1), which is supplied with 1) a rupture disk that is connected to a hose to exhaust in case of malfunction, like boiling point retardation, the synthesis mixture and 2) a small hole through which the sleeve of the thermocouple goes into the synthesis solution/mixture.
- * A thermocouple in a sleeve and a recorder. The metal sleeve must be connected to earth and
- * Perforated metal shields in the form of cylinders that can be placed around the Teflon autoclave. This way microwave radiation at a setting of 100 W can be reduced to 20, 40, 60 or 80 W. Reduced and homogeneous radiation is needed to keep the temperature in the synthesis mixture constant after an initial heating up with hundreds of watts.

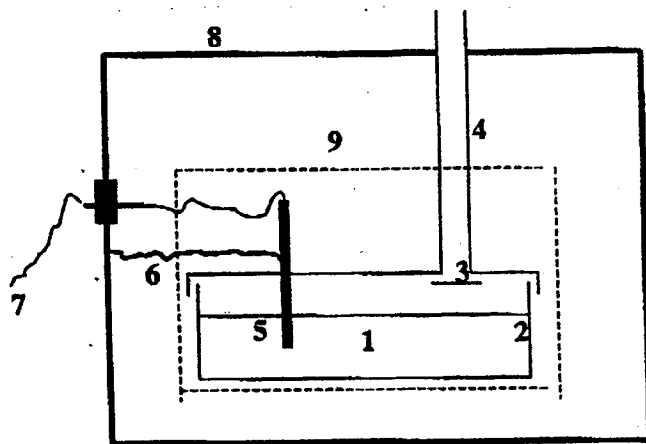


Figure 2. A general picture of the set-up in a household microwave oven to perform zeolite syntheses. [1,2]

- 1) zeolite synthesis mixture
- 2) 1 cm thick Teflon autoclave (up to 170°C)
- 3) rupture disk
- 4) exhaust channel
- 5) metal sleeve around thermocouple
- 6) connection of sleeve to earth
- 7) connection thermocouple to recorder
- 8) microwave oven
- 9) perforated metal shield around the autoclave.

The synthesis is carried out as follows: A regular, not viscous synthesis mixture of a zeolite is placed in the Teflon autoclave. The autoclave is closed and the thermocouple connected. An initial heating step is then applied which can be up to 1000 W. In this way the mixture is at the

projected synthesis temperature within tens of seconds. Subsequently the synthesis mixture must be kept at a constant temperature. The minimum oven setting is 100 W which is too high to compensate for the heat losses. Thus a lower power which is needed is accomplished by reducing the amount of radiation at 100 W. This is achieved with a screen of perforated metal installed around the autoclave. At a setting of 100 W and depending on the size of the holes in the perforation, only a few tens of watts will reach the autoclave and thus maintain the synthesis temperature at the projected value.

Crystallization times of zeolites were reduced to two minutes in particular cases. The main advantage of microwave heating compared to conventional heating is the high, even extremely high, up to 170°C in 20 seconds, controllable heating rates under homogeneous conditions, if the right configurational dimensions are applied.

One aspect, the formation of pure product, is of interest if microwaves are applied as heating technique for zeolite synthesis mixtures. The formation of pure product is related to the heat-up rate which is different in conventional heating compared to microwave heating as given in Tab. 2.

Table 2. Autoclaves of 0.5 liters were used. Stainless steel in a preheated hot air oven and Teflon in a microwave oven.

Mode of heating	projected synthesis temperature (°C)/time (minutes)	
Conventional	100 / 30	170 / 60
Microwave	100 / 0.2	170 / 0.3

If sources, in particular silicate and aluminate, are not extremely well mixed, and immediately after the mixing step exposed to rapid heat-up with microwaves, it is most likely that a mixed product distribution is observed. The product contains partly zeolite, silicate, aluminate and mixtures thereof, not yet converted into zeolite. [1] This is not observed a) after extensive stirring of the mixture at room temperature and subsequently immediate exposure to microwaves or b) after relatively short stirring and next placed in a preheated hot air oven. Apparently the nutrients need to be mixed on a molecular scale to obtain pure zeolite. This is achieved either through extremely long stirring after which the pure zeolite phase forms immediately when the projected synthesis temperature is rapidly reached with microwaves, or slowly heating up the synthesis mixture in a hot air oven which allows for further mixing upon heating up for a relatively long time before the projected synthesis temperature is reached.

References

- [1] P. M. Slangen, Thesis, TU-Delft (1998)
- [2] A. Arafat, Thesis, Helwan University, Cairo (1993)

Preparation of zeolite membranes

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1. Introduction

Separation processes are widely used in industry since the chemical conversions are often incomplete. Membrane technique is one of the most attractive separation methods because of its low cost and high selectivity. A membrane is an intervening phase acting as an active or passive barrier between phases adjacent to it under a driving force. Zeolitic membranes have gained considerable attention during the last decade. Detailed information can be found in the current literature and in several excellent reviews dealing with the subject of zeolitic membranes which have appeared over the last five years. [1-7]

The regularly structured pores and cages make the zeolites a unique material for designing thin films, coatings and membranes that can be utilized for a variety of purposes. Since the early 1990s, intensive research efforts have been underway to develop the synthesis and separation applications of zeolitic membranes. The specific properties of zeolite membranes which have attracted the attention of academic and applications scientists are: (i) long-term stability at high temperature, (ii) resistance to harsh environments, (iii) resistance of high pressure drops, (iv) inertness to microbiological degradations, and (v) easy cleanability and catalytic activation.

One of the most challenging problems in the preparation of zeolitic membranes is the complete exclusion of pinholes from the membranes, particularly under conditions of severe thermal cycling.

2. Preparation of zeolitic membranes

Zeolitic films and membranes are completely different from simple crystalline zeolite powders and their preparation requires new strategies. Methods which have been developed for the preparation of zeolite membranes are as follows:

2.1. Zeolite-filled polymeric membranes

One of the most direct methods of preparation of zeolite-containing membranes is to embed zeolite crystals in a matrix. [2,6] Sealing the gaps between zeolite crystals with a gas-tight matrix can provide a membrane configuration. The application of this method of membrane preparation, however, is limited. The clogging of zeolite pores by the matrix is a serious concern. Furthermore, gaps between binder and zeolite or a porosity in the matrix could introduce nonselective diffusion pathways.

2.2. Free-standing zeolite films

For molecular sieving applications a dense, pin-hole free zeolite film with limited thickness ($<1 \mu\text{m}$) would be an ideal configuration. Such films have been grown on temporary supports like Teflon and cellulose or at the interface between two phases. [2,6] This route for the preparation of zeolitic membranes is abandoned now because of the fragility of self-supported zeolite membranes.

2.3. Supported zeolite membranes

The most frequently used and probably the most promising seems to be the so-called composite membranes. This type of membrane is prepared by *in situ* hydrothermal synthesis. A relatively thin zeolite layer is crystallized on the surface or in the pores of a pre-shaped porous support. Among different types of inorganic materials, like ceramics, metal glasses, carbon used as

supports, porous alumina has been the most popular for these preparations. The nucleation and crystal growth on the support can be self-induced or induced by attachment of seed crystals on the substrate. The latter procedure requires a pretreatment of the support before the hydrothermal synthesis. [7]

Zeolite-containing composite membranes have been prepared by a vapor phase transport method called "dry synthesis." The zeolite layer in this case is prepared by conversion of a previously deposited silica or silica-alumina layer under joint action of vapors containing water and a structure-directing agent. [4]

The zeolite type prepared most often as a membrane is MFI, which is interesting for industrial applications with its suitable pore diameter, high thermal and chemical stability, easy synthesis and modification of the chemical composition. The experience gained in the preparation of MFI and other zeolitic membranes has shown that as well as the pin-holes there are many factors critical for the performance of the composite membranes. Some of them are (i) the adhesion of the zeolite layer on the support surface, (ii) the difference of the thermal expansion coefficients of support and zeolite, (iii) the orientation of zeolite crystals, (iv) the thickness of the zeolite layer, (v) the anisotropy of mass transport due to an anisotropic pore geometry, and (vi) the influence of crystal boundaries on the permeation properties.

3. Concluding remarks

The first zeolitic membranes are already on the market. Nevertheless, the control and fine tuning of the properties of the zeolite-containing membrane configurations remains a challenge. A common problem is that, despite the use of a pre-defined methodology, it is difficult to obtain membranes with consistent and predictable properties. However, the steeply increasing interest in this field suggests that zeolitic membranes with excellent separation properties will soon be available.

Lately the zeolitic membranes have attracted considerable attention for catalytic membrane reactors, where the zeolite phase can carry the dual function of separator and catalyst.

Other potential applications of zeolite film and layers include chemical sensors, zeolite electrodes, solar energy conversion, zeolite batteries, optical and data storage materials.

References

- [1] R. D. Noble, J. L. Falconer, *Catal. Today* 25 (1995) 209
- [2] T. Bein, *Chem. Mater.* 8 (1996) 1636
- [3] M. J. den Exter, J. C. Jansen, J. M van de Graaf, F. Kapteijn, J. A. Mouliun, H. van Bekkum, in *Stud. Surf. Sci. Catal.* 102, H. Chon, S. I. Woo, S.-E. Park (eds.), Elsevier, Amsterdam, 1996, p. 413
- [4] M. Matsukata, E. Kikuchi, *Bull. Chem. Soc. Jpn.* 70 (1997) 2341
- [5] J. Coronas, J. Santamaria, *Separation and Purification Methods* 28 (1999) 127
- [6] A. Tavoraro, E. Drioli, *Adv. Mater.* 11 (1999) 975
- [7] J. Caro, M. Noack, P. Kolsch, R. Schäfer, *Micropor. Mesopor. Mater* 38 (2000) 3

Safety considerations for zeolite synthesis

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In general, synthesis experiments are neither complex nor hazardous, and normal precautions which apply to any chemistry laboratory are adequate to protect both equipment and the investigator. But certain precautions should be called to the attention of the inexperienced operator.

1. Source Materials

Silica and alumina are inert in most forms, but ingestion of dust should be avoided. The alkoxides are skin irritants and should be handled with gloves and in a hood. Hydrofluoric acid (HF) is corrosive and skin contact or inhalation must be avoided. Likewise strong caustic is corrosive to skin and equipment. Gloves and a face mask are indicated, and the experiment should be done in a hood.

In one case an "overflow" occurred when an inexperienced student put all the powdered aluminum required for a synthesis into a caustic solution. The exothermic dissolution heated the solution, accelerated the dissolution autocatalytically, and resulted in "boil over." Obviously, if hydrogen is given off, danger of explosion exists. The use of aluminum wire, which dissolves more slowly, is suggested.

Organic templates cover a wide range of volatility and toxicity. In many cases these materials are quite rare and their toxicity may not be well defined. Some are known to be biologically active; in all cases the investigator should avoid skin contact or inhalation by using gloves and working in a hood.

In some cases, the potential exists for explosive decomposition of the template under crystallization condition. There is no good way to rule out this possibility, but a strong exotherm in the thermal analysis curve of the template indicates it should be treated with caution.

No preparations in this book use beryllium (Be) or thallium (Tl), but reports can be found in the literature of zeolite syntheses using these materials. Be and Tl are extremely toxic and should be used only by experts who thoroughly understand the necessary precautions.

2. Batch Preparation

The hazards of handling strongly caustic materials are increased when the solutions are hot. Gloves and face mask are still more important. Hydrolysis of the alkoxides produces heat; this may not be a problem in gram quantities but becomes so with scale-up. The alcohol produced is often removed by evaporation which can be a fire hazard. High-speed mixers can be splash hazards unless totally contained.

3. Crystallization

Zeolite crystallization is usually done at autogenous pressure at temperatures up to 200°C. With water present, this can mean pressure up to 15 atm. When organic templates are present, the pressure can be considerably higher. The manufacturer's specifications for the autoclave must be carefully considered. The liquid fill of the cold autoclave should not exceed 75%; the expansion of liquid water between 25 and 200°C is not negligible. Teflon loses its strength above 200°C. Teflon gaskets and liners must be treated with caution at these temperatures. When working in metal autoclaves without liners, stainless steel exposed to caustic mixtures undergoes caustic embrittlement at temperatures above 200°C, which can quickly ruin an autoclave. To clean autoclave liners between experiments, strong, hot mineral acids are usually used, for example HNO₃. It takes copious amounts of rinse water to remove all the acid.

Polypropylene jars may be used for crystallizations below 100°C. After extended use, they

tend to spring a leak, as the bottom begins to separate. Although there is no danger of the jars bursting at this temperature, organic vapors are liberated, so that the oven or bath used for heating should be placed under a hood or have otherwise good ventilation.

Sealed quartz tubes are often used as the crystallization container, especially for small quantities and high throughput. Also one can monitor progress of crystallization visually. Quartz is a poor conductor of heat, but prolonged heating for sealing can heat the synthesis batch to boiling if the neck is too short. After crystallization, the quartz reactor should be opened behind a shield to protect the operator in case of residual gas pressure.

Heat transfer by air, for example in an oven, is slow, and heating in a bath is preferred. As heating fluid, a polyglycol-type, which does not attack polypropylene, is recommended. A silicon oil leaches plasticizer out of the polypropylene thus making the jar brittle and subject to cracking. Glycerol can be used, but has a relatively high vapor pressure (vapors condense on all surfaces in the lab making them sticky) and should be used under a hood. The temperature controls of a liquid bath should have a high-temperature shut-off to prevent overheating, in case the temperature controller fails.

Combinations of organic templates and strong oxidizing agents such as chromate and permanganate are potential explosives, particularly in low-water conditions.

4. Product Recovery

Opening the reaction vessel after crystallization should be treated with caution. Even thoroughly cooled, residual gas pressure should be expected. Organic templates may degrade during the reaction; the products may be toxic and often cause a stench problem. The mother liquor after a templated synthesis may be a disposal problem. In most cases it should be collected for disposal as a hazardous chemical.

The synthesis batch may crust over during crystallization and retain residual gas pressure. When the crust is penetrated, the contents may constitute a splash / missile hazard.

A template not removed by washing is usually expelled by calcination. The template or its decomposition products are usually combustible and it is easy to start a fire. The heating equipment should be properly vented; if necessary nitrogen blanketed.

**With contributions by Kenneth Balkus, Günter Kühl and Robert Thompson*

Product characterization by x-ray powder diffraction

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1. Introduction

Different features of a powder diffraction pattern can be exploited in the characterization of a material (see Table 1). Of course, powder diffraction data is most commonly used as a "fingerprint" in the identification of a material, but the other information that can be gleaned from a diffraction pattern should not be forgotten. If possible, the diffraction experiment should be adapted to optimize that feature which provides the information desired.

Table 1. Information contained in a powder diffraction pattern

<u>Feature</u>	<u>Information</u>
Peak positions (2θ values)	Unit cell dimensions
Non-indexable lines	Presence of a crystalline impurity (or incorrect indexing)
Systematically absent reflections	Symmetry
Background	Presence (or absence) of amorphous material
Width of peaks	Crystallite (domain) size
	Stress / strain
	Stacking faults
Peak intensities	Crystal structure

Although there are a number of different powder diffractometer geometries on the market, each one with its positive and negative attributes, all have an X-ray source, a specimen holder and a detector, and almost all are capable of recording a respectable powder diffraction pattern. The difficulty arises when one wants to compare data from different instruments or even from the same instrument with different operators. It is not possible to go into detail in the space available here, but the basic considerations and a few common sources of error will be discussed. For more information, the reader is referred to the volume entitled "Modern Powder Diffraction" edited by Bish and Post [1] or to the article entitled "Practical Aspects of Powder Diffraction Data Analysis" by Baerlocher and McCusker [2].

2. Data Collection

2.1 Peak positions

If the pattern is to be indexed (Miller indices hkl assigned to each of the peaks and thereby the unit cell dimensions extracted from the pattern), it is essential that the peak positions be determined accurately. In this case, the instrument's 2θ scale needs to be carefully calibrated using a standard material such as the NIST silicon standard 640b. The sharper a peak, the better its 2θ value can be determined, so the diffractometer should also be adjusted to optimize resolution. As a guide, almost any laboratory instrument can be adjusted to give a full width at half maximum (FWHM) for the Si 111 reflection ($28.44^\circ 2\theta$ with $\text{CuK}\alpha_1$ radiation) of $0.10^\circ 2\theta$ or less. The measured 2θ values for the peaks in the standard material's pattern should agree with the literature values to within $0.01^\circ 2\theta$.

If the sample is off-center, this will affect the 2θ zeropoint correction, so ideally, the sample should be mixed with a small amount of the standard (that is, measured with an internal standard), so that the 2θ calibration can be done simultaneously. However, if care is taken in positioning of the sample, a 2θ calibration using an external standard is usually sufficient. In reflection mode,

thin samples are preferred for peak position determination, so effects of sample transparency can be eliminated.

2.2 Peak intensities

For indexing purposes, the intensities of the peaks are irrelevant, but for identification or for structure analysis, accurate relative intensities are essential. There are three commonly ignored factors which can severely affect the relative peak intensities: 1) sample thickness, 2) preferred orientation, and 3) divergence slit(s).

Bragg-Brentano reflection geometries require an "infinitely thick" sample. That is, it is assumed that the sample is thick enough that all the X-rays interact with the sample (by absorption or diffraction) before they reach the sample holder. In this way, the volume of sample effectively irradiated remains constant as 2θ changes. If this is not the case, the intensities must be adjusted for the transparency of the sample. In general, the relative intensities of the low angle reflections will be too large if the "infinite thickness" criterion is not met. For transmission geometries, on the other hand, the sample must be thin enough that the X-rays are not too strongly attenuated.

Most powder diffraction data analyses assume that the sample consists of millions of randomly oriented crystallites. If this is not the case, relative intensities will be distorted. For example, if the crystallites have a plate-like morphology, they are likely to lie flat. Assuming that the c -axis is parallel to the short dimension, crystallites aligned in the $00l$ diffraction condition will be overrepresented, and those in the hkl diffracting condition underrepresented. This will then lead to a bias in the relative intensities recorded. Various sample preparation techniques have been used to reduce preferred orientation (such as back or side loading of flatplate sample holders, mixing amorphous glass beads with the sample, or spray drying), but none is foolproof. Measurements in transmission mode with the sample loosely packed in a rotating capillary are less susceptible (but not immune) to this problem. An easy way to establish whether or not preferred orientation is present is to measure the diffraction pattern in both reflection and transmission mode. The two measured patterns should be comparable, and if their relative intensities differ significantly (in an hkl -dependent manner), there is probably preferred orientation present in the sample.

At low angles, the X-ray beam is spread over a larger surface of the specimen than it is at high angles. To ensure that the X-rays interact only with the sample (and not the edges of the specimen holder) a slit is inserted between the X-ray source and the sample to confine the beam to the sample (divergence slit). As the 2θ angle increases, this slit can be opened wider to allow more X-rays through and thereby increase the counting rate, but then the resulting data must be corrected for the increased volume of sample irradiated. The slit size can be varied during the measurement either continuously (using an automatic divergence slit) or manually (using a series of calibrated slits). For data comparison purposes, the data should then be transformed to constant sample volume (single constant slit) data. In many laboratories, data are recorded using a relatively wide single slit that is appropriate for higher angle data, but not for the lower 2θ values. In such a measurement, the relative intensities of the low angle peaks will appear to be too low, because only a part of the X-ray beam interacts with the sample.

3. Identification

In a zeolite laboratory, powder diffraction data are most commonly used to identify a newly synthesized material or to monitor the effects of a post-synthesis treatment. In both cases, the measured pattern is compared with an existing one, whether it be a pattern in the *Collection of Simulated XRD Powder Patterns for Zeolites* [3], the Powder Diffraction File (PDF) of the ICDD [4] or an inhouse data file. Such comparisons are not easy for zeolites, especially if the data collection or sample preparation conditions differ. A few practical considerations are presented briefly below.

- (1) Intensities are important for identification, so the data should be collected bearing the points discussed in the previous section in mind.
- (2) Data should be in the form of a constant volume measurement if the *Collection*, the PDF or any of the common databases is to be used in a search/match process.

- (3) Peak position information is often given in terms of d -values rather than 2θ values, because d -values are independent of the X-ray wavelength (λ) used. ($d = \lambda / 2 \sin\theta$)
- (4) The low angle lines are the ones most strongly affected by non-framework species (see Ref. [2] p. 418). In general, these lines are more intense in the calcined material than in the as synthesized form, and similar materials containing different cations or different organic species may have quite different relative intensities at low angles. However, the intensities of the higher angle reflections are generally dominated by the positions of the framework atoms, so these can be compared quite well.
- (5) Different synthesis conditions or different post-syntheses treatments can cause subtle distortions in a zeolite framework structure that can complicate identification. The symmetry may be reduced (and thereby produce many more peaks in the pattern), although the basic framework topology (connectivity) remains unchanged. In such a case, indexing the pattern to obtain the dimensions of the unit cell can facilitate the identification.

4. References

- [1] Modern Powder Diffraction, D. L. Bish, J. E. Post (eds.), Review in Mineralogy 20 (1989)
- [2] Ch. Baerlocher, L. B. McCusker, Stud. Surf. Sci. & Catal. 85 (1994) 391
- [3] M. M. J. Treacy, J. B. Higgins, R. von Ballmoos, "Collection of Simulated XRD Powder Patterns for Zeolites," Zeolites 16, 1996
- [4] PDF Database (Sets 1-44), Copyright 1994, International Centre for Diffraction Data, 12 Campus Blvd., Newtown Square, PA 19073-3273, USA

Determination of the elemental composition of zeolitic materials

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1. Introduction

The determination of the bulk elemental composition of zeolites is of importance in many aspects of zeolite synthesis, characterization and applications. This information is used to verify the synthesis formulations, the bulk silica/alumina ratio, the cation(s) concentration, degree of ion exchange, and the detection of contaminant elements (impurities, poisons). The elements of interest can be grouped into two broad categories, metals and non-metals. The latter commonly include sulfur, chlorine, carbon and nitrogen. Generally the results are reported on volatile free basis, thus the Loss on Ignition (LOI) at a specified temperature and time is also determined. The concentration of water is determined if the request is for the results to be based on anhydrous basis and volatile components other than water are present. The information herein is a brief review of the techniques and their characteristics as used for the determination of bulk elemental compositions of zeolites.

2. Determination of metals

The most common techniques for the determination of compositional metals are Inductively Coupled Plasma Emission Spectroscopy (ICP), Atomic Absorption Spectroscopy (AAS) and X-Ray Fluorescence Spectroscopy (XRF). Because these methods offer the benefit of reduced interferences and matrix effects, and have improved accuracy, precision and speed, the use of "classical wet chemistry" methods (for example, gravimetric silica, titrimetric or spectrophotometric alumina) has been greatly diminished.

ICP is probably the most widely used technique for the determination of the elemental composition of zeolites. It offers the capability for the simultaneous (or sequential) determination, with good sensitivity and precision, of most compositional matrix metals of interest, for example silicon, aluminum, phosphorous, titanium, and many others. Relative standard deviations of 1% can be routinely obtained for the major and minor compositional metals. In general, the sensitivity of ICP is better than that possible with conventional flame AAS for most refractory-like metals and phosphorus. However, flame AAS has somewhat better sensitivity for Group IA elements, including sodium and potassium, and relatively similar sensitivity for many metals of interest, such as calcium, magnesium and iron. Because the cesium emission lines are above 800 nm, conventional ICP instrumentation is incapable of its determination and AAS has to be utilized.

Wavelength dispersive X-Ray Fluorescence (XRF) is also used for the determination of the elemental composition of zeolitic materials. As compared to ICP/AAS, the benefits of XRF include the ability to determine some non-metals, conceptually simpler sample preparation and improved precision. Relative standard deviations of -0.1 to 0.2% are possible for samples introduced as glass discs. The disadvantages include poor sensitivity for light elements and sensitivity to changes in the matrix composition. This means that in many cases XRF can not perform the complete characterization. ICP/AAS has to be employed for some of the determinations, for example, lithium and low concentrations of sodium. Also, especially for best accuracy, changes in the matrix compositional elements require the use of matrix matched calibration standards and the use of mathematical models. Thus XRF has its greatest impact in a controlled, manufacturing environment, while in an R & D environment ICP/AAS is often the technique of choice.

3. Sample decomposition for ICP and AAS

Both conventional ICP and AAS require that the sample be introduced as a liquid, thus decomposition is necessary prior to analysis and similar preparation schemes apply for both techniques. There are two main approaches for sample dissolution in order to determine major and

minor compositional elements (including silicon). The sample can be solubilized by a fusion with lithium tetraborate (or a similar flux) followed by dissolution of the flux in dilute hydrochloric acid, or it can be digested with acid in a beaker.

a. Beaker digestion for ICP or AAS analysis

Although this approach is used widely and can produce good data, it has several areas of concern. The acid digestion may not completely solubilize binders, such as clay. Increasing the severity of the decomposition conditions (e.g., higher temperature) can generally ensure complete dissolution, but such a modified digestion may require elevated pressures in a Teflon lined bomb. The digestion requires the addition of hydrofluoric acid in order to solubilize the silicon, and because of the volatility of the resulting fluorides, special care must be taken to avoid the loss of silicon.

A more serious problem is the fact that fluoride will attack a conventional ICP sample transport system that contains quartz/glass components, thus necessitating the complexation of the fluoride. This can be accomplished utilizing boric acid, or a commercial complexing agent. In the author's experience these solutions mostly extend torch life, they do not completely eliminate attack on the quartz and thus accurate determination of silicon is not possible. Hydrofluoric acid resistant sample transport systems are available from instrument manufacturers. We have found these to be inadequate because the typical alumina sample delivery torch tube is attacked by fluoride thus contributing to increased aluminum and silicon (impurity in the alumina) backgrounds. Replacing the alumina tube with sapphire eliminates this problem, unless very high concentrations of fluoride are present. [1] A commercial sapphire torch tube is currently available from at least one manufacturer.

Typical AAS sample introduction systems are silica free and the fluoride containing solutions can be analyzed, but the precision for silicon and aluminum is generally inadequate. If the silicon is of no interest, these issues, except for completeness of dissolution, become irrelevant. In fact, for the determination of minor and trace metals, it is often desirable to volatilize the silica during sample decomposition, thus reducing the total dissolved solids.

b. Dissolution by Fusion for ICP or AAS analysis

It is the author's experience that sample dissolution by fusion results in better precision and accuracy than possible by a beaker digestion. Although other fluxes can be used, the author fuses the sample, in a platinum crucible, using a 15:1 ratio of lithium tetraborate to sample. The fusion can be accomplished using automated fusion devices, via a muffle furnace or air boosted natural gas burners. The resulting melt is allowed to cool to room temperature and is then dissolved with dilute (5-10%) hydrochloric acid. In case of the automated devices, the hot melt is poured directly into the dilute acid. This is preferable as it enables faster and less troublesome dissolution. In order to facilitate the pouring of the hot melt, a small amount of cesium iodide (same weight as the sample) is weighed into the platinum crucibles together with the flux and the sample material.

4. Sample preparation for X-ray fluorescence analysis

There are two main approaches utilized for sample preparation in order to achieve the best precision for major compositional elements. The sample is fused akin to the fusion described above. The resulting hot melt is poured into a platinum mold and forms a glass disc that is introduced to the XRF. While a number of fluxes can be used, lithium tetraborate is often the flux of choice for zeolitic materials. In order to reduce the sensitivity of XRF to the matrix composition, lanthanum oxide (20%) can be added to the lithium tetraborate flux. A number of approaches can be taken in order to prepare calibration standards; however, the fusion based sample preparation approach enables the addition of elements of interest (usually as oxides) directly into the platinum crucible prior to the fusion.

Pressing pulverized samples into pellets is also a viable approach. The drawback is that this technique is likely to have poorer precision than the fusion and be more sensitive to changes in the matrix composition. However, it is satisfactory for many applications and it enables the

determination of non-metals, such as halogens and sulfur, that would be volatilized during the fusion. Often, if the desired precision can be achieved, the samples can be introduced to the XRF simply as ground powders, without pressing. The author routinely determines sulfur and chlorine with a detection limit of 100 ug/g.

5. Determination of non-metals

a. Determination of carbon, hydrogen and nitrogen (CHN)

The determination of CHN is generally requested because these elements are present in an organic amine template used during synthesis or because the zeolite adsorbs these during a specific application. In either case conventional CHN analyzers are frequently used for this determination. Alternative approaches include the determination of nitrogen by classical Kjeldahl digestions and the determination of carbon by combustion analyzers specific for only carbon. The hydrogen concentrations from a CHN will include hydrogen from water and hydrocarbons. Karl-Fischer based determination of water, at specified temperature, can be used to differentiate the two sources of hydrogen.

b. Determination of sulfur

The determination of sulfur is generally accomplished via a combustion type analyzer, often together with carbon. Commercial equipment exists for single or multi-element analysis of C, H, N, and S. There are several alternative non-oxidative techniques; these include XRF with a detection limit of about 100 ug/g, or specialized reduction-distillation of the sulfur as hydrogen sulfide followed by calorimetric detection via methylene blue.

c. Determination of chlorine

The determination of chlorine can be accomplished via a variety of leaching or closed vessel (microwave) digestions followed by silver nitrate titrations of the liberated chloride. Alternatively, leaching (which may include full dissolution by addition of hydrofluoric acid) followed by Ion Chromatography has been found very useful as it enables the detection of chloride as well as nitrate, sulfate and ammonium. Also, XRF can be used, with a detection limit of about 100 ug/g chlorine.

d. Determination of fluorine and chlorine via pyrohydrolysis [2]

A specialized technique has been implemented for the determination of fluorine. The sample is pyrolyzed in a nickel combustion tube in a steam atmosphere at 1000°C. The steam/analyte eluent is scrubbed and the fluoride concentration is then determined via Ion Chromatography or Ion Selective Electrode. Chlorine is volatilized together with the fluorine and can also be determined.

6. Summary

All the techniques described herein have their strengths and weaknesses and areas of overlap. The selection is dictated by specific sensitivity and precision requirements and by instrument availability. Each approach described above can be modified to address specific requirements. For example, a graphite furnace and hydride AAS can be used with great sensitivity for the determination of trace contaminants such as arsenic or mercury.

7. References

- [1] Walter Zamechek, Robert G. Pankhurst, in Proceedings of the International ICP Winter Conference, San Juan Puerto, 1980, Heyden Press, p 121
- [2] Analytical set-up based on Anal. Chem. 32 (1960) 118

Characterization of zeolites by SEM

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1. Introduction

In the scope of this contribution the reader is referred to the regular textbooks for technical information on the Scanning Electron Microscope (SEM).

The resolution of SEM in the world of microscopy clearly bridges Optical Microscopy (OM) with Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM) as is depicted in Figure 1.

The size of the zeolites that can be studied with SEM is thus between 20 nm and 20 μm .

Regarding zeolite sample preparation, two approaches are possible: for the ultimate picture and for fast exploration.

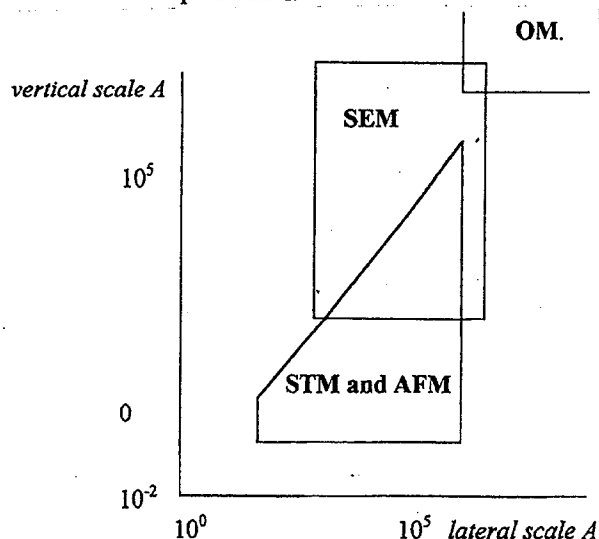


Fig. 1: Comparison of resolution between OM, SEM and STM

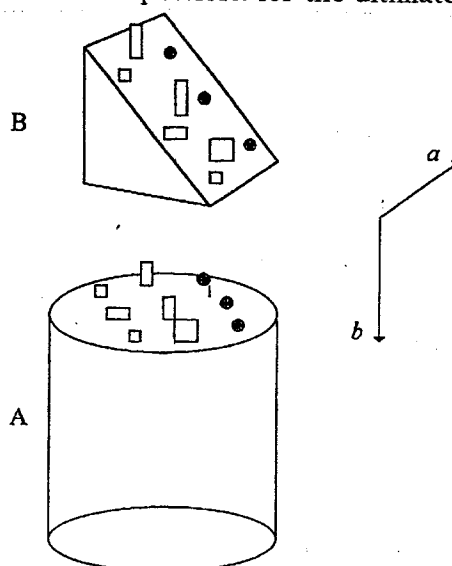


Fig. 2: Sample holder (A) with optional prismatic holder (B). Three rows of samples are shown. Rotation axis are indicated.

2. Approach for the ultimate picture

Start with a metal holder of which the surface is polished. The background is then smooth and even and does not interfere with the contours of the crystals.

Bring a hair from your head in contact with a glue in a way that you get individual small drops of glue on this hair. Touch the sample holder with this hair and a row of very tiny spots of glue are now present on the holder. Either powder or, preferably, crystal(lites) can be fixed on this row of glue spots, thus representing one type of zeolites. More rows with the same or another zeolite material can be arranged this way on one sample holder. Next, the samples need to be coated via a sputter technique with a conduction layer of preferably noble metal. This layer must be thin so that details of the sample are not blurred. Thus, in the case of an Edwards sputtering chamber, one minute for gold at the proper setting is enough.

In case the crystals are very small ($< 0.1 \mu\text{m}$) or flat oriented on the support, it is difficult to make a picture of the crystallite with enough contrast to the background, actually the support. To

observe the crystal clearly it is convenient to use an additional prismatic shaped support that is mounted on the primary support as shown in Figure 2. Not only the form, but also the aspect ratio of crystals, can be well studied. In particular, the crystal size and aspect ratio of crystals are determined with accuracy only when a crystal face is oriented perpendicular to the beam. With the additional support, the crystal can be oriented either perpendicular to the beam, which means rotation around the lateral axis as indicated in Figure 2, or almost parallel to the beam. With the rotation around the axial axis *b*, shown in Figure 2, at least three crystal faces perpendicular to each other can be studied on one crystal.

Regular sample tables of SEM apparatus only rotate thirty degrees in the lateral orientation.

3. Approaches for fast exploration

Start with a metal holder on which a preshaped, double-sided, sticky, conducting layer is applied. Divide the sticky area in, for instance, six segments. Dust each segment with a sample and remove loose material. Sputter for one or two minutes. Pictures can now be made.

In all cases the samples need to be dry and/or free of volatile material in the high vacuum chamber.

The information that can be drawn from SEM pictures of zeolites is given in Table 1.

Table 1. Subjects and details that can be observed.

Subjects	Details
Crystal form	Type of zeolite
	Aspect ratio
	Influence on crystal growth, for example, inhibition of crystal faces that indicate the presence of an unknown factor
	Crystal size distribution phenomena, for example, aggregation / twinning / intergrowth
External surface	Indication of single crystals
	Relative roughness
	Secondary nucleation effects
Purity of the phase	Other zeolite types
	Amorphous material
Unknown species	New material?

Product characterization by NMR

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The impact of solid-state NMR as a powerful tool for studies of micro- and mesoporous molecular sieves has been dramatic during recent years. Tremendous progress has been made, aiming towards enhanced resolution, sensitivity and improved multinuclear capabilities. Solid-state NMR is nowadays a well established technique for characterization of zeolites and related materials with respect to structure elucidation, catalytic behavior and mobility properties.

Solid-state NMR is a complementary technique to XRD, since both crystalline and amorphous material as well as powders can be investigated. While XRD (preferably on single crystals) provides information about the long range ordering and periodicities, NMR allows investigations on the short range ordering (local environment) and structure.

The potential of high-resolution solid-state NMR has been known for a long time. However, the challenge has always been to overcome the problems in connection with recording solid-state NMR spectra with sufficient resolution. Distinct nuclear spin interactions like chemical shift anisotropy (CSA), dipolar and quadrupolar interactions which lead to excessive line broadening, are averaged in liquids due to fast thermal/molecular motions of molecules, but are operative in the rigid lattice of solids (the molecules are less mobile). As a consequence, the fine structure is lost since broad lines are obtained, hiding the essential information of analytical character. In addition, long spin-lattice relaxation times, due to the lack of translation- and rotation-motions, are controlling the repetition of a NMR experiment and, consequently, the entire recording time. During recent years, several techniques have been developed for averaging those interactions / phenomena to zero, or reduce them to the isotropic values, allowing the registration of high-resolution NMR spectra of solids as well. Those techniques and their relations to the mentioned interactions / phenomena are:

Techniques	Handling of the following interactions / phenomena
Dipolar decoupling (DD)	Heteronuclear dipolar interactions
Multiple pulse sequences (MPS)	Homonuclear dipolar interactions
Magic angle spinning (MAS)	Chemical shift anisotropy (CSA), dipolar and first-order quadrupolar interactions
Dynamic angle spinning (DAS)	Second-order quadrupolar interactions
Double orientation rotation (DOR) or Multiple-quantum NMR	
Cross polarization (CP)	Long spin-lattice relaxation times

During MAS, the sample is rotated quickly about an angle of $\theta = 54^{\circ}44'$ in relation to the axis of the external magnetic field, and the three interactions mentioned have a dependence on the second-order Legendre polynomial $3 \cos^2\theta - 1$. That means, if θ is chosen to be $54^{\circ}44'$ (the so-called magic angle), the expression $3 \cos^2\theta - 1$ becomes equal to zero and the interactions are averaged to zero or reduced to the isotropic values.

Quadrupolar nuclei interact not only with the magnetic field in which the sample is placed but also with the electric field gradient. The combination of both effects results in an anisotropy that can no longer be removed by MAS alone. A detailed analysis of the averaging process of quadrupolar nuclei shows that second-order quadrupolar interactions depend on a fourth-order Legendre polynomial $35 \cos^4\theta - 30 \cos^2\theta + 3$. Therefore, the introduction of two independent angles averages the effect of both tensors and high resolution solid-state NMR spectra of nuclei possessing quadrupole moments can be recorded. In principle, two different techniques can be used: Applying DAS, the sample is rotated sequentially about two different angles, whereas during DOR, the sample is spun simultaneously about the two axes. However, using multiple-quantum NMR

spectroscopy the same information can be obtained.

The spinning speed of a rotor during MAS or DAS/DOR experiments should be at least in the range of the line width of the signal recorded under static conditions, otherwise the main resonance line is accompanied by a series of spinning side bands occurring at integral multiples of the spinning speed. Cross polarization (CP) allows transfer of magnetization (or polarization) from an abundant species (usually ^1H) to a dilute species which is under observation. The benefits are primarily an intensity enhancement of the dilute spin signal and a reduction of the recycle time between experiments, since the rate-determining relaxation time is now that of the abundant species. Usually the relaxation of the abundant spins are much faster than the dilute spin relaxation. In order to obtain optimum line narrowing and improved sensitivity in a solid-state NMR spectrum, the experimental techniques mentioned are often applied in combination, as, for example, CP/MAS or CRAMPS (combined rotation and multiple pulse spectroscopy).

All of the relevant basic nuclei contributing to the framework of zeolites and AlPO_4 molecular sieves are detectable to NMR investigations by their natural isotopes (natural abundance in parentheses): ^{29}Si (4.7%), ^{27}Al (100%), ^{31}P (100%) and ^{17}O (0.037%). Both ^{27}Al and ^{31}P spectra are easily detected within reasonable time, however, ^{27}Al has a quadrupole moment which can cause line broadening due to interaction with the electric field gradient. Investigations of ^{17}O NMR can be done by using enriched material, since the natural abundance is quite low.

The obtained resonance lines for ^{31}P and ^{29}Si are usually narrow, and, due to their important role as framework elements (besides ^{27}Al), these nuclei have been widely used in solid-state NMR studies of microporous and mesoporous molecular sieves for structural investigations. The most important application of ^{29}Si NMR is due to the relationship between the ^{29}Si chemical shift sensitivity and the degree of condensation of the Si-O tetrahedra, that is, the number and type of tetrahedrally coordinated atoms connected to a given SiO_4 unit: $\text{Si}(n\text{ Al})$, with $n = 0, 1, 2, 3$ or 4 [chemical shift range: -80 to -115 ppm, with the high-field signal for $\text{Si}(0\text{ Al})$]. Here n indicates the number of Al atoms sharing oxygens with the SiO_4 tetrahedron under consideration. Differences in chemical shifts between $\text{Si}(n\text{ Al})$ and $\text{Si}(n+1\text{ Al})$ are about 5-6 ppm. Furthermore, ^{29}Si MAS NMR spectra can be used to calculate the framework Si / Al ratio from the NMR signal intensities (I) according to eq. (1):

$$\frac{\text{Si}}{\text{Al}} = \frac{\sum_{n=0}^4 I_{\text{Si}(n\text{ Al})}}{\sum_{n=0}^4 0.25 n I_{\text{Si}(n\text{ Al})}} \quad (1)$$

^{27}Al NMR spectra reveal the existence of extra-framework Al (about 0 ppm) besides the lattice aluminum (tetrahedrally coordinated Al at about 40-65 ppm). However, in special cases aluminum atoms can be "invisible" and are not observable by NMR. The introduction of DAS and DOR as well as nutation NMR (where in a two-dimensional way the effect of the quadrupole interaction is separated from other line broadening interactions) allow a much more detailed insight with respect to the structural information available by ^{27}Al NMR. Usually, the only Al transition recorded in microporous and mesoporous materials is the central $+1/2 \leftrightarrow -1/2$ transition, which is dependent only on the second order quadrupolar interaction. This interaction decreases with increasing magnetic field strength, and better resolution can be obtained by applying higher magnetic fields and/or DAS/DOR. Both ^{29}Si and ^{27}Al MAS NMR spectra are widely used to follow dealumination processes, as well as direct synthesis procedures concerning ^{29}Si NMR.

Solid-state ^1H NMR of protons, OH groups, adsorbed water, organic sorbates and probe molecules containing hydrogen in microporous and mesoporous molecular sieves has been developed as a usable method for getting information about different kinds of hydrogens in terminal or bridging OH groups, varying environments for hydrogen containing probe molecules and, finally, acidity investigations. In this way, four distinct types of protons have been identified and quantified by their chemical shifts: (1) non-acidic, terminal SiOH groups (1.5-2 ppm), (2) AlOH

groups at non-framework Al (2.6-3.6 ppm), (3) acidic, bridging hydroxyl groups SiO(H)Al (3.6-5.6 ppm) and (4) ammonium ions (6.5-7.6 ppm). Cross polarization measurements are used to emphasize signals of nuclei connected to hydrogen containing environments.

Other nuclei which can substitute isomorphously for the usual framework elements in microporous and mesoporous materials are observable by solid-state NMR, for example, ^{11}B , ^{73}Ge and $^{69,71}\text{Ga}$. Charge compensating cations, like ^7Li , ^{23}Na , ^{39}K , ^{133}Cs or ^{195}Pt , are suitable for NMR measurements. However, most of those elements possess a quadrupole moment which usually limits the application. Furthermore, organic compounds used as templates during hydrothermal synthesis or as sorbates in the zeolite framework (adsorbed guest molecules can cause frame transitions) as well as catalytic organic reactions on microporous and mesoporous molecular sieves (even *in situ*) can be detected by applying ^{13}C CP/MAS NMR.

Finally, ^{129}Xe (natural abundance of 26.4%) is a very suitable and sensitive isotope for probing the pore architecture of zeolites and AlPO_4 's. The extended Xe electron cloud is easily deformable due to interactions, for example, the Xe atoms and the channel wall of a zeolite framework. The deformation results in a large low-field shift of the Xe resonance. Probe molecules like water and hydrocarbons have been used to study the pore architecture of mesoporous materials by monitoring the ^1H NMR intensity of the liquid water signal when decreasing the temperature. The intensity of the liquid water ^1H NMR signal drops drastically when the water is frozen, however, the temperature for this transition depends strongly on the pore diameter of the porous material. A surprising consistency between the nitrogen adsorption-desorption isotherms and the proton NMR signal intensity versus temperature was observed (see Figure 1).

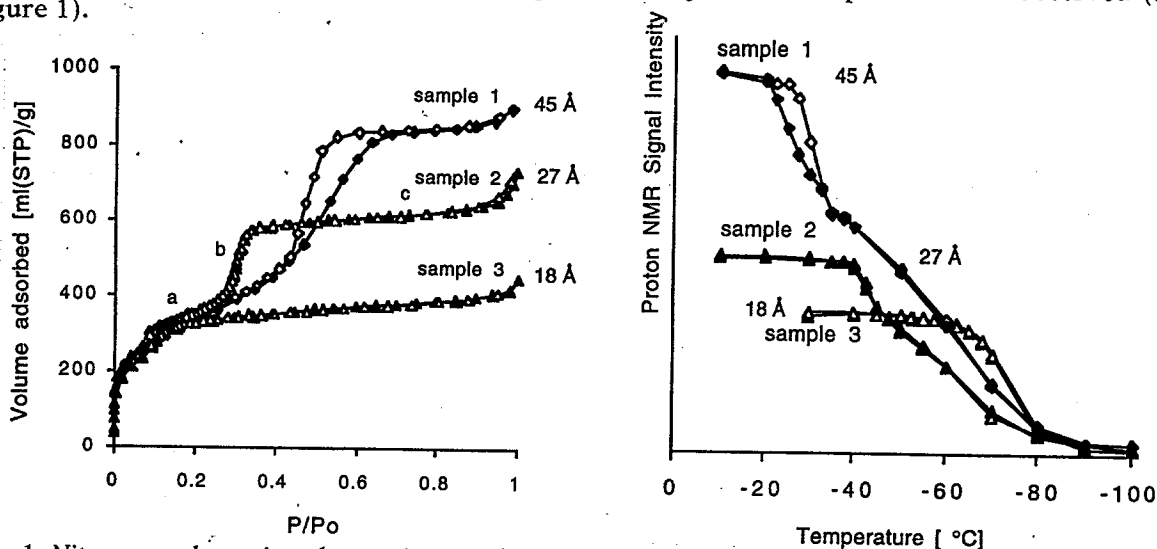


Fig. 1: Nitrogen adsorption-desorption isotherms at 77 K (left) and ^1H NMR signal intensities of pore water confined in different siliceous MCM-41 samples versus temperature (right) (pore diameters are given in Å). Filled symbols denote adsorption (left) and cooling (right), open symbols denote desorption (left) and heating (right).

The introduction of two-dimensional (2D) solid-state NMR spectroscopy enables us to follow the three dimensional connectivities within a zeolite lattice (Si-O-Si), by applying 2D homonuclear ^{29}Si COSY (Correlated Spectroscopy) or 2D ^{29}Si INADEQUATE (Incredible Natural Abundance Double Quantum Transfer Experiment) sequences.

The mobility/dynamics of small molecules and the intracrystalline mass transfer in porous materials can be followed by diffusion NMR measurements. Most known is the pulsed field gradient (PFG) technique, where the spins have a state which is spatially dependent upon their location along B, (with pulses of linear gradients of B_0).

Characterization of zeolites by sorption capacity measurements

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1. Introduction

Sorption capacity measurement provides one of the simplest and most direct ways of characterizing a zeolite sample. However, the information derived from capacity measurement generally provides only an estimate of sample purity and/or evidence of consistency with a known structure, rather than a means of differentiation between different structures.

The adsorption equilibrium isotherm for a microporous adsorbent, such as a zeolite, is of type I form in the Brunauer classification and, in the appropriate temperature range, the isotherm is highly favorable with a well defined saturation limit corresponding to complete filling of the intracrystalline pores. [1] The molecular volume of the adsorbed phase corresponds closely to that of the saturated liquid sorbate at the same temperature so the measured saturation capacity can be easily converted to the specific micropore volume (cm^3/gm) or, knowing the crystal density, to the intracrystalline void fraction. Representative isotherms are shown in Figure 1 (a) and (b), and the calculation of the specific pore volumes is summarized in Table 1.

Table 1. Calculation of specific micropore volumes (Fig. 1)

Figure	System	Temperature (K)	Saturation capacity (g g^{-1})	Density of saturated liquid sorbate (g ml^{-1})	Specimen micropore volume
1 (a)	O_2/CoY	78	0.324	1.2	0.27
1 (b)	Ar-silicalite	77	0.205	1.42	0.144
1 (c)	N_2 -silicalite	77	0.116*	0.81	0.143

*First plateau. Second plateau yields essentially the same pore volume if the density of solid N_2 (1.02 g/mL) is used.

2. Experimental Technique

Several different techniques may be used to measure the capacity. The essential features of the apparatus used for gravimetric and piezometric measurements are shown in Figure 2. [4]

2.1 Gravimetric Method

In a gravimetric experiment the mass of the sample is measured directly using a microbalance connected to a vacuum line, equipped with a pressure gauge and a system for introducing the sorbate vapor. The sample is first degassed under vacuum at elevated temperature and then cooled to the measurement temperature. Successive doses of sorbate are introduced and the sorbate pressures and corresponding masses are recorded. Provided that the temperatures and range of sorbate pressures are correctly selected, the isotherm should be almost rectangular. Under these conditions accurate measurement of the sorbate pressure is not necessary since the capacity is almost independent of pressure.

2.2 Piezometric Method

In the piezometric method the quantity of sorbate adsorbed is deduced from measurements of the change in pressure in a system of known volume when a known quantity of sorbate is introduced. The system volume can be easily determined using a calibrated doser volume. Accurate

pressure measurements are needed, and of course the entire system should, ideally, be maintained at a uniform constant temperature. This requirement imposes significant practical difficulties when the measurements are to be made at a temperature far from ambient. For this reason the gravimetric method is generally preferred.

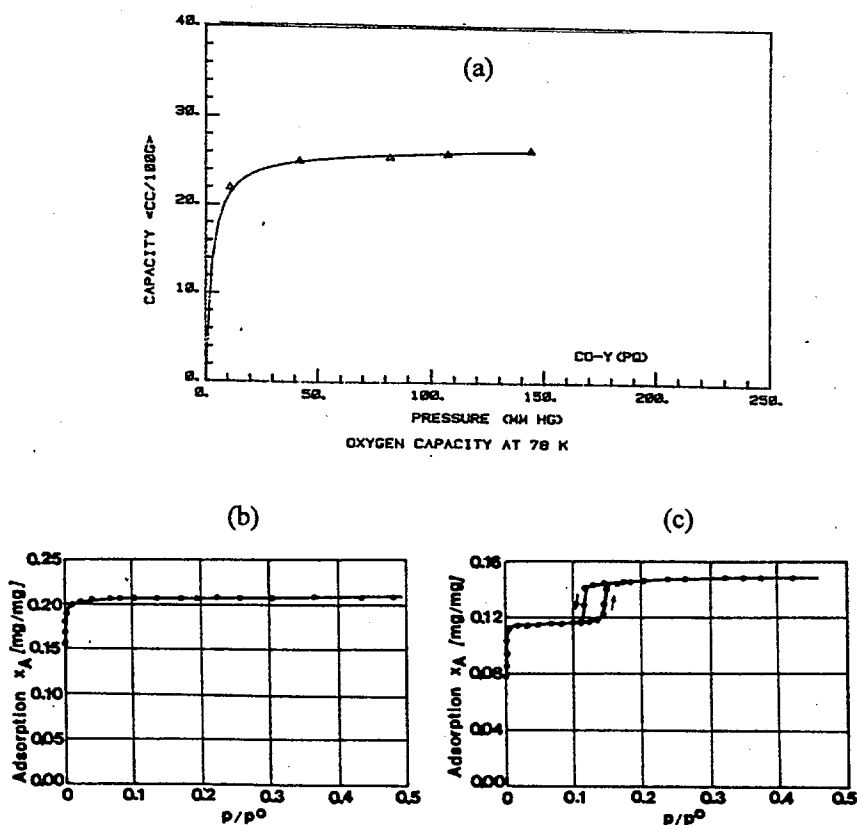


Fig. 1. Experimental isotherms at 77 K: (a) O_2 on CoY [2], (b) Ar on silicalite [3], (c) N_2 on silicalite [same sample as in (b)] [3]

2.3 Automated BET System

Automated BET measurement systems such as *Omnisorb* can also be used to measure saturation capacity. In such devices a dilute stream of sorbate in an inert (He) carrier is passed through the sample and the capacity is found by integration of the measured breakthrough curve, thus providing essentially the same information as is obtained from a gravimetric or piezometric measurement.

Although the basic experiment is very simple, a number of precautions are necessary to obtain accurate results:

- (1) In principle a buoyancy correction is needed to allow for the mass of vapor displaced by the zeolite sample. However, except at high pressures, such corrections are generally negligible.
- (2) It is important to minimize any temperature gradient in the region of the sample in order to

avoid errors due to thermal transpiration and convection. This can normally be achieved simply by ensuring that the hangdown tube containing the sample pan dips well below the surface of the thermostat liquid.

- (3) To avoid the possibility of capillary condensation in the interstices between crystals the sample should be dispersed on the balance pan and the relative pressure (p/p_s) should not exceed about 0.25. (p_s is the saturation vapor pressure at the relevant temperature).
- (4) At high relative pressures significant (multilayer) physical adsorption can occur on the external surface of the crystals. If the crystals are small (sub-micron), this can give rise to a significant error in the measured capacity. This problem can also be avoided by keeping the relative pressure below about 0.25.
- (5) To correct for the positive slope of the saturation plateau the Dubinin-Radushkevich equation is sometimes used to extrapolate to zero pressure. However, with a near rectangular isotherm of the kind shown in Figure 1, the difference between this extrapolation and the actual value at the plateau is minor.

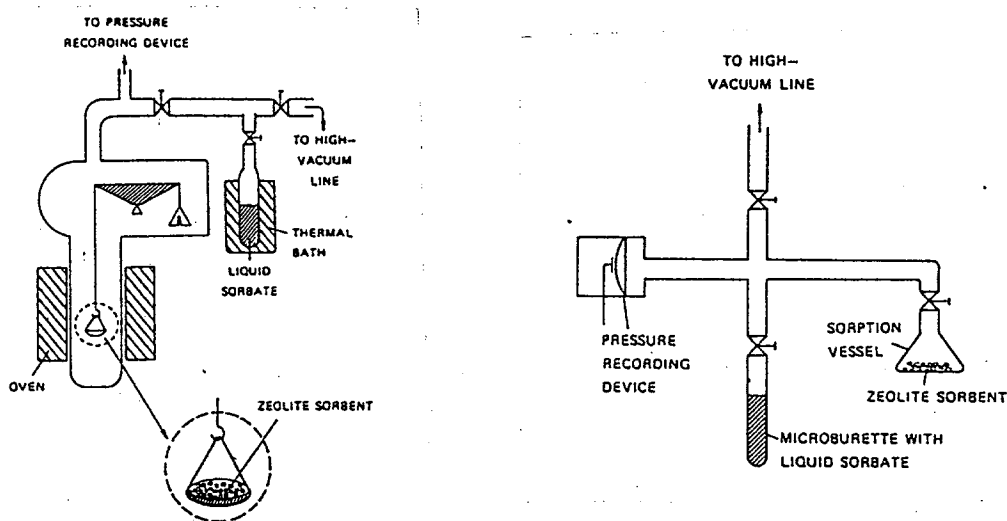


Figure 2. Schematic diagrams showing apparatus for gravimetric and piezometric isotherm measurements [4]

3. Preconditioning

Prior to a capacity measurement any organic template from the synthesis must be removed by oxidation and the sample must be thoroughly degassed. If the synthesis does not include a template then only the degassing step is needed. Oxidation to remove the template is generally carried out by exposure to air for several hours at the highest temperature that can be tolerated by the zeolite without structural degradation—typically 500-550°C for silicalite/ZSM-5. Degassing is conveniently carried out at elevated temperature in the vacuum system. Temperatures in the range 350-400°C are commonly used, but for less stable materials somewhat lower temperatures can be used. To some extent a reduction in temperature can be compensated for by using a higher vacuum for a longer period of time. The aluminum rich zeolites have poor hydrothermal stability, that is, they are unstable in the presence of water vapor at elevated temperatures. In degassing such samples it is therefore important to raise the temperature slowly maintaining a good vacuum all the time so that water vapor is removed as soon as it is desorbed.

A typical procedure for degassing a sample of A or X zeolite is as follows:

- (1) Increase temperature under vacuum from ambient to 400°C over a period of 4-5 hours.
- (2) Maintain the temperature at 400°C under vacuum overnight.
- (3) Cool (under vacuum) to the experimental temperature (1-2 hours.).

4. Choice of Sorbate and Measurement Temperature

In principle almost any of the common small molecules can be used as the probe sorbate although, in practice, the choice is generally restricted to Ar, O₂ or N₂. Linear paraffins such as n-hexane have sufficient flexibility to pack within the micropores almost as effectively as the smaller molecules so n-hexane capacities are also commonly used to measure specific micropore volume. Bulkier molecules such as i-butane pack less efficiently and thus yield erroneously low estimates for the micropore volume. Molecules such as Ar, O₂ and N₂ do not penetrate 6-membered oxygen rings, at least at low temperatures, so the saturation capacity determined from measurements with these sorbates includes only the pore volume accessible through 8-rings (or larger). Although N₂ is the usual choice of probe molecule for BET surface area measurements, it is not the best choice for measuring the micropore volume of a zeolite, since, probably as a result of quadrupole interactions, N₂ isotherms commonly show complex changes in packing density leading to hysteresis of the isotherm, even for an ideal pore system. [3,5] In contrast, the low temperature isotherms for Ar and O₂ are generally close to the ideal rectangular form (see Fig. 1).

The choice of measurement temperature is dictated by the practical requirement that the desired relative pressure range ($0.05 < p/p_s < 0.2$) should correspond to an easily measured range of absolute pressures. This means that if the measurements are to fall within the convenient subatmospheric pressure range, the temperature should not be too far from the normal boiling point of the sorbate.

Water is a very small molecule, and, as a result of its strong dipole, it is strongly adsorbed, especially in Al-rich zeolites. Water isotherms at ambient temperature generally show the characteristic rectangular form observed for other small molecules. However, the saturation capacities for water (based on the molecular volume) are often higher than the values determined using Ar, O₂ or even N₂ since water can penetrate regions of the framework (for example, sodalite and cancrinite cages) which are not accessible to Ar, O₂ and N₂. Comparison between the saturation capacities measured with water and with Ar, O₂ or N₂ can therefore provide additional structural information.

5. B.E.T. Area

BET areas are commonly determined for zeolite samples by the same method as is used for larger pore materials. [6] Under the conditions of the BET measurement the N₂ molecules condense, filling the micropore volume. Thus the BET area of a zeolite is really the equivalent area that would be covered by the quantity of sorbate required to fill the intracrystalline pores if the molecules were arranged as a close packed monolayer. It does *not* correspond to the internal area of the framework.

6. Mesoporosity

As a result of structural defects the intracrystalline pores of a zeolite sometimes contain a significant proportion of mesopores (20-50 Å) in addition to the ideal zeolite pores (< 15 Å). The presence of significant mesoporosity leads to a positive slope instead of the almost horizontal saturation plateau characteristic of an ideal microporous structure.

7. Determination of Pore Size

In this article we have considered only the use of capacity measurement to determine specific micropore volume. Such measurements using molecules of different critical diameter may also be used to establish the controlling pore dimensions in an unknown structure (see, for example Gaffney, et al., [7]) but this is outside the scope of the present review.

8. References

- [1] D. M. Ruthven, *Principles of Adsorption and Adsorption Process*, John Wiley, New York, 1984, p. 49
- [2] D. T. Hayhurst, J. C. Lee, *AIChE Symp. Series 230*, Vol. 79, Am. Inst. Chem. Eng., New York, (1983) pp. 67-78
- [3] U. Müller, K. K. Unger, *Characterization of Porous Solids*, K. K. Unger (ed.), Elsevier, Amsterdam, 1988, p. 101
- [4] M. F. M. Post, *Introduction to Zeolite Science and Practice*, H. van Bekkum, E. M. Flanigen, J. C. Jansen (eds.), Elsevier, Amsterdam, 1991, Ch. 11
- [5] D. W. Breck, R. W. Grose, *Molecular Sieves*, Adv. Chem. Ser. 121, W. M. Meier, J. B. Uytterhoeven (eds.), Am. Chem. Soc., Washington, DC, 1973, p. 319
- [6] S. J. Gregg, K. S. W. Sing, *Adsorption, Surface Areas and Porosity*, Academic Press, London, 1967
- [7] T. R. Gaffney, T. A. Braymer, T. S. Ferris, A. L. Cabrera, C. G. Coe, J. N. Armor, *Separation Technology*, E. F. Vansant (ed.), Elsevier, Amsterdam, 1994, p. 317

Ion exchange capacity

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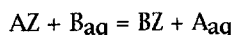
1. Natural Zeolites

In a traditional aluminosilicate zeolite the source of the ion exchange capacity is the extent of isomorphous substitution of Al for Si in the tetrahedral framework. The theoretical exchange capacity thus can be derived from the elemental composition.

To estimate the CEC (cation exchange capacity, meq/g) in a natural zeolite it is usual to observe the uptake of the ammonium cation at room temperature when equilibrium conditions are known to have been attained in the presence of a 1M ammonium salt solution. This working capacity can be obtained by batch or column exchange techniques. [1]

2. Synthetic zeolites and related materials of SAPO, MeAPO type ("zeotypes") [2]

When synthetic materials are to be characterized, prior careful elemental analysis will provide the expected, theoretical cation capacity. It is now important to establish equilibrium conditions with a specific cation for which the synthetic product has a highly selectivity; consider:



At equilibrium the "as-synthesized" cation A, in the zeolite phase Z, has been completely displaced by the selective uptake of cation B from the aqueous phase (aq). The following procedure is recommended assuming that the ammonium cation will be the B species.

2.1 Determination of cation exchange capacity at equilibrium.

- (1) Weigh suitable aliquots of the zeolite into sealable polyethylene tubes.
- (2) Add equal volumes of a known concentration of ammonium nitrate solution to the tubes and mix at room temperature. It is preferable to mix by rolling the tubes slowly about their horizontal axis. Mineralogical rollers of the type used to polish gemstones can easily be adapted for this purpose. The solid/solution volume ratio should be at least 1/20.
- (3) At appropriate time intervals remove each tube in turn and determine the concentrations of the displaced cation (A) in solution.
- (4) Construct a plot of the concentration in solution of A as a function of time (Fig 1. plot 1). The vertical axis can be expressed as fractional attainment of equilibrium assuming the calculated theoretical capacity as 100%.

2.2 Notes

- (a) To quote the capacity in meq/g it will be necessary to determine the equilibrium water capacity of the end member (for example, the B form of the zeolite).
- (b) If the expected theoretical capacity is not reached (Fig 1. plot II) it means that, at room temperature, cations in certain sites are not being displaced. This is the ion-sieving phenomenon and can be used to help in structural interpretation of the zeolite structure. Increasing the temperature at which exchange is performed should enable the attainment of full capacity. Usually temperature in the range 60° - 70°C are adequate.
- (c) Choice of conditions are a function of the expected theoretical capacity. A "rule of thumb" is to aim for a 5-fold solution excess of ingoing cation (B). The time for attainment of equilibrium depends on the openness of the zeolite framework and will vary from about 1 hour to 1 week.

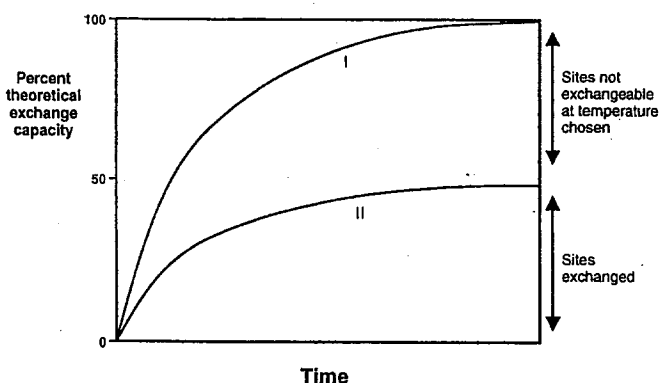


Fig. 1.

3. Experimental methods

The most sensitive analytical technique available is to use radioisotopes to prelabel the A cation and follow its replacement by increase in solution activity with time. (Isotope dilution technique). This will be possible for the as synthesized cations Na, K, Rb, Cs, Ca, Sr and Ba.

In the absence of radiochemical facilities, flame photometry, atomic absorption are perfectly adequate. An alternative is to monitor the ammonium concentration by Kjeldahl titrimetry. Ammonium concentrations can be determined in either the zeolite or solution phase.

4. Other points

- (1) When an organic template has been used to synthesize the zeolite, careful calcination is needed to remove it from the framework. This leaves the zeolite in the H form (H_3O^+ cation in solution). In these cases it is possible to use pH titration to follow ammonium (or other cation) uptake as the H_3O^+ has a low affinity for most zeolites. An exception can be in exchanges observed in materials of SAPO / MeAPO types. These materials sometimes show an unusual affinity for the H_3O^+ ion, especially over Na^+ . [3]
- (2) It is advisable to limit washing to a minimum. Zeolite frameworks are well known to hydrolyze. This is not confined to just those with Si/Al ratio $\rightarrow 1$. [4] It is always advisable to check for the presence of extra framework Al (by MAS NMR). This can arise from template removal and from instability of P-containing frameworks. Obviously, extra framework Al contributes to cation exchange capacities, but can be quantified. [5]
- (3) Some zeolite like materials and high silica materials may have cation and anion capacities due to the presence of framework hydroxyls. This will be pH dependent, but experience is that these OH groups make small contributions to exchange capacities. [6]

5. References

- [1] B. W. Mercer, I. L. Ames, *Natural Zeolites, Occurrences, Properties, Use*, L. B. Sand. F. A. Mumpton (eds), Pergamon, Oxford, 1988, p. 451
- [2] A. Dyer, *An Introduction to Zeolite Molecular Sieves*, J. Wiley & Sons, Chichester, 1988, Ch. 10
- [3] C. M. G. Jones, R. Harjula, A. Dyer, *Stud. Surf. Sci. Catal.* 98 (1995) 131
- [4] R. Harjula, A. Dyer, R. P. Townsend, *J. Chem. Soc., Faraday Trans.* 89 (1993) 977
- [5] A. Dyer, S. Amini, H. Enamy, H. A. El-Naggar, M. W. Anderson, *Zeolites*, 13 (1993) 281
- [6] A. Dyer, T. I. Emms, unpublished work

Characterization by IR spectroscopy

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1. Techniques

The KBr pellet technique is frequently used for investigations of vibrations of the framework. [1-3] Also well-established are (i) infrared (IR) spectroscopy of self-supporting wafers (usually in transmission mode [4]) and (ii) diffusive reflectance IR Fourier transform (DRIFT) spectroscopy of zeolite powders. [5] Both methods (i) and (ii) enable us to investigate cation vibrations in the far IR region [6, 7], to employ heat treatment, to achieve complete dehydration (in high vacuum or a stream of inert gas) and, if desirable, to admit probes (see below). Also, the (thermal) stability of zeolitic materials against, for example, dehydration, dehydroxylation and interaction with sorbates, may be characterized by (*in situ*) transmission IR or DRIFT. In the case of method (i) it is easier to carry out quantitative measurements, while method (ii) is in many instances more sensitive.

2. Framework vibrations

Vibrations of the frameworks of zeolites give rise to typical bands in the mid and far infrared. A distinction is made between external and internal vibrations of the $\text{TO}_{4/2}$ tetrahedra (with, for example, T = Si or Al). The original assignments of the main IR bands [1] were as follows: internal tetrahedra: 1250 - 920 cm^{-1} , asymmetrical stretch (n_{asym}); 720 - 650 cm^{-1} , symmetrical stretch (n_{sym}); 500 - 420 cm^{-1} , T-O bend; external linkages: 650 - 500 cm^{-1} , double ring vibrations; 420 - 300 cm^{-1} , pore opening vibrations; 1150 - 1050 cm^{-1} , asymmetrical stretch; 820 - 750 cm^{-1} , symmetrical stretch. The positions of bands due to vibrations of external linkages are often very sensitive to structure. More recent detailed analysis, however, showed that these assignments may have to be revised in some respect. Computation of normal modes suggested that the concept of strictly separated external and internal tetrahedral vibrations must be modified in that zeolite framework vibrations appear to be strongly coupled. Similarly, the proposed pore opening vibrations seem to be related to a complex motion which in total includes an opening (rupture) of the rings (4-rings, 6-rings) of the structure. [2] Nevertheless, clear-cut linear relationships were found between the frequency of, for example, n_{asym} and n_{sym} of X- or Y-type zeolite and the atom fraction of Al (related to the ratio $n_{\text{Si}}/n_{\text{Al}}$) of the framework. [1] Thus, the frequencies of lattice vibrations could be used in certain cases to determine the $n_{\text{Si}}/n_{\text{Al}}$ ratio of the framework in a similar manner as the lattice parameters obtained by X-ray diffraction as a function of this ratio. Also, shifts of the bands of lattice vibrations are characteristic of cation movements upon dehydration. [1] In several cases a typical lattice vibration is observed around 950 cm^{-1} , indicating the isomorphous substitution of framework Si, Al by other T atoms. The most prominent example is Ti substituted for Si into silicalite (TS-1, TS-2). [8]

3. Cation vibrations

In the far infrared region (200 - 50 cm^{-1}) vibrations of cations against the framework occur. [6, 7] The wave number of the corresponding IR bands depend on the nature of the cations as well as on their siting. The IR bands of alkali metal-exchanged zeolites X, Y and ZSM-5 shift to lower frequencies (red shift) in the sequence of Na^+ , K^+ , Rb^+ , Cs^+ , that is, with increasing cation mass. [6, 7]

4. Extra-framework species

Extra-framework species such as aluminium-containing entities, (for example Al_xQ^{n+}), which occur upon dehydroxylation, [9] may be detected and quantitatively determined by IR spectroscopy when suitable probe molecules are employed as adsorbates. [10,11] The most frequently used probe is still pyridine. Pyridine attached to Lewis acidic centres such as Al_xQ^{n+} gives rise to a typical band at about 1450 cm^{-1} . Adsorption of pyridine on cations of zeolite structures produces bands in the range from 1438 to 1452 cm^{-1} . The exact positions of these bands depend on the nature of the cation, that is, on the Coulomb potential q/r (q : electric charge; r : radius of the respective cation). [10] In cases where the pyridine molecule is too bulky to have access to the extra-framework species, smaller probe molecules such as NH_3 , CO , CH_3CN , H_2 , N_2 can be used advantageously. [5,11,12]

5. Hydroxyl groups

Hydroxyl groups attached to zeolite structures are most important for the chemistry of these materials. They may be detected and characterized by IR spectroscopy as such due to their vibration modes (OH fundamental, overtone and combination vibrations) or with the help of probe molecules (see preceding paragraph and Refs. [5, 11, 12]). A distinction is made among (i) lattice termination silanol groups, (ii) hydroxyl groups occurring at defect sites (hydroxyl nests), (iii) OH-groups attached to extra-framework T atom-containing species (iv) OH groups attached to multivalent cations which compensate the negative charge of the framework and, most importantly, (v) bridging OH-groups (such as =Al(OH)Si= groups with Brønsted acidic character). Hydroxyls of type (i), (ii), (iii), (iv) and (v) give rise to bands in the fundamental stretch region at about 3740 , 3720 , 3680 , $3580 - 3520$ and $3600 - 3650\text{ cm}^{-1}$ (free bridging OH-groups), respectively. Bridging OH-groups exhibiting additional electrostatic interactions to adjacent oxygens are indicated by lower wavenumbers, for example, at ca. 3550 cm^{-1} in the case of the hydrogen forms of faujasite type (X and Y) zeolites and at 3520 cm^{-1} in the case of H-ZSM-5. Moreover, the fundamental stretching vibrations of free bridging OH-groups, which are responsible for important catalytic properties of the hydrogen forms of zeolites, depend on the nature of the T atoms in the =T(OH)Si= configuration. It is, for instance, frequently observed that the respective wavenumbers decrease in the sequence $\text{T} = \text{Al, Ga, Fe, B}$. [13] From the intensity (integrated absorbance) of the bands being typical of the above-mentioned types of hydroxyls, the density (concentration) of the corresponding entities can be estimated. To obtain the absolute data the appropriate extinction coefficients must be determined through independent measurements. [14] This is particularly valuable in the case of defect sites and acid Brønsted (bridging) OH groups. Similarly, there seems to exist a correlation between the wave number indicative of bridging OH groups of zeolites and their acidic strength. [15]

Investigation of the overtone and combination vibrations of hydroxyls via DRIFT spectroscopy is a valuable means for characterization of zeolite materials since it frequently reveals more detailed features than are obtained from the fundamental stretch region. [16]

Adsorption of probes such as ammonia, pyridine or less basic molecules (such as benzene, CO , alkanes, $\text{C}_2\text{Cl}_4\text{H}_2$, N_2 , etc.) also enables zeolitic OH-groups, especially acidic Brønsted sites, to be characterized. Pyridine, for instance, produces a band around 1540 cm^{-1} when adsorbed on Brønsted acid sites, resulting in the formation of pyridinium ions. In view of the bulkiness of pyridine and its strong basicity (low selectivity with respect to acidic strength of the Brønsted sites), other probes should sometimes be preferred. Finally, it should be mentioned that Lewis and Brønsted acidity of zeolites is often advantageously characterized by a combination of IR spectroscopy and other techniques such as temperature-programmed desorption or microcalorimetric measurements of adsorbed probe molecules.

6. Adsorbates

IR spectroscopy is extensively used to characterize zeolite/adsorbate systems. Adsorption and desorption of water (hydration and dehydration) may be easily monitored by IR, since adsorbed H₂O gives rise to a typical deformation band around 1640 cm⁻¹. Adsorbed or occluded template molecules (or their decomposition products) are detectable by, for example, CH and/or NH vibration bands.

7. References

- [1] E. M. Flanigen, H. Khatami, H. A. Seymenski, in *Adv. Chemistry Series* 101, E. M. Flanigen, L. B. Sand (eds.), American Chemical Society, Washington, D. C. 1971, pp. 201-228
- [2] E. Geidel, H. Böhlig, Ch. Peuker, W. Pilz, in *Stud. Surf. Sci. Catalysis* 65, G. Ohlmann, H. Pfeifer, R. Fricke (eds), Elsevier, Amsterdam, 1991, pp. 511-519
- [3] F. Bauer, E. Geidel, Ch. Peuker, W. Pilz, *Zeolites* 17 (1996) 278
- [4] H. G. Karge, W. Niessen, *Catalysis Today* 8 (1991) 451
- [5] V. B. Kazansky, V. Y. Borovkov, H. G. Karge, *J. Chem. Soc., Faraday Trans.* 93 (1997) 1843
- [6] I. A. Brodskii, S. P. Zhdanov, in *Proc. 5th Int. Zeolite Conf*, Naples, L. V. Rees, (ed.), Heyden, London, 1980, pp. 234-241
- [7] H. Esemann, H. Förster, E. Geidel, K. Krause, *Micropor. Mater.* 6 (1996) 321 (and references therein)
- [8] G. Perego, G. Bellussi, G. Corno, M. Taramasso, F. Buonomo, A. Esposito, in *Stud. Surf. Sci. Catalysis* 28, Y. Murakami, A. Iijima, J. W. Ward (eds.), Elsevier, Amsterdam, 1986, pp. 129-136
- [9] G. H. Köhl, *J. Phys. Chem. Solids* 38 (1977) 1259
- [10] J. W. Ward, in *ACS Monograph* 171, J. A. Rabo (ed.), American Chemical Society, Washington, D. C., 1976, pp. 118-284
- [11] H. Förster in *Spectroscopic and Computational Studies on Supramolecular Systems*, J. E. Davies (ed.), Kluwer Academic, Dordrecht, 1992, pp. 29-60
- [12] V. B. Kazansky, in *Stud. Surf. Sci. Catalysis*, 65, H. Pfeifer, R. Fricke (eds.), Elsevier, Amsterdam, 1991, pp. 117-131
- [13] V. A. Tuan, PhD Thesis, Free University of Berlin, 1994
- [14] S. Khabtou, T. Chevreau, J. C. Lavalley, *Micropor. Mater.* 3 (1994) 133
- [15] E. Brunner, H. G. Karge, H. Pfeifer, *Z. Phys. Chemie*, 176 (1992) 173
- [16] K. Beck, H. Pfeifer, B. Staudte, *Micropor. Mater.* 2 (1993) 1

How to read a patent

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Patents contain information useful in zeolite synthesis, but they are hard to read. So why read them? Because they are often the first and sometimes the only source of this information. Much of it is eventually published in the open literature with the arcane language of the patent discarded along the way. But for those on the cutting edge of discovery, the delay may be intolerable. To one "experienced in the art," the inventor discloses more of his/her thought and research than is generally realized. Finally the inventor's summary of the state of the art may be useful to one new to the field.

In reading a patent, it helps to know what to look for and what to ignore. For example, ignore the claims section at the end of the patent. These are lawyers talking to lawyers; rarely is there useful data there. On the other hand, Example 1 usually tells you what works. Pay progressively greater attention to examples where the product has been extensively analyzed and/or used in subsequent applications experiments. Examples which define the limits of operability are warnings for what can go wrong in replicating his/her work. Ignore examples written in the present tense; these are not experiments but the inventor's best guess as to what might happen under hypothetical conditions.

To the beginner, the "state of the art" summary may be a good source of references. The inventor is obliged to cite all pertinent art because failure to do so weakens the case, but the reader should be aware that the inventor is obliged to show that his/her invention is superior to existing art.

"Summary of the invention" may be useful for a long and complex case. At this point, Claim 1 may be a help. Patent attorneys struggle to get the inventor to define exactly what he/she has invented. It helps to be aware of the process by which a patent case is written and prosecuted. The inventor, pushed by the attorney, rushes to assemble the data to support the case and get it filed. The attorney presses the inventor for wide ranging examples to support broad claims. This is the reader's window for discerning the working of the research organization. The case may be refiled during prosecution to delete some of this superfluous and revealing data, but most often it is not. Bad data weakens the case so the inventor is obliged to be truthful about the data, but there is no obligation to present data damaging to the case. This data selectivity makes patents a suspect source in the opinion of many scientists.

Notes

- a. Of the aluminosilicate ABW type analogues, only the hydrated Li-form and the anhydrous Rb-, Cs-, and Tl-forms may be directly synthesized. [2]
- b. Addition of small amounts of potassium fluoride are reported to have a marked mineralizing effect. [3]
- c. In a gold-lined steel autoclave, the reaction was performed at 285°C in 72 hours.
- d. Good results have been obtained by crystallization at 200°C for 93 hours.
- e. At temperatures above 350°C α -eucryptite is formed. Li_2SiO_3 may occur. [1]
- f. Upon dehydration of zeolite Li-A(BW) the framework topology is retained, but the 8-ring channel is considerably narrowed. The lithium cation coordinates across the channel, preventing rehydration of the material even when submerged in water. However, by hydrothermal treatment at temperatures above 110°C, rehydration to the original zeolite is possible.
- g. The Si/Al ratios of ABW type are close to 1. Though Li-A(BW) may be synthesized from oxide compositions with Si/Al ratios from 0.5 to 7, there is no evidence of variation in the Si/Al ratio of the product. [3]
- h. Reversible dehydration of Li-A(BW) is possible to a limited extent. [4] The anhydrous ABW-types do not show any sorption of water at ambient conditions.
- i. In one experiment (sodium bromosodalite and LiBr, hydrothermal 260°C, 72 h), single crystals large enough for single crystal diffraction were obtained (0.1 x 0.05 x 0.01 mm) [1,5]