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The Hydrothermal Synthesis of Zeolites: History and Development from the Earliest Days to the Present Time

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I. Introduction

A. The Nature and Uses of Zeolites

Zeolites are crystalline aluminosilicates containing pores and cavities of molecular dimensions. Many occur as natural minerals, but it is the synthetic varieties which are among the most widely used sorbents, catalysts and ion-exchange materials in the world.[1−3] Zeolite crystals are porous on a molecular scale, their structures revealing regular arrays of channels and cavities (ca. 3−15 Å), creating a nanoscale labyrinth which can be filled with water or other guest molecules. The resulting molecular sieving ability has enabled the creation of new types of selective separation processes (ion exchange, sorption), and in their acid form, zeolites are probably the most important heterogeneous acid catalysts used in industry. The majority of the world's gasoline is produced by the fluidized catalytic cracking (FCC) of petroleum using zeolite catalysts. Their key properties are size and shape selectivity, together with the potential for strong acidity. Figure 1 illustrates the relationship of a representative zeolite crystal to its micropore system, showing the existence of crystallographically defined channels and cavities and the cation-exchange centers resulting from the periodic replacement of $[AlO_4]^-$ for $[SiO_4]$.

In view of the industrial importance of zeolites and also because of the intrinsic scientific interest in their structural complexity and diverse chemistry, considerable effort has been directed into zeolite synthesis. The main aims of this work have been the synthesis of new materials and the building up of an understanding of the synthesis process. In recent years, many new zeolite-like materials (zeotypes) containing elements other than silicon and aluminum have been synthesized,[3,4] and related structures with much larger pore sizes (up to around 200 Å) have also been discovered.[5,6] These new materials have potential applications in (for example) fine chemicals synthesis, electronic arrays, and biomaterials. Further information on such microporous and mesoporous materials can be found in recent extensive reviews.[7−10]

Aluminosilicate zeolites are usually synthesized[1−3,7,8] under hydrothermal conditions from reactive gels in alkaline media at temperatures between about 80 and 200 °C. An alternative route is based on fluoride-containing compositions as mineralizing media, in which case the pH can be much lower. This latter approach has the advantages that (i) nucleation rates are reduced so that larger crystals are formed and (ii) in zeotype synthesis[3,4,7,8] the acid or neutral pH regime facilitates the structural incorporation of those heteroatoms where the precursor species would be precipitated (e.g., as hydroxides) at higher pH. The advent of new families of zeotypes has considerably

Colin Cundy gained his B.Sc. and Ph.D. degrees from the University of Bristol, U.K., working on fluorocarbon nickel complexes with Dr. M. Green and Professor F. G. A. Stone. Research Fellowships in organometallic chemistry took him to Munich (1970) and then to Sussex University. During his subsequent career in Industry (ICI, 1974–1995), he developed research interests in inorganic materials, applied mineralogy and, particularly, the relationship between solution chemistry and the solid state. He began an ongoing research program on fundamental aspects of zeolite synthesis in the early 1980s. In 1995, he moved to the University of Manchester Institute of Science and Technology (UMIST) to work with John Dwyer in setting up the UMIST Centre for Microporous Materials, where he is currently Associate Director.

Paul Cox obtained a first-class degree in Chemical Physics from University College London in 1985. His PhD, undertaken at the University of Keele under the direction of Professor Richard Catlow, involved a combined experimental and theoretical investigation into the structure of superionic conductors. After completing his doctoral studies, he spent three years in industry working as part of the modeling team at ICI Wilton, Teesside, U.K. He moved to Portsmouth in 1992, where he is currently Principal Lecturer in the School of Pharmacy and Biomedical Sciences. His research interests focus on the application of molecular modeling methods to investigate the structure and properties of solid-state materials.

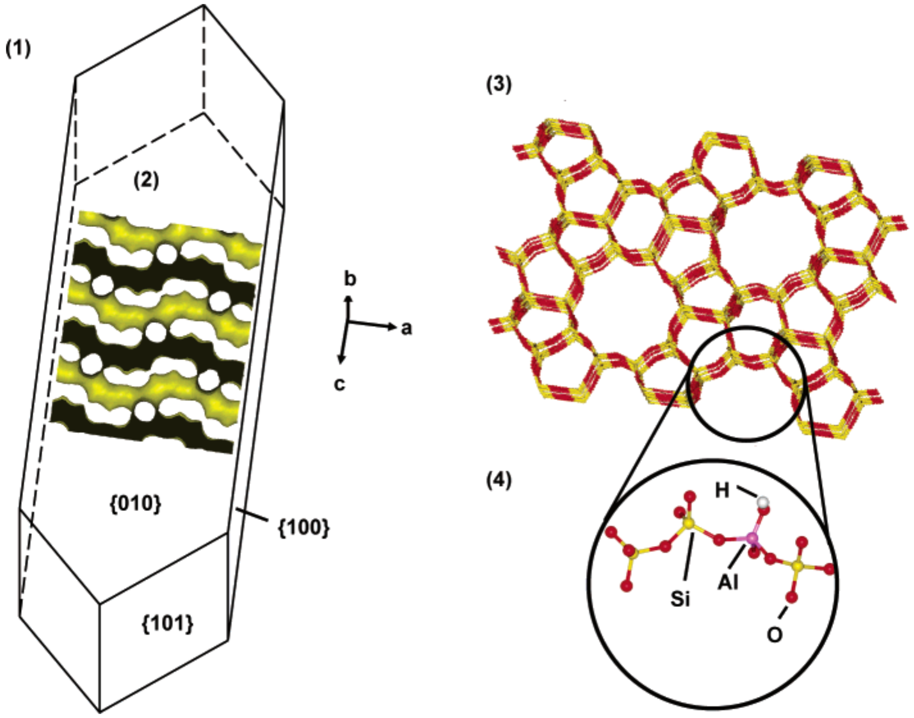


Figure 1. The key features of a representative zeolite, ZSM-5: (1) crystal morphology, showing the relationship to the major axes (*a*, *b*, *c*); (2) section of pore map, showing zigzag channels in the a-direction, intersecting with straight channels in the *b*-direction; (3) part of the crystal structure—these sheets of 5- and 10-membered T-atom rings lie in the *ac* plane, giving the vertical straight channels shown in (2); (4) detail of the atomic structure, illustrating the linked TO_4 tetrahedra. For ZSM-5, T = Si predominantly, but this insert shows an Al substituent (purple) with a hydrogen atom (white) occupying the associated cation exchange site.

broadened the scope of zeolitic catalysis, which was formerly confined largely to strong acid reactions such as hydrocarbon cracking and rearrangement. The titanosilicate TS-1, for example, is now used commercially as an oxidation catalyst, particularly in olefin epoxidation.

Many zeolites (and some zeotypes) can be made using only inorganic reactants, and all the phases studied up to 1961 (such as the classical synthetic zeolites A, X, and Y) were synthesized in this manner. However, in the 1960s, increasing use was made of organic compounds, particularly quaternary ammonium salts. These are often referred to as templates since the zeolite structure appears to form around them, in some cases encapsulating them with a very close fit between the organic groups and the pore walls. Clearly, this steric requirement will limit the number of organic units which can be accommodated. Thus, for templates such as quaternary salts which also act as charge-balancing cations, the organic guest species impose a restriction on the zeolite framework charge density, resulting in products of increased Si/Al ratio (since only the Al-sites are anionic). Most high-silica zeolites (Si/Al > 10) are synthesized using organic templates, which have to be removed from the structure (usually by calcination) to produce the open-pore materials for use in sorption and catalysis. In general, crystal growth rates tend to decrease as the Si/Al ratio increases so that the relatively short preparation times of aluminous zeolites (minutes to hours) become more extended for the high-silica materials (hours to days) and the synthesis temperatures of the latter are usually considerably higher (100−200 °C rather than 80−120 °C).

Members of the aluminophosphate family of molecular sieves ($AlPO_4$-*n* series)[3,4,7,8] also almost invariably require the use of organic templates in their synthesis. However, with these neutral frameworks, amines are more often used than quaternary compounds. As with high silica zeolites, synthesis temperatures are in the 100−200 °C range, and synthesis times are most often measured in hours or days. The most recent development in the growing family of ordered porous materials is the discovery that mesoporous materials with regular pore sizes of ca. 20−200 Å (M41S and related families)[5,6,7−10] can be synthesized by using long-chain surfactant molecules as templates. Lamellar (e.g., MCM-50), hexagonal (e.g., MCM-41), and cubic (e.g., MCM-48) types are known. The materials are ordered, but not conventionally crystalline, since the pore walls are usually amorphous. Silicate, nonsilicate, aluminosilicate, and heterosubstituted varieties have been synthesized, usually at moderate temperatures (25−150 °C).

The major pathway to all of the above materials is that of hydrothermal synthesis. It is unfortunately fairly common to see in the scientific literature statements to the effect that this process is still at an empirical stage, or poorly understood, or even steeped in some form of alchemical mystery. There is also a tendency to evoke special explanations for some of the phenomena observed, as if they were somehow outside the legitimate realm of classical orthodoxy. Such implications are misleading. Although we do not yet have a complete and detailed understanding of this area of science, a great deal is already established with a fair degree of certainty. Hydrothermal zeolite synthesis is a multiphase reaction-crystallization process, commonly involving at least one liquid phase and both amorphous and crystalline solid phases. Although the complexity of the system underlines the need for careful observation and analysis, it should not be necessary to invoke any "zeolite-specific" explanations beyond those provided by the normal physical laws.[11]

B. The Historical Development of Hydrothermal Zeolite Synthesis: Structure and Scope of this Review

In this survey, an account is given of the main discoveries and advances in thinking in the field of zeolite synthesis from the 1940s up to late 2002. Some of the early work is treated in greater depth than that afforded to some later items. This is partly because it is not now so well-known and partly to emphasize the astonishing insight of the pioneers, who, working without the benefit of present-day methods of characterization, penetrated almost to the core of the problems surrounding zeolite synthesis. The text is confined to hydrothermal methods of synthesis and concentrates on aluminosilicate zeolites, mentioning alternative zeotypes or other porous materials only when this is necessary to illustrate or broaden the main argument. While it is not possible to offer a comprehensive account of the totality of the synthetic work carried out over so long a period, it is hoped that at least some mention of all the more important developments has been included. Fortunately, many areas of the subject have been reviewed elsewhere (Table 1).

This present survey is principally concerned with the pattern of discovery and the consequent progression of ideas. Discussion of our current perception of the mechanism of zeolite synthesis is limited to this evolutionary context. However, by drawing upon this assembly of information, an attempt will be made in a forthcoming study[12] to expand this critical argument and to describe in detail the most probable steps by which amorphous aluminosilicate reagents are converted to crystalline molecular sieves.

II. 1940s and 1950s: The Founding Fathers

Reviews by Morey and co-workers[73,74] cover developments in hydrothermal chemistry from 1845 to 1937, while the general evolution of the hydrothermal preparative method from the nineteenth century to the mid-1980s is described by Rabenau.[75] The first claim to have made a named zeolite (levynite) in the laboratory was that of St. Claire Deville in 1862.[76] However, the two scientists who can justly be regarded as the founders of zeolite synthesis science and practice are pictured in Figure 2. Richard Barrer began his studies in the early 1940s, initially investigating the conversion of known mineral phases under the action of strong salt solutions at fairly high temperatures (ca. 170−270 °C). Using this approach in 1948, he synthesized the first zeolite unknown as a natural mineral—as two variants, species P and Q.[77−79] (These materials were later found to have the KFI structure[80] determined subsequently for zeolite ZK-5.[81,82]) There followed a lifetime of contributions to all aspects of zeolite science.[83,84]

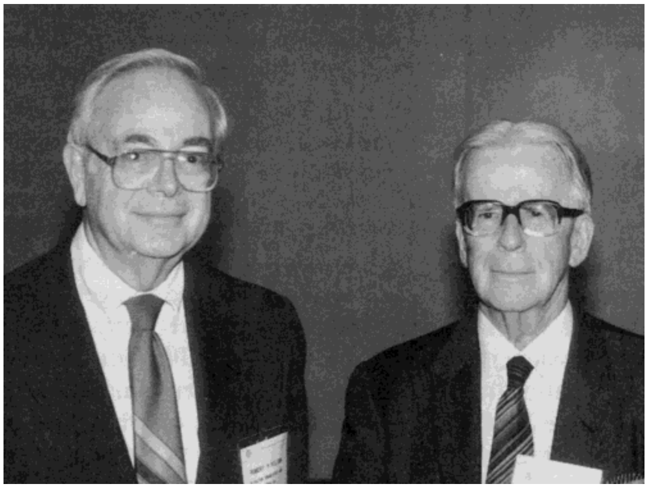


Figure 2. The Founding Fathers. R. M. Barrer (1910−1996) (right) and R. M. Milton (1920−2000) photographed by M. L. Occelli at the ACS Symposium in Los Angeles on September 22, 1988. (Reprinted with permission from ref 33. Copyright 1989 American Chemical Society.)

Robert Milton began his synthesis program in the laboratories of the Linde corporation in 1949. The use of more reactive starting materials (freshly precipitated aluminosilicate gels) enabled reactions to be carried out under milder conditions. The rate of progress was astonishing.[85] By the end of the year, zeolites A, B (now known as Na−P), and C (hydroxysodalite) had been prepared, together with a crystalline impurity designated X. In 1950, pure zeolite X (isostructural with the naturally occurring mineral faujasite) was isolated and also synthetic chabazite. The latter is notable as the original objective of both the Barrer and the Linde groups, since the scarce natural counterpart was the only material known at that time which was considered suitable for industrial separation applications, especially air separation and purification. By 1953, Milton and his colleagues (including, by that time, D. W. Breck) had synthesized 20 zeolites, including 14 unknown as natural minerals. The patents on zeolites A[86] and X[87] were filed in the same year, the publication date of 1959 reflecting the battles with the patent examiners over the novelty of these new types of materials. Many other achievements were to follow.[88,89]

III. 1960s: The Pioneers

Following the foundations laid in the 1950s, the next decade saw many significant developments, both in terms of new discoveries and also in the beginnings of investigative work aimed at gaining an understanding of the synthesis process.

In a major advance (although its full significance took a while to be appreciated), two groups of workers disclosed in 1961 the effect of introducing quaternary ammonium cations into zeolite synthesis. Barrer and Denny described amine-associated routes to zeolites A and X, the products eventually being termed "N−A" and "N−X" (although designated "N−Q" and "N−

Table 1. Reviews and Surveys Relating to Zeolite Synthesis

author(s)	year	title	ref
Barrer	1966	Mineral synthesis by the hydrothermal technique	13
Barrer	1968	Synthesis of molecular sieve zeolites	14
Zhdanov	1971	Some problems of zeolite crystallization	15
Flanigen	1973	A review and new perspectives in zeolite crystallization	16
Breck	1974	The synthetic zeolites (Chapter 4 of book)	1
Robson	1978	Synthesising zeolites	17
Rollmann	1979	Templates in zeolite crystallization	18
Sand	1980	Zeolite synthesis and crystallization	19
Barrer	1981	Zeolites and their synthesis	20
Barrer	1982	Hydrothermal chemistry of zeolites (book)	2
Barrer	1983	Zeolite synthesis: some chemical aspects	21
Lok, Cannan, & Messina	1983	The role of organic molecules in molecular sieve synthesis	22
Lechert	1984	New routes in zeolite synthesis	23
Rollmann	1984	Synthesis of zeolites, an overview	24
Barrer	1985	Synthesis of zeolites	25
Thompson & Dyer	1985	Mathematical analyses of zeolite crystallization	26
Moretti, Contessa, & Padovan	1985	Zeolite synthesis in the presence of organic components	27
Bajpai	1986	Synthesis of mordenite type zeolite	28
Guth & Caullet	1986	Zeolite synthesis − status and future prospects	29
Jacobs & Martens	1987	Synthesis of high-silica aluminosilicate zeolites (book)	30
Lowe	1988	Synthesis mechanisms for zeolites and molecular sieves	31
Barrer	1988	Zeolite synthesis: an overview	32
Occelli & Robson (Eds)	1989	Zeolite synthesis (symposium proceedings)	33
Barrer	1989	Zeolites: their nucleation and growth	34
Keijsper & Post	1989	Precursors in zeolite synthesis − a critical review	35
Guth et al.	1989	Zeolite synthesis in the presence of fluoride ions	36
Bell	1989	Applications of NMR spectroscopy to the study of zeolite synthesis	37
McCormick & Bell	1989	The solution chemistry of zeolite precursors	38
Kessler	1989	Recent advances in zeolite synthesis	39
Di Renzo et al.	1989	Are the general laws of crystal growth applicable to zeolite synthesis?	11
Szostak	1989	Hydrothermal zeolite synthesis (Ch. 2 of book), Process of zeolite formation on a molecular level (Ch. 3)	3
Knight	1990	Are zeolite secondary building units really red herrings?	40
Guth et al.	1990	New mobilizing and templating agents in the synthesis of crystalline microporous solids	41
Zhdanov, Khvoshchev, & Feoktistova	1990 (1981)	Synthetic zeolites: crystallization (book)	42
Jansen	1991	The preparation of molecular sieves: (a) Synthesis of zeolites	43
Jacobs	1992	Some thermodynamic and kinetic effects related to zeolite crystallization	44
Gilson	1992	Organic and inorganic agents in the synthesis of molecular sieves	45
Davis & Lobo	1992	Zeolite and molecular sieve synthesis	46
Thompson	1992	Population balance analysis of zeolite crystallization	47
Occelli & Robson (Eds)	1992	Synthesis of microporous materials (symposium proceedings)	48
Kessler	1993	Recent advances and perspectives in molecular sieve synthesis	49
Feijen, Martens & Jacobs	1994	Zeolites and their mechanism of synthesis	50
Livage	1994	Sol−gel chemistry and molecular sieve synthesis	51
Gonthier & Thompson	1994	Effects of seeding on zeolite crystallization, and the growth behavior of seeds	52
Kessler, Patarin & Schott-Darie	1994	The opportunities of the fluoride route in the synthesis of microporous materials	53
Davis	1995	Strategies for zeolite synthesis by design	54
Lewis, Catlow & Thomas	1997	Application of computer modeling to the mechanisms of synthesis of microporous catalytic materials	55
Cox, Casci & Stevens	1997	Molecular modeling of templated zeolite synthesis	56
Morris & Weigel	1997	The synthesis of molecular sieves from nonaqueous solvents	57
Occelli & Kessler (Eds)	1997	Synthesis of porous materials (symposium proceedings)	58
Coker et al.	1998	The synthesis of zeolites under micro-gravity conditions: a review	59
Catlow et al.	1998	Computer modeling of nucleation, growth and templating in hydrothermal synthesis	60
Thompson	1998	Recent advances in the understanding of zeolite synthesis	61
Cundy	1998	Microwave techniques in the synthesis and modification of zeolite catalysts	62
Francis & O'Hare	1998	The kinetics and mechanisms of the crystallization of microporous materials	63
Weller & Dann	1998	Hydrothermal synthesis of zeolites	64
Cheetham, Férey & Loiseau	1999	Open-framework inorganic materials	65
Millini, Perego & Bellussi	1999	Synthesis and characterization of boron-containing molecular sieves	66
Camblor, Villaescusa, & Díaz-Cabañas	1999	Synthesis of all-silica and high-silica molecular sieves in fluoride media	67
Matsukata et al.	1999	Conversion of dry gel to microporous crystals in gas phase	68
Guth & Kessler	1999	Synthesis of aluminosilicate zeolites and related silica-based materials	69
Fricke et al.	2000	Incorporation of Ga into zeolites: syntheses, properties & catalysis	70
Serrano & van Grieken	2001	Heterogeneous events in the crystallization of zeolites	71
Balkus	2001	Synthesis of large pore zeolites and molecular sieves	72

R" in the original paper).[90] Kerr and Kokotailo published[91] data on a silica-rich version of zeolite A named ZK-4 (Si/Al up to 1.7) although no mention of its method of preparation was made in the open literature until a later publication.[92] Interestingly, Barrer and Denny predicted, but did not themselves confirm, the silica-rich nature of these materials. Their surmise was based on the low nitrogen content of the products and the difficulty of accommodating sufficient of the bulky R_4N^+ cations to balance the accustomed framework charge. Both groups filed patents on their discoveries, the Barrer patent[93] being a little earlier than that of their Mobil competitors.[94]

It is doubtful whether anyone in 1961 could have appreciated the full significance of the application of organic components in zeolite synthesis. However, the key step followed quite rapidly in 1967[95] with the disclosure of the first high-silica zeolite, zeolite β ($5 < \text{Si/Al} < 100$), made using the tetraethylammonium cation. The first zeolite with a silica content far beyond anything known hitherto in nature or the laboratory had been made.

A. Early Views of the Synthesis Mechanism

At the ACS Inorganic Chemistry Meeting in Cleveland, Ohio, in April 1960, Edith Flanigen and Donald Breck presented a remarkable paper entitled "Crystalline Zeolites, V. Growth of Zeolite Crystals from Gels". In this report[96,97] the authors sought to elucidate (1) the formation of the aluminosilicate gel or reaction mixture and (2) the nucleation and growth of zeolite crystals from the reaction mixture. In what was almost certainly the first study of its type, the authors used XRD measurements to follow the crystallization with time of zeolite Na−A (at 100 °C) and Na−X (at 50 °C and 100 °C). They showed the now-familiar S-shaped growth curves and described an induction period followed by a sudden rapid growth. The morphological changes observed[98] were interpreted as a successive ordering of the gel as crystallization proceeds, leading to a conclusion that crystal growth takes place predominantly in the solid phase.

Only the Abstract[96] from the Cleveland paper was published, although sections from the full paper did appear in later publications.[1,99,100] The final paragraph of the Abstract (quoted in full or in part several times (e.g., refs 101 and 102)) reads:

> "A mechanism of crystal growth is proposed; extensive heterogeneous nucleation occurs during formation of the highly supersaturated gels. Crystal growth in the solid phase then proceeds by a series of depolymerization-polymerization reactions, catalyzed by excess hydroxyl ion. There is no significant solution of the solid phase during crystallization."

However, this summary does not fully reflect the authors' views (see Appendix I), since in their complete discussion they state that "growth of the crystal proceeds through a type of polymerization and depolymerization process which involves both the solid and liquid phases",[97] mentioning also the polyhedral building units suggested earlier by Barrer et al.[103]

In a subsequent review,[99] Breck gave what is believed to be the first schematic representation of zeolite formation (Figure 3). The gel structure is depolymerized by hydroxide ions. Rearrangement of the aluminosilicate and silicate anions present in the hydrous gel is brought about by the hydrated cation species present. Tetrahedra regroup about hydrated sodium ions to form the basic polyhedral units (24-hedra). These then link to form the massive, ordered cystal structure of the zeolite. A very similar scheme appeared later in Breck's book (p. 341).[1] At around this time, Barrer also considered that the growth of aluminosilicate crystals from alkaline media was unlikely to proceed by the capture of single monomeric silicate and aluminate tetrahedral ions TO_4^{n-} since "in the elaborate porous crystalline structures of the zeolites, for instance, it would seem difficult for the lattice to persist in its very open pattern when rapidly adding such small units".[13] He felt that "a plausible process would be the accretion in simple coordination of polygonal or polyhedral anions by condensation polymerization", giving as examples the 4-ring, 6-ring, cube, and hexagonal prism.

Several authors responded to the stimulus provided by these early studies, and among these, the paper published by George Kerr in 1966 stands as one of the classics of the zeolite synthesis literature.[101] He describes an experiment carried out before the observations of Breck and Flanigen were made public and designed to test the hypothesis that[104] "a zeolite could be formed via dissolution of gel by sodium hydroxide solvent followed by deposition of zeolite crystals from gel-derived species in solution." In the experiment, shown conceptually in Figure 4 (note that this is not a diagram found in the original paper), a sodium hydroxide solution at 100 °C was circulated through two filters. The first (filter A) contained a specially prepared amorphous sodium aluminosilicate and the second (Filter B) held crystals of zeolite Na−A. When the experiment was terminated after about 4 h, nearly all of the amorphous solid had been dissolved and the zeolite sample (estimated to be essentially 100% zeolite A by water sorption) had approximately doubled in mass. From these (and other[101]) observations, it was concluded that

> "amorphous solid dissolves rapidly in the alkaline solution to form a soluble active species. The concentration of this species remains constant during most of the growth period but decreases sometime during the last half, as the amorphous substrate is depleted. This depletion explains the decrease in the slope of the [growth] curves near completion of reaction. The rate-determining step is the reaction of the soluble species with nuclei or zeolite crystals to yield zeolitic product:
>
> $$\text{amorphous solid} \xrightarrow{\text{fast}} \text{soluble species (S)}$$
>
> $$\text{(S)} + \text{nuclei (or zeolite crystals)} \xrightarrow{\text{slow}} \text{zeolite-A"}$$

Largely as a result of the 1960 Union Carbide Abstract[96] and the 1966 Mobil paper,[101] an unfortu-

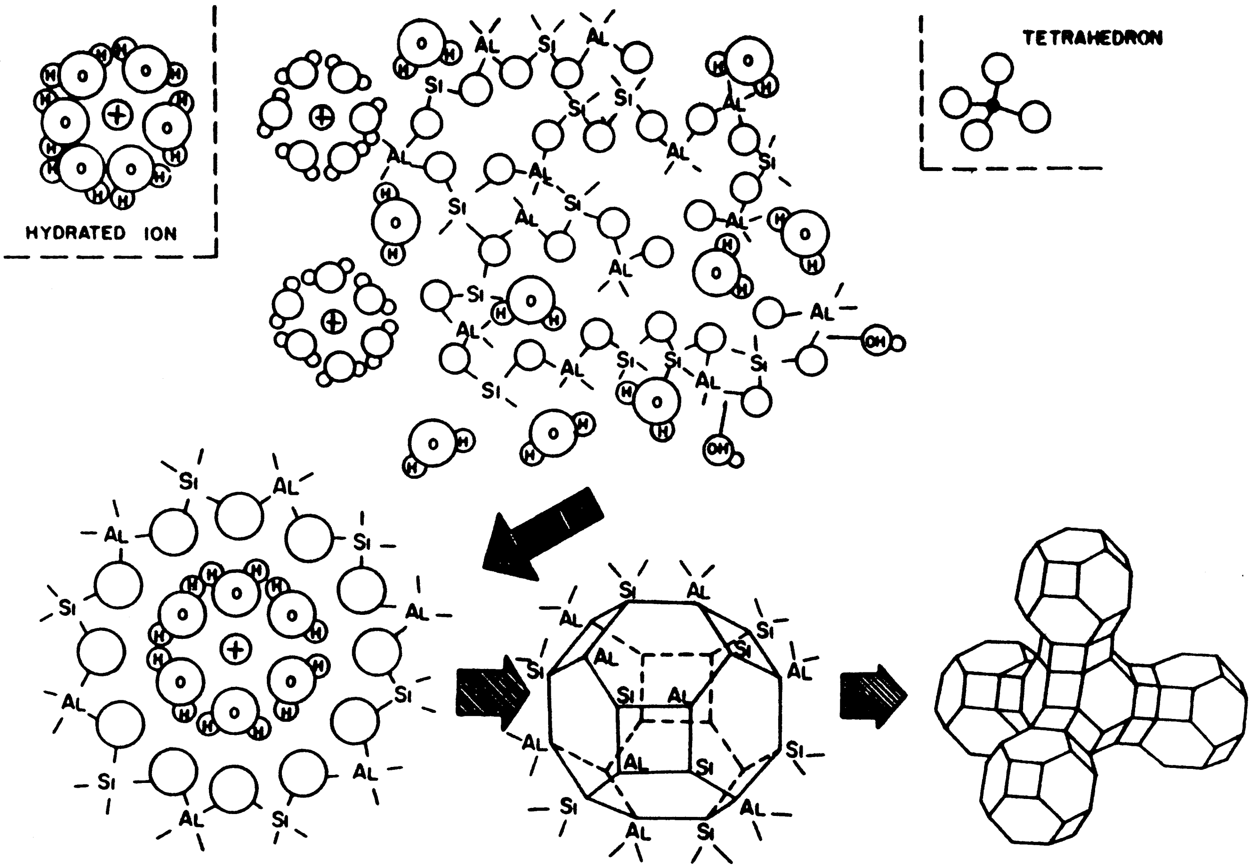


Figure 3. The first pictorial depiction of zeolite synthesis (D. W. Breck). "Schematic representation of the formation of zeolite crystal nuclei in a hydrous gel". (Reprinted with permission from ref 99. Copyright 1964 Division of Chemical Education, Inc., American Chemical Society.)

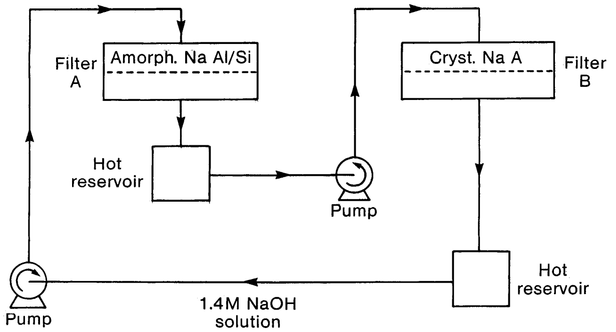


Figure 4. The classic dissolution/crystallization experiment of G. W. Kerr (1966) (ref 101, conceptual realization by the present authors). The circulating alkaline solution dissolved the amorphous material on Filter A, while the mass of zeolite A on Filter B increased.

nate controversy has grown up concerning the nature of the zeolite synthesis mechanism. A useful summary of the divergence of opinion was provided by Caullet and Guth in 1986[29] and revisited more recently.[69] As illustrated diagrammatically in Figure 5, at one extreme the amorphous precursor ("gel") is dissolved to yield small soluble species from which the product crystals grow by a solution-mediated mechanism. In the other limiting case, the zeolite lattice is formed via an in situ rearrangement (ordering) of the gel, apparently in the absence of solution participation. However, Breck and Flanigen clearly did not believe the solution phase to be a mere spectator in the synthesis process[97] (see Appendix I), while Kerr stressed[104] that what he had shown may not universally apply. The true situation involves both solution and solid phases in a cooperative process, as discussed elsewhere.[12]

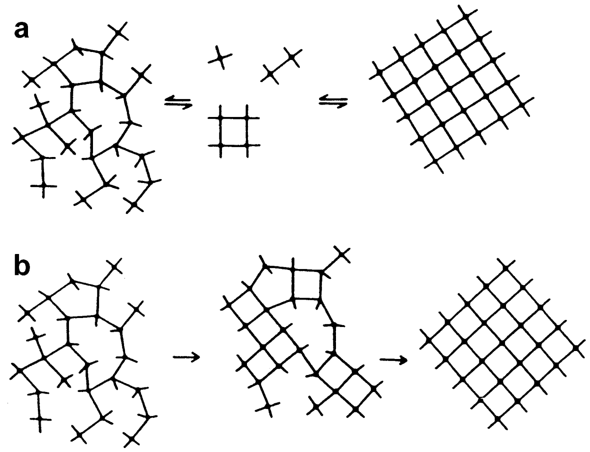
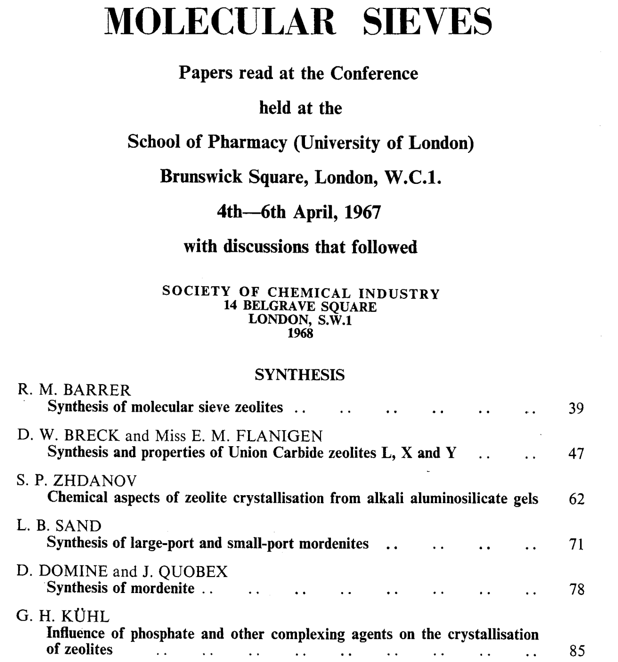


Figure 5. The two extreme views of the zeolite synthesis mechanism as pictured by Caullet and Guth in 1986: (a) zeolite formation through gel dissolution and solution-mediated crystallization, (b) zeolite formation by "in situ" rearrangement of the gel. (Reprinted with permission from ref 29. Copyright 1986 Société Française de Chimie.)

B. First International Conference, London, 1967

The state of knowledge in zeolite science and technology toward the end of the sixties is well



MOLECULAR SIEVES

Papers read at the Conference
held at the
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4th—6th April, 1967
with discussions that followed

SOCIETY OF CHEMICAL INDUSTRY
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LONDON, S.W.1
1968

SYNTHESIS

R. M. BARRER
Synthesis of molecular sieve zeolites 39
D. W. BRECK and Miss E. M. FLANIGEN
Synthesis and properties of Union Carbide zeolites L, X and Y 47
S. P. ZHDANOV
Chemical aspects of zeolite crystallisation from alkali aluminosilicate gels 62
L. B. SAND
Synthesis of large-port and small-port mordenites 71
D. DOMINE and J. QUOBEX
Synthesis of mordenite 78
G. H. KÜHL
Influence of phosphate and other complexing agents on the crystallisation of zeolites 85

Figure 6. Extracts from the published Proceedings of the 1967 London Meeting, showing the Synthesis section. This symposium led directly to the formation of the IZA. (Reprinted with permission from ref 105. Copyright 1968 Society of Chemical Industry.)

illustrated by the papers presented at a meeting held in London in 1967. This symposium led directly to the formation of the International Zeolite Association (IZA) and was to become the first in a continuing series of International Conferences organized under the auspices of that body (first IZC). The Synthesis section from the contents pages of the published proceedings[105] is reproduced in Figure 6.

Barrer's paper was concerned mainly with the outcome of syntheses in terms of crystallization fields. It also contains an early account of his quantitative treatment of the zeolite reaction product as a sorption complex in which the porous crystals are stabilized thermodynamically by the presence of water or salts as guest molecules. (These ideas were subsequently developed in a number of ways[106] which included the concept of water as a "space catalyst", facilitating the formation of the porous tectosilicate framework through lattice stabilization but subsequently removable unchanged without alteration of the framework topology.) Breck and Flanigen present a comprehensive (for its time) account of the synthesis and properties of zeolites L, X, and Y. However, discussion of mechanism is very limited, although some elements of the 1960 Cleveland paper (e.g., the growth curves and activation energies) do appear in print for the first time. Particularly interesting are the early ideas of Zhdanov, most of whose carefully considered work had been published only in Russian at that point. His group had investigated the gel, solution, and crystal composition during zeolite synthesis and shown the importance of the composition of the solution phase but had not yet formulated the ideas on mechanism which were to be so influential later (see section IV.D). An appreciation of the life and work of Sergey Petrovich Zhdanov has recently appeared on the occasion of his 90th birthday.[107]

Sand's account of his pioneering work on mordenite was also essentially factual. However, in an interesting pre-echo of Sand's later work, the Air Liquide representatives gave a detailed account of mordenite synthesis with growth curves derived from nitrogen sorption data. They also discussed, but did not actually calculate, how activation parameters could be obtained from these curves. Kühl's paper is both interesting in itself and for its significance in the light of later events.[108] At that time, Kühl, in reply to a question from Breck, stated that he had found no evidence for phosphorus substitution in tetrahedral atom sites.[109] In a further question, D. P. Shoemaker suggested that "it might be possible to make 'zeolites' containing tetrahedral PO_4 groups in the framework by a synthesis in an acid medium (syrupy phosphoric acid) somewhat analogous to the present alkaline syntheses of zeolites",[109] a prediction fulfilled 15 years later (section V.A).

Although a separate publication and unconnected with the 1967 London meeting, mention must be made at this point of the paper "Kinetics of Zeolite A Crystallisation" by Julius Ciric,[102] whose untimely death clearly robbed zeolite science of one of its most able proponents. This remarkable report presented the most detailed study of zeolite synthesis published at that date. Kinetic curves were determined from water sorption and chemical analyses were carried out on reaction filtrates. In addition, data were obtained by particle counter, optical microscopy, and BET surface area methods. It is impossible to summarize in a few words the insights provided by this paper. However, in essence the work adds to and greatly expands the ideas set out in the Kerr report,[101] pointing to a solution-mediated growth mechanism modified by the presence of the gel phase (so that transport of growth species to crystals embedded in gel is restricted by diffusion through the gel).

IV. 1970s: High-Silica Zeolites and the Growth of Systematic Studies

If the world had been a little slow to appreciate the significance of the discovery of zeolite β in 1967,[95] this was certainly corrected in the next decade which saw a tremendous growth in work on high silica zeolites. Most of the well-known materials (e.g., from the EU, NU and ZSM series[3]) were patented in the 1970s or early 1980s. The key to this acceleration in interest was the discovery of ZSM-5 and the publication of the first patent in 1972.[110] At the same time, the 1970s saw an expansion of ideas on zeolite synthesis and the growth of systematic studies of kinetics and mechanism.

A. ZSM-5

The original patent on ZSM-5[110] disclosed a material of composition

$$0.9 \pm 0.2\ M_{2/n}O:W_2O_3:5-100\ YO_2:zH_2O$$

where M is a cation of valence n, W is Al or Ga, Y is Si or Ge, and $z = 0-40$.

The examples were all based on a mixture of tetrapropylammonium (TPA) and sodium cations using a synthesis temperature of 125−175 °C for a reaction time of 5−9 days. It is interesting to contrast these reaction conditions with those of a recently reported microwave synthesis[111] which could be completed in about 3 min at similar temperatures − perhaps an indication of the extent of progress in both theory and practice during the intervening years.

In 1978, an article appeared in *Nature* which was to have wide-ranging consequences. A new polymorph of silica (silicalite, refractive index 1.39, density 1.76 g cm^{-3}) was found to have a novel tetrahedral framework enclosing a three-dimensional system of intersecting channels defined by 10-T-atom rings wide enough to absorb molecules up to 0.6 nm in diameter.[112] The material was prepared by hydrothermal synthesis using alkylammonium (for example TPA) cations.[112,113] In fact, the material was (nominally) Al-free ZSM-5, and the ensuing legal battle over definitions, ownership, and patent rights was most regrettable in that it dissipated the resources of two major companies and imposed a great strain upon many sincere and hard-working scientists and their colleagues. However, the concept of silicalite was very significant in that it brought about a number of important realizations, namely:

1. High-silica zeolites are essentially impure silica polymorphs and bear at least as much relationship to silicas as they do to Al-rich zeolites, feldspars and similar aluminosilicates.
2. High-silica zeolites are intrinsically hydrophobic and organophilic, a trend which reverses only with increasing aluminum content as their surface polarity and cation content increases.
3. For a given structure, there is usually a smooth transition in properties as the aluminum content is varied from zero to a limiting value,[114] thus generating families of isostructural materials.
4. Traces of aluminum are likely to be incorporated into the lattice in tetrahedral positions, as may be confirmed by ^{29}Si and ^{27}Al MAS NMR spectroscopy.[115]
5. Proposals for the mechanism of synthesis of highly siliceous zeolites must cover the whole family of compositions since it is very unlikely that the presence or absence of a small quantity of aluminum will radically alter the manner in which the structure comes together.

B. Synthesis of ZSM-5 in the Absence of Organic Compounds

Following the discovery of ZSM-5,[110] there developed a belief that this zeolite could only be made using a suitable organic template (usually TPA) or through the addition of existing ZSM-5 seeds. (Interestingly, the latter admission implies that the zeolite will grow but not nucleate in the absence of an organic template.) The first publication to disprove this by demonstrating substantial yields of well-crystallized ZSM-5 from the $Na_2O-SiO_2-Al_2O_3-H_2O$ system appears to be that initiating the series of patents by Grose and Flanigen,[116−118] although Chao, in very early work on ZSM-5 synthesis, also reported the formation of partially crystalline ZSM-5 from a sodium aluminosilicate system in the absence of any organic compound.[119,120] Even after the publication of these results, a remnant of opinion attributed the reaction products to the effects of adventitious seeding. At least two laboratories (ICI,[121] Union Carbide[122]) put this to the test by carrying out successful syntheses of organic-free Na−ZSM-5 in new equipment which had never previously been used for zeolite synthesis. Many papers have since been published on inorganic ZSM-5,[120,123] and this synthetic result is significant for a number of reasons. First, the synthesis shows that Na−ZSM-5 is essentially a sodium zeolite[123,124] and no different from other sodium zeolites such as A, X, or mordenite. This observation provides a link between high-silica zeolites and the traditional, more aluminous varieties and suggests that there is in principle no fundamental difference between them nor is there likely to be any fundamental difference between their mechanisms of formation. Furthermore, it is clear that the ZSM-5 structure can nucleate and grow perfectly well in the absence of organic materials so that any suggested mechanism of formation must take this into account. The range of compositions over which the inorganic structure can be formed is much reduced in comparison with that of Na,TPA−ZSM-5. This is only to be expected since the individual precursors which crystallize ($Na-ZSM\text{-}5{\cdot}xH_2O$ and Na,TPA−ZSM-5) are different materials with different free energies. The inorganic product is void-filled only with hydrated cations and will be more soluble (in water) than the tetrapropylammonium organic clathrate complex.

C. Some Other Important Discoveries of the 1970s

Although the 1970s were notable primarily for the growing number of high silica zeolites, there were other important discoveries in the areas of materials and synthetic methods.

1. Use of F^- as a Mineralizer in Zeolite Synthesis

From the development of the low-temperature gel synthesis around 1950 up to 1978, nearly all zeolite syntheses had shared a similar chemistry in which hydroxide ion acted as mineralizer in high pH hydrothermal conversions. However, there is no reason other mineralizing agents should not be used to mobilize reaction components, and in 1978 a patent to Flanigen and Patton demonstrated the use of fluoride ion in the synthesis of silicalite.[125] This procedure lay dormant for some time but has in recent years come to great prominence, particularly in the synthesis of large crystals, novel structures and heterosubstituted materials.[36,39,41,45]

2. Polymeric Templates

This is another area which became becalmed after launch[18,126] but is now showing promise once again.[127,128] The original work was carried out by Rollmann and colleagues, employing a series of 1,4-diazbicyclo[2.2.2]octane-based polyelectrolytes.[18,126]

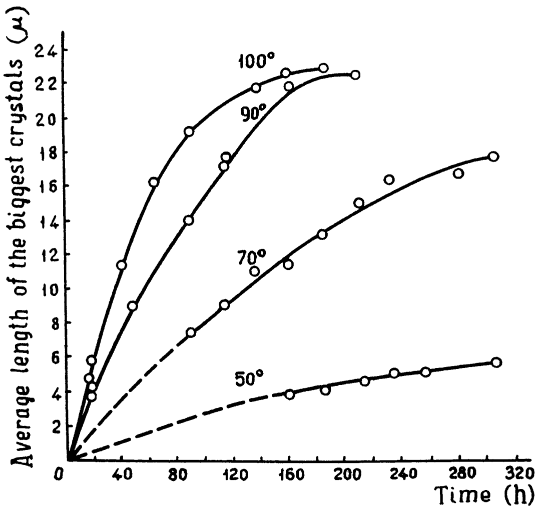

Figure 7. The first measurement of zeolite crystal linear growth rates (Zhdanov, 1970). Growth of zeolite A from gels of the same composition at different temperatures. (Reprinted with permission from ref 15. Copyright 1971 American Chemical Society.)

This must at first have seemed an attractive breakthrough but the initial promise was not fulfilled. No completely new materials were produced and the polymeric templates are believed to have proved difficult to burn out of the structures. The area is one of considerable mechanistic challenge since the chain lengths of the (preexisting) polymers are such that they must extend through, and be encapsulated by, many framework unit cells. Any explanation of the formation process must explain how an entire crystal can be assembled under these conditions.

3. Mazzite—First Synthetic Phase Found as a Mineral

Since the earliest days of zeolite synthesis, laboratory products have been found which possess the same structure as known natural minerals. However, in 1974 there occurred the first (of several) cases in which a newly discovered zeolite mineral was found to have the same structure as an existing synthetic phase. In this case, mazzite from Mont Semiol, France[129] was determined to be isostructural with the tetramethylammonium aluminosilicate ZSM-4[130] which itself was essentially the same as the independently synthesized zeolite omega.[131]

D. Advances in the Study and Understanding of Zeolite Synthesis

No account of zeolite science in the 1970s could be complete without noting the appearance in 1974 of "Zeolite Molecular Sieves—Structure, Chemistry and Use" by D. W. Breck.[1] It is a measure of Breck's achievement to consider how many such books remain (unrevised) standard texts nearly thirty years since they first appeared.

Some striking advances in thinking and technique occurred between the first IZC meeting in 1967 (section III.B) and the second Conference in 1970. In the proceedings of the latter, Zhdanov reported the first measurements on crystal linear growth rates (Figure 7: zeolite A, 2−20 μm, 50−100°C).[15] These showed directly for the first time the effect of temperature in increasing growth rate and that the crystals grew at a near-constant rate over the majority of the synthesis period. Moreover, by working back from the product crystal size distribution and assuming a constant linear growth rate under fixed conditions, Zhdanov was able to deduce the nucleation rate profile over the course of the reaction (Figure 8). This enabled him to begin to separate the contributions of nucleation and growth to the overall growth curve, a task he completed in a later classic paper.[132] These considerations, together with measurements of chemical changes in the solution phase of the reaction mixture and detailed consideration of such phenomena as the induction period and seeding effects, led to the schematic representation of zeolite crystallization shown in Figure 9. In this view, the solid and liquid phases are connected by the solubility equilibrium. Condensation reactions give rise to "primary aluminosilicate blocks (four- and six-membered rings)" and crystal nuclei. Crystal growth occurs from solution until dissolution of the amorphous phase is complete. Analytical data supported the proposition that the composition of the crystals depended on that of the liquid phase from which they crystallized.

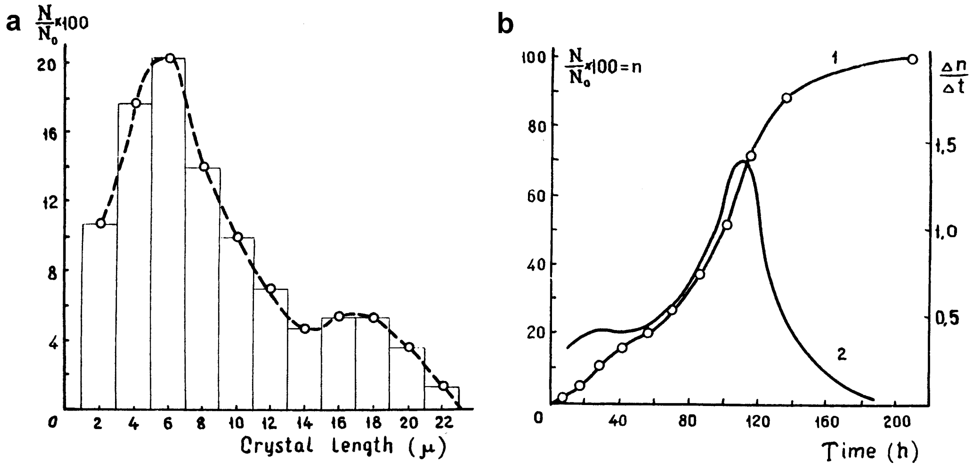

Figure 8. Crystal size distribution (a) and consequent nucleation profile (b) for zeolite A crystallization at 90 °C (Zhdanov, 1970). In panel b are shown (1) the growth in the number of nuclei and (2) the change in the rate of their formation. (Reprinted with permission from ref 15. Copyright 1971 American Chemical Society.)

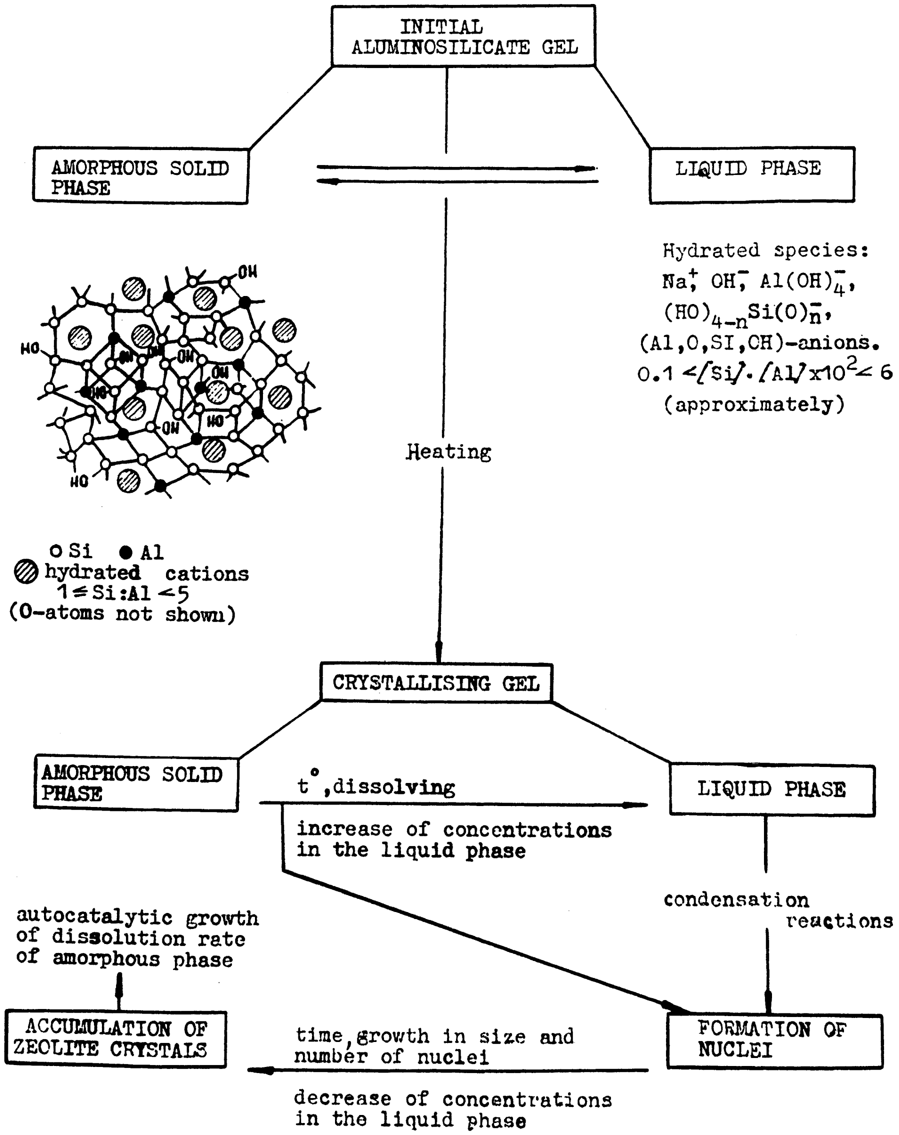

Figure 9. "Schematic representation of aluminosilica gel crystallization". (Zhdanov, 1970). (Reprinted with permission from ref 15. Copyright 1971 American Chemical Society.)

In 1973, Culfaz and Sand introduced a simple method for calculating apparent activation energies for zeolite nucleation and growth.[133] In essence, this consists of assuming that the rate-limiting step is crystal growth and measuring this as the percentage conversion per hour at the highest rate (50% conversion), where the assumption has the greatest validity. An Arrhenius plot of this value as a function of temperature gives an activation energy for growth, E_g. A similar treatment of nucleation rate, taken as the reciprocal of the induction period, gives an activation energy for nucleation, E_n (Figure 10). This approach has been justly criticized[134,135] since the figures obtained are compound values with many variables rolled up inside them. Its great advantage is its simplicity, and provided that the pitfalls are appreciated, the method does provide a semiquantitative comparison of significant parameters for a set of reactions in a series, e.g., when a single reaction mixture is crystallized at a series of temperatures. Beyond this, great caution is necessary, as can be seen from the huge range of activation energy values reported in the literature for ZSM-5 syntheses, some of which are chemically implausible. When carried out carefully, the E_g measurements are probably fairly realistic since they correspond quite well to the more reliable values obtained from crystal linear

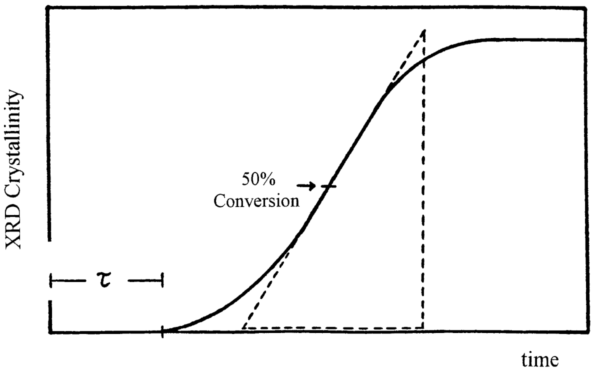

Figure 10. The two parameters used by Culfaz and Sand in their derivation of apparent activation energies for nucleation and growth (ref 133). Nucleation rate is taken as the reciprocal of the induction time ($1/\tau$) and crystallization rate as the slope of the crystallinity curve at 50% conversion.

growth measurements (see, e.g., ref 135 and references therein). The E_n values are more problematic, since so many factors can influence induction times. However, this is a very difficult parameter to measure and even now there are no reliable published values obtained by alternative methods.

In the mid 1970s, Kacirek and Lechert published the first[136,137] in a series of distinguished papers on zeolite synthesis, concentrating principally on understanding the formation of faujasite. The reports present a large quantity of high quality data. Growth rate constants (k, dimension l/t) were not determined directly from size measurements of growing crystals but were calculated from % crystallinity and final size:

$$k = [(x/x_o)^{1/3} - 1]\,\bar{r}_o/t$$

where x is the mol fraction for the amount of faujasite already crystallized (mol = formula unit $NaAlO_2 \cdot nSiO_2$) and x_0 is the mol fraction at time $t = 0$ (equal to the amount of seed crystals of average radius $\bar{r}_o$ suspended in the gel). However, these measurements provided the first accurate quantitative evidence of (for example) the qualitative observation that the formation rate of faujasite decreases as the material becomes more siliceous:

$$\begin{aligned} k &= 0.2\ \mu\text{m/h} && (\text{Si/Al} = 1.4) \\ &\quad 0.00053\ \mu\text{m/h} && (\text{Si/Al} = 3.4) \end{aligned}$$

A further important point established in these papers concerns the control of nucleation and particle size. In a series of experiments, the growth of faujasite was controlled by working in an area of the phase diagram in which the FAU phase would grow but not nucleate (the spontaneous product being NaP1). By adding different quantities of faujasite seed crystals, the product particle size could be controlled with considerable accuracy (Figure 11), and a similar result was obtained in an experiment where the quantity of seed was kept constant but its crystal size was varied.

In a landmark paper reminiscent of that of Ciric in 1968,[102] Freund in 1976 published an extraordinarily comprehensive paper entitled "Mechanism of the Crystallisation of Zeolite X".[138] As with the Ciric report, it must be left to the reader to discover the treasures of this publication but in summary two different nucleation mechanisms are proposed, linear growth rates are measured directly and relative growth rates are given for faujasite, zeolite P and mordenite. In addition, both clear solution synthesis and room-temperature growth are described, together with a detailed account and interpretation of the effects of stirring. The overall rationale is that of a solution-mediated reaction-crystallization process.

Finally, mention is made of three papers relevant to the role of the solid phase in zeolite synthesis. A very interesting observation was made by Aiello, Barrer, and Kerr using electron microscopy to monitor the changes in very dilute reaction mixtures.[139] From the clear solutions, the solid phase appeared initially as laminae, mostly amorphous. Crystalline material was then seen in the laminae which began to develop holes and gaps, presumably through partial dissolution. Finally, the laminae were completely replaced by zeolite crystals. Thus, heterogeneous nucleation appeared to occur on gel lamellae which separated at an early stage from the solution phase. Some spectroscopic studies of zeolite synthesis were beginning to appear at this time, and in 1972 workers from the Shell Amsterdam laboratories reported studies of zeolites A and X synthesis by phosphorescence and laser Raman spectroscopy. Their results "were indicative of a zeolite crystallisation in the solid gel phase".[140,141] However, in a much more thorough later study, Angell and Flank from the Union Carbide laboratories deduced a "mechanism involving formation and subsequent dissolution of an amorphous Al−Si intermediate, with solution transport from the gel to the growth surface of the crystallite".[142]

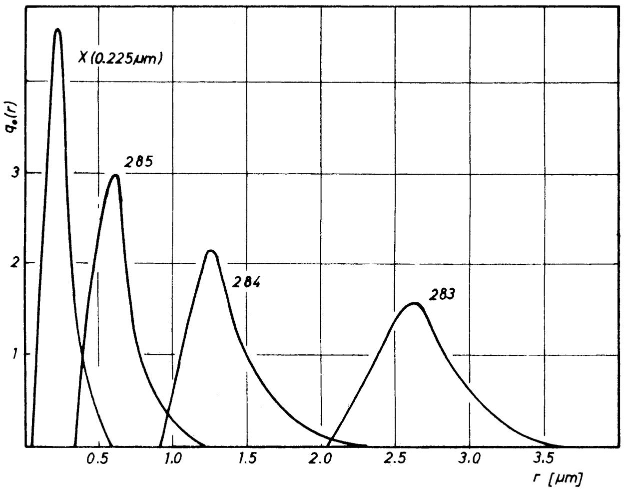

Figure 11. Distribution density curves of the radii of Na−Y particles grown using the same reaction composition but with different quantities of seed crystals (Kacirek and Lechert, 1975). The crystal sizes of the seeded reactions (numbered) corresponded well to the quantity of seed crystals (x) added (run 285, 4.4% seeds; 284, 0.44%; 283, 0.044%), showing that particle numbers were not increased by the nucleation of new crystals under these conditions. (Reprinted with permission from ref 136. Copyright 1975 American Chemical Society.)

V. 1980s: AlPO$_4$s and the Decade of Spectroscopy

The 1980s were characterized by the discovery of a completely new family of molecular sieves, the aluminophosphates ($AlPO_4$s), and by the rapidly increasing application of improved spectroscopic methods to the study of zeolite synthesis. Among other advances, better quantitative descriptions of the synthesis process in the form of mathematical models were developed, and there was the emergence of "global" investigations in which a wide variety of characterization methods were brought simultaneously to bear on a synthetic problem.

A. AlPO$_4$ Molecular Sieves and the Breaking of the 12-T-Ring Barrier

Just as silicalite had forced a realization of the silica-like nature of high-silica zeolites, the discovery

Table 2. Mathematical Models of Zeolite Crystallization

	model type	key features
kinetic	empirical	not based on fundamental theory arbitrary convenient (some predictive ability)
	reaction engineering	classical kinetic treatment of defined phases contains assumptions but has scientific basis some predictive capability
	population balance (chemical)	based on fundamental theory contains much information predictive
thermodynamic	equilibrium	based on fundamental theory no kinetic information predictive

of the $AlPO_4$ family[143,144] demonstrated that microporous materials need not contain any silica at all. Any three-dimensional and appreciably covalent framework could probably be persuaded to behave similarly. Furthermore, the subsequent finding that a large number of other elements could be substituted into $AlPO_4$ frameworks (giving the SAPO and MeAPO series of materials)[3,4] lent credibility to earlier claims of heterosubstitution into the frameworks of zeolites themselves. Although same-group substitutions or replacements (e.g., Ga for Al, Ge for Si) had been respectable for some time, claims for ferrisilicates, chromosilicates, and the like[3] had been treated with considerable scepticism.[145,146] It now began to be realized that, although substitution of widely different elements (e.g., transition metals) into aluminous zeolites was indeed either difficult or impossible, such substitutions, albeit at modest levels, were quite possible into materials of lower lattice charge such as the silica-like high-silica zeolites.

It also soon became apparent that other barriers could be broken by new materials having greater flexibility in bond lengths, bond angles, and coordination number. Up to this point, the largest rings found in the frameworks of either natural or synthetic zeolites contained 12 T-atoms. This limited applications in sorption and catalysis to molecules no larger than about 8.5 Å.[1] Hypothetical structures (section VII.C) containing larger ring sizes had been predicted by Barrer and Villiger,[147] Smith and Dytrych,[148] and Meier.[149] Also, the natural iron phosphate mineral cacoxenite had been found to possess rings of ca. 15 Å diameter comprising oxygen-linked octahedral Fe,Al(III) units and tetrahedral phosphate groups.[150] However, the synthesis of the aluminophosphate VPI-5 in 1988 provided the first, well-characterized microporous material having 18-T-atom rings and a pore size of around 13 Å.[151] The new material was able to adsorb perfluorotributylamine (10.5 Å). In a reflection of the earlier theoretical work, the framework topology of VPI-5 was found to correspond to that of net 81(1) described by Smith and Dytrych.[148] It was perhaps a sign of the times and an interest in the potential of catalysts which might have the ability to crack larger hydrocarbons that carried rapid publicity for this discovery beyond the primary scientific journals[152] and even into the world of commerce and business affairs.[153]

B. Mathematical Models of Zeolite Synthesis

Both R. W. Thompson[154] and the late[155] B. M. Lowe[156] published their first papers on zeolite synthesis in 1980, and both went on to encapsulate their ideas in mathematical models. Such models are of great importance and utility since they represent, in a concentrated and succinct fashion, a quantitative expression of much basic theory on how such systems operate. Furthermore, the information is in such a form that it can readily be tested, both retrospectively and predictively. Mathematical models are categorized in Table 2, which is based on Table 1 in the review by Thompson and Dyer.[26] Of these, the most chemically significant are the population balance model[157] (a kinetic model) and the equilibrium model[158] (a thermodynamic model).

The population balance model[47,157] is built upon the basic equation (for a well-mixed reactor)

$$\frac{\partial n}{\partial t} + Q\frac{\partial n}{\partial L} = -\frac{n}{\tau}$$

where n is a number density function (characterizing the crystal size distribution at any time), t is time, L is crystal length, Q is the crystal linear growth rate, and τ is residence time. Further relationships set boundary conditions and the material balance. Solutions for the resulting cohort of equations can be developed to provide simulations covering a wide variety of conditions. Thus, hypothetical reactions can readily be explored to assess the effect of changing reaction variables and introducing other components such as seed crystals. Some examples of this approach are (a) prediction of zeolite crystal size distribution in batchwise hydrothermal synthesis,[159] (b) modeling the effect of gel aging,[160] and (c) the analysis of zeolite crystallization with autocatalytic nucleation.[161−163] A similar approach has subsequently been adopted by other workers.[164] Related kinetic analyses form part of the extensive studies on zeolite crystallization and dissolution published by B. Subotić and colleagues in a series of papers starting[165] in the 1980s. The evolution of zeolite crystal growth in a semicontinuous reactor has been explored by Cundy et al. in experimental and modeling studies also carried out during this period and later published.[166,167]

The equilibrium model[158] was initially developed to provide insight into the pH changes which occur

Table 3. The Equilibrium Model: Some Output Functions

pH	[base (Q^+)] = [$(HO)_3SiO^-$] + 2[$(HO)_2SiO_2^{2-}$] = $(K_1K_s/[H^+]) + (2K_1K_2K_s/[H^+]^2)$
ΔpH (difference between initial and final pH)	$\Delta pH = -F \log (K_{s,zeolite}/K_{s,gel})$, F varies from 1 (low pH) to 0.5 (high pH)
solution silica concentration	[solution silica] = [$Si(OH)_4$] + [$(HO)_3SiO^-$] + [$(HO)_2SiO_2^{2-}$] = $K_s + (K_1K_s/[H^+]) + (K_1K_2K_s/[H^+]^2)$
solution supersaturation	$\Delta G = -RT \ln(K_{s,gel}/K_{s,zeolite})$

in the course of high-silica zeolite syntheses.[168] The resulting analysis enabled the solution chemistry, and in particular the effects of solubility and pH, to be understood at a fundamental level. The model considers the zeolite synthesis process as a series of pseudoequilibria:

$$\text{amorphous solid} \leftrightarrow \text{solution species} \leftrightarrow \text{crystalline zeolite}$$

$$\xrightarrow{\text{progress of reaction}}$$

In the initial situation, amorphous solid is in equilibrium with solution species. As the reaction proceeds, this initial equilibrium is maintained while product crystals grow from the supersaturated solution. Finally, all amorphous precursor has been consumed and the crystalline zeolite equilibrates with its mother liquor.

Examples of output functions from the model are given in Table 3 (derived from ref 158). Computer modeling of the pH function provides a good simulation of the types of pH curve observed experimentally.[31] The most notable feature is the sharp rise in pH which occurs when all of the solid gel phase has been consumed and control of the solubility is transferred to the crystalline product. The ΔpH term is directly related to the difference in solubility between zeolite product and gel precursor, providing a measure of the strength of the templating effect for a series of organic additives.[169] The most effective template gives the most stable (least soluble) product and hence the largest pH rise. Solution silica concentration (and hence, by difference, product yield) can be derived from the third function shown and its value calculated as a function of alkalinity and extent of reaction.[31] The final term illustrated (ΔG) represents the solution supersaturation and hence the driving force for the crystallization reaction. This is again related to the ratio of precursor and product solubility constants (K_s).

Before leaving the topic of modeling work related to zeolite synthesis, mention should be made of the important background research carried out at around this time in the laboratories of the Mulhouse group. Following the early studies of Zhdanov,[15] this was the first work to investigate experimentally the nature of aluminosilicate solutions in relation to the solubility of zeolites and their formation.[170−172] A further aspect, closely allied to the territory of Lowe's equilibrium model,[31,158] was the investigation of speciation in silicate solutions by ^{29}Si NMR spectroscopy[173] and the formulation of a model which derived, to a good agreement with experiment, the distribution of oligomeric silicate anions from known or estimated equilibrium constants.[174,175]

C. Advances in Spectroscopy

The increasing availability of laser-powered instruments greatly augmented the utility of vibrational spectroscopy—and, in particular, for aqueous studies—of Raman spectroscopy. A study by Roozeboom et al.[176] added to the data generated earlier[142,170] in providing convincing evidence for a solution-mediated mechanism in the crystallization of zeolites A, X, and Y and gave some indications as to the nature of the soluble complex polymeric aluminosilicates which were believed to lead to crystal nuclei. The spectroscopic observations were complemented by data from chemical analyses and X-ray diffraction. Raman spectroscopy was also the principal investigative method employed in a series of papers by Dutta and colleagues on the synthesis of zeolites A,[177] Y[178], and ZSM-5.[179] Formation of entities interpreted as the first zeolite crystals could be detected from Raman and IR spectra before crystallinity was evident from diffraction patterns. In the ZSM-5 study, a proportion of the TPA cation was found to be trapped in the amorphous solid phase at the earliest stage of the synthesis and was seen to undergo a major conformational change upon crystallization of the zeolite.

The other spectroscopic technique which (in zeolite terms) came of age at around this time was NMR spectroscopy, in particular, high-resolution solution measurements for nuclei such as ^{27}Al and (especially) ^{29}Si, and also MAS NMR for solid-state studies. The state of the art (for zeolite synthesis) in the late 1980s for the former can be judged from reviews written by A. T. Bell and colleagues.[37,38] However, a problem seldom addressed is that, to achieve reasonable signal intensities, most of the studies involved solutions of high concentrations and alkalinities which were unrepresentative of those used in most zeolite syntheses. Under synthesis conditions, over 90% of the solution components are present as polymeric species which are invisible to the NMR measurements. Thus, while the resulting spectra provide much information about the nature of true solution species in silicate solutions, their relevance to zeolite synthesis is questionable. In general, only broad changes in synthesis mixtures are observable by MAS NMR,[180−182] although the technique is a valuable complement to vibrational spectroscopy in determining the location, mobility, and conformation of occluded template molecules.[183−185]

As the degree of detail observable by spectroscopic and related analytical techniques increased, so too did the extent to which individual samples could be characterized. One consequence of this was to highlight differences between samples of the same, nominally pure zeolite phase in which the synthesis procedure had been varied. In some cases, the result was to improve the correlation between complementary characterization techniques. A case in point was the achievement of an ultrahigh resolution ^{29}Si MAS NMR spectrum for a specially prepared sample of completely siliceous ZSM-5 (silicalite).[186] The spectrum obtained showed natural line widths of ca. 5

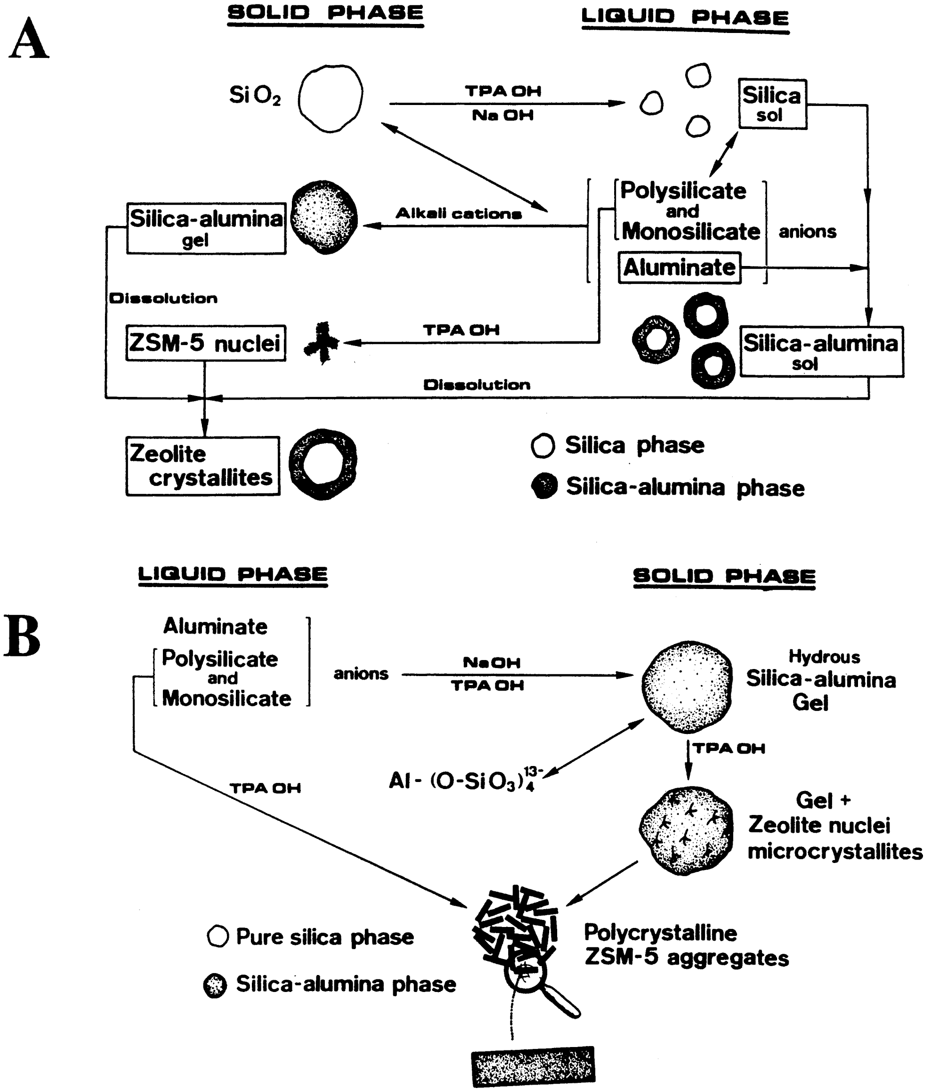

Figure 12. The two different types of ZSM-5 synthesis (type A and type B) envisaged by Derouane, Detremmerie, Gabelica, and Blom, as summarized by Gabelica, Derouane, and Blom. (Reprinted with permission from ref 196. Copyright 1984 American Chemical Society. The original version of this diagram appeared in ref 193, published by Elsevier Science Publishing Co.)

Hz (an order of magnitude improvement) and gave clearly resolved resonances for 21 of the 24 lattice sites postulated on the basis of the X-ray diffraction data. Also using ^{29}Si MAS NMR, detailed silicon-aluminum (lattice) distributions were derived for a series of 14 different synthetic faujasite samples.[187] As noted below (section V.D), the increasing power of spectroscopy also became linked to advances in a wider range of analytical techniques. This had both practical and theoretical consequences. In some cases, a more comprehensive approach to synthesis and characterization led to new ideas on synthesis mechanism. Other investigations employing an augmented range of analytical techniques set out to exploit variations which would be expected to influence product properties, for example catalytic behavior.

D. “Global” Investigations of Zeolite Synthesis

Whereas earlier investigations of synthesis tended to focus on a limited variety of characterization techniques, the rapidly expanding power and availability of such methods produced a general trend toward “global” investigations, in which a large number of complementary techniques were focused upon the problem. In a carefully planned series of papers,[188−191] Debras and co-workers carried out a detailed examination of two series of ZSM-5 samples. Although both series were based on Na,TPA-syntheses, different preparative procedures were followed to afford two groups of products having a comparable range of compositions. A systematic analysis was then undertaken of the differences in (for example) crystal size, radial aluminum distribution, spectroscopic properties, and thermal and steam stability. Studies of this type provided valuable information about the relationship between synthetic method and product properties. This knowledge could then be used to tailor zeolite syntheses toward particular applications, e.g., in sorption and catalysis.[192]

A different aspect of 1980s detective work is found in the series of investigations on pentasil synthesis carried out by the Namur group and their collaborators[193−195] and reviewed in 1984.[196] The overall conclusions are illustrated diagrammatically in Figure 12 and can be summarized as follows. The use of Al-rich ingredients and polymeric silica are pictured as generating a small number of nuclei which grow involving a liquid phase ion transportation process and yield large ZSM-5 single crystals (synthesis A). When high Si/Al ratios and monomeric Na silicate are used (synthesis B), the results are interpreted in terms of numerous nuclei which rapidly yield very small ZSM-5 microcrystallites: these appear directly within the hydrogel and are not detectable by X-ray diffraction. A related study comparing the crystallization of zeolite Y, mordenite, and ZSM-5 appeared in 1986.[197]

E. Studies on the Genesis of Zeolite Crystal Morphology

The concept of manipulating zeolite syntheses to provide products tailored toward particular applications has been mentioned earlier (section V.D). An important aspect of this is the control of crystal size and shape.[192] During the 1980s, several studies explored the wide variations observed in zeolite crystal morphology under different synthesis conditions. Most work was directed at the ZSM-5 system, where the crystalline reaction products were seen in habits varying from ovate to needle-shaped. (The basically orthorhombic ZSM-5 crystals are most typically found as pseudo-rectangular tablets, often with the smallest (end) face rounded. A typical aspect ratio would be $c:a:b = 3:2:1$, where the crystals are sometimes described as “cubic”. An example in which the aspect ratio is around 3:2:0.5 is shown later in the inset to Figure 14.) Some research addressed directly the relationship between crystal morphology and product properties, such as the comparison of molecular transport behavior in ZSM-5 crystals of different habit by Kärger et al.[198]

Following pioneering studies by Sand and coworkers,[199,200] additional information on crystal size and habit as a function of compositional variables (metal cation, salt anion, silica source, alumina content, template type, alkalinity, dilution, seed crystals) was provided by Mostowicz and Berak[201] and Choudhary and Akolekar.[202] The former group identified alkalinity as the most important factor but (unusually) found no effect of aluminum level. In work related to the equilibrium model for zeolite crystallization,[158] the effects of alkalinity on reaction kinetics, yield, pH profile, and crystal size and shape were discussed in detail by Fegan and Lowe.[203]

However, the most detailed investigation of crystal growth regulation and the evolution of single-crystal morphology appeared among the continuing series of papers from the Delft group[204] and has formed the basis for extensive subsequent developments on zeolite coatings and membranes.[205−207] In this work, reagents of carefully defined purity were used in two types of synthesis formulations. The majority of the work was devoted to a detailed study of the system $20Na_2O:20(TPA)_2O:12SiO_2:<0.5Al_2O_3:2000H_2O$ in a static crystallization at 180 °C. Under these conditions, transparent silica bodies up to several millimeters in size were formed after 24 h. From these gel spheres, the evolution of a series of ZSM-5 crystal morphologies could be followed. Initially (ca. 48 h), pyramids in which the basal (*ac*) plane coincided with the sphere surface were seen to form and penetrate into the sphere body. As growth in the *b*-direction (toward the center of the sphere) proceeded, a new ac plane was observed at the apex of the pyramid, and it was the protrusion of this surface (growing in the liquid interface) which became the well-known “cubic” ZSM-5 crystal. The liquid interface was also believed to provide the necessary supply of TPA template cations from the liquid phase.

It should be noted that the synthesis mixture used for the Delft experiments is exceptionally high in base ($OH^-/SiO_2 = 6.7$). One manifestation of this, noted by the authors, was that “during the first day, about two-thirds of the TPA^+ reacts with OH^- according to the Hofmann degradation reaction yielding tripropylamine and propane”. Thus, the phenomena observed should not necessarily be taken as representative of the majority of ZSM-5 syntheses.

F. X-Ray Amorphous Zeolites and Early Development of Zeolitic Structure

In 1981, a paper by Jacobs, Derouane, and Weitkamp presented evidence for the existence of entities which were amorphous to XRD but, on the basis of the appearance of a vibration at 550 cm^{-1}, appeared to be fully crystalline by infrared spectroscopy (Figure 13) and showed catalytic activity similar to macrocrystalline ZSM-5 in the hydroconversion of *n*-decane.[208] Work by Coudurier et al.[209] adds usefully to the infrared evidence. The summarized investigation mentioned earlier[196] makes further reference to X-ray amorphous zeolites, this time based on DTA evidence but citing also ^{13}C NMR data. These results are difficult to explain satisfactorily within a consistent picture of the early stages of zeolite synthesis and the term “X-ray amorphous zeolite” is probably something of a misnomer.[12] However, that there exist entities amorphous to X-rays which have some of the characteristics of zeolites is indisputable. In the case of zeolite Y, Fahlke et al.[210] tested the activity for

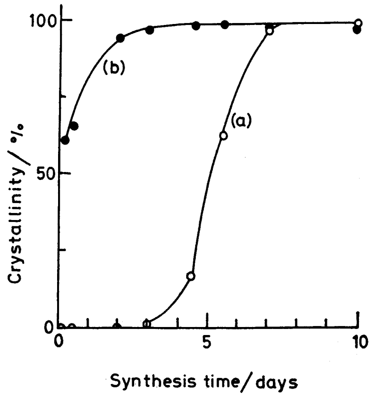

Figure 13. Evidence for “X-ray amorphous zeolites” from Jacobs, Derouane, and Weitkamp (1981). “Change of the crystallinity of ZSM-5 materials with synthesis time: (a) X-ray crystallinity derived from peak summation between $2\theta = 22°$ and $25°$; (b) IR crystallinity using the 550 cm^{-1} skeleton vibration in a KBr pellet technique with the 2200 cm^{-1} vibration of KCN as internal standard”. (Reproduced from ref 208 by permission of The Royal Society of Chemistry.)

cumene cracking of intermediate samples taken during the course of a 72 h synthesis at 363 K. The sample taken at 48 h had 69% of the catalytic activity of the final fully crystalline sample (72 h) but was X-ray amorphous. Samples taken up to 10 h showed only 4% of the final activity. In an interesting reflection of the observations of Angell and Flank,[142] the authors also concluded that the silica-rich primary gel (obtained immediately after mixing the reactants) undergoes redissolution as the reaction mixture equilibrates, whereupon a new amorphous phase, having the same composition as the final product, is precipitated. The same pattern was observed in later work by the Montpellier group[211] in a study of Na, TEA−aluminosilicate gels (TEA = tetraethylammonium). Similar materials would yield crystalline zeolite β under appropriate hydrothermal treatment. However, after heating for a limited period at 150 °C, the products formed were amorphous but differed from the gels initially precipitated at room temperature. These secondary products had been formed by dissolution and reprecipitation and were silicoaluminates sharing several properties with high-silica zeolites but differing in their degree of order. Whereas zeolites feature well-defined and repeatable site geometries, these equilibrated, amorphous products present irregular and hence aperiodical, local organization.

G. Other Significant Advances of the 1980s

1.The Role of Organic Templates

The use of X-ray diffraction methods to determine the location of template molecules inside the host framework gave a unique insight into the geometric match between framework and template. The first of these determinations (for TPA(F)−silicalite) was published by Price and co-workers in 1981.[212] Studies of this type provided hard data with which to validate molecular modeling methods, allowing these approaches to be used in the prediction of template−framework relationships for systems less amenable to experimental investigation (section VII.A).

In the mid-1980s, two reviews were published which focused attention on the role of organic templates in molecular sieve synthesis.[22,27] These were very useful in concentrating the minds of research groups on this area of host−guest chemistry and were instrumental in engendering some of the theoretical and modeling work which followed.

2. Alkali-Metal Free Zeolite Synthesis—Use of NH_4^+–R_4N^+ Systems

The first demonstration of this procedure was in the synthesis of ZSM-5 and ZSM-11 by Bibby, Milestone, and Aldridge.[213] The method subsequently became of great utility in systems where alkali metals were deleterious and in the growth of very large crystals.[214−216] For applications in acid catalysis, no ion exchange step is necessary since calcination of the product leads directly to the metal-free, protonic form of the zeolite.

3. Syntheses in Nonaqueous Media

The earliest work in which reactions carried out in nonaqueous media afforded a hitherto unknown zeolite-type product was the preparation of an all-silica form of sodalite by Bibby and Dale in 1985.[217] The reaction medium was an oxygenated solvent such as ethylene glycol or propanol. No water was added, but neither was any attempt made to ensure an absolutely anhydrous system, the reagents themselves (NaOH, silica, glycol) generating some water. However, this was not the first disclosure of zeolite formation in a nonaqueous system, since a BASF patent from 1982 had described the synthesis of ZSM-5-type materials from NaOH, silica, and $Al(OH)_3$ in ethereal solvents or in ether−water mixtures.[218] Among the patent examples, some of those with diglyme (diethyleneglycol dimethyl ether) employ no added water, although the quantity of moisture carried in with the $Al(OH)_3$ (made in situ) is not clear. Subsequent research did not fulfill the early promise of this technique for the synthesis of new zeolites, yielding only known materials.[219−221] However, a variation of the method (adding the template as an amine-HF complex) later proved very successful for growing large (millimeter-sized) crystals.[222] Application of nonaqueous and mixed-solvent techniques to the synthesis of microporous phosphates has produced a richer variety of results, including the discovery of some novel phases such as the 20-T-ring aluminophosphate JDF-20.[223,224] A useful review discusses much of this area.[57]

As pointed out by Bibby and Dale,[217] reactions of silica in nonaqueous solvents are not unexpected, as silica is readily solvated by many polar organic molecules.[225] Indeed, a subsequent study by Herreros and co-workers of the original silica-sodalite synthesis detected the 5-coordinate silicoglycolate complexes which are present in the reaction solution.[226] The rather slow reaction rates usually found for the above solvent-mediated syntheses presumably reflect the fact that the available solvating power falls rather short of that of water. In some cases, the organic solvents may be acting largely as heat-transfer media, with residual water providing the necessary solvation at the reaction sites. In these respects, it is apparent that the chemistry of such reactions is closely related to that taking place in the “dry” or “vapour phase” synthesis of zeolites (see section VI.F).

4. Deuterium Isotope Effect

If the making and breaking of SiO−H bonds can affect the rate of processes critical to zeolite formation, it might be expected that zeolite syntheses would be susceptible to a kinetic isotope effect when carried out in deuterated media. The first evidence showing that this might be the case was presented in 1989 by Dutta, Puri, and Bowers, who observed a deceleration (measured from the overall XRD growth curves) in the rate of growth for zeolite A at 90−95 °C in D_2O.[227]

5. Secondary Synthesis and Lattice Lability

The term secondary synthesis has come to be used rather broadly in describing a variety of postsynthesis treatments (not all of which are hydrothermal) which may be used to modify zeolites and, particularly, the properties of zeolite catalysts.[228] Brief mention is made of it here in the specific context of hydrothermal insertion (or reinsertion) of heteroelements into existing zeolite structures. In the mid-1980s, several reports appeared showing that, following the preparation of a zeolite by direct synthesis, its aluminum content could be increased by further chemical treatment and that at least some of the new aluminum entered lattice positions. For example, Al was found to migrate from the alumina binder to high-silica ZSM-5 under extrusion or steaming conditions[229,230] and re-incorporation of aluminum occurred on treating ultrastable zeolite Y (containing 35% extraframework Al) with 0.25M potassium hydroxide solution under mild conditions (80 °C for 24 h).[231,232] The aqueous method has also been used to introduce gallium into silicate and aluminosilicate frameworks, by both hydroxide[233] and fluoride[234] routes and will undoubtedly prove to be a useful alternative to direct synthesis for other heteroatom-substituted zeolites and zeotypes. The success of the technique is a useful reminder of the reversible nature of zeolite synthesis reactions and of the remarkable lability of the zeolite lattice. On this latter point, von Ballmoos and Meier showed from ^{18}O-exchange between liquid water and NH_4−ZSM-5 at 95 °C that not only hydroxyl groups but also T−O−T bridges are cleaved under these relatively mild conditions.[235]

6. Titanium Silicalite (TS-1)

In 1983, Taramasso, Perego, and Notari reported the synthesis of a titanium-substituted analogue of silicalite, given the name titanium silicalite or TS-1.[236] Synthesized in a TPAOH system substantially free of metal cations, TS-1 contains low levels (up to about 2.5 atom %) of titanium substituted into tetrahedral positions in the silicalite lattice. The product has proved to be an extremely useful oxidation catalyst, particularly in conjunction with a peroxide, and is now in commercial use. In epoxidations and related reactions, TS-1 is an active and selective catalyst[237] and, in addition to being the first authenticated Ti-containing porotectosilicate, provides the first example (excluding acid catalysis) in which a heterosubstituted atom in a zeolite has shown significant chemical activity.

7. Titanium Molecular Sieves (ETS-4 and ETS-10)

The greater structural diversity found in non-aluminosilicate zeotypes has been mentioned earlier (section V.A). This increased flexibility is also apparent in the manifestation of coordination numbers greater than four in some zeolitic metallophosphates.[238] However, the first well-established examples of microporous materials having nontetrahedral coordination as a regular and major feature of their structures were the titanosilicates ETS-4 and ETS-10 discovered by Kuznicki of the Engelhard Corporation in the late 1980s.[239] The extraordinary structure of ETS-10, in which a zeolite β-like wide pore framework is additionally supported by rods of titanate octahedra, was elucidated by an inspired collaboration of workers using state-of-the-art microscopic and spectroscopic techniques.[240] The titanosilicate family is growing rapidly[241] and will present many new challenges to those seeking to understand hydrothermal zeotype synthesis.

VI. 1990s: Mesoporous Materials and the Decade of High Technology

The 1990s saw further innovation in the field of porous solids with the discovery of new families of materials having regular arrays of mesopores and formed by the interaction of silicate and aluminosilicate species with surfactants. These materials not only gave access to far larger pore sizes but also represented a new class of structures, since their pore walls were amorphous rather than crystalline. While this discovery in itself provided a new perspective on the zeolites and zeotypes available previously, advances in technology provided new insights into those materials themselves. Two achievements stand out. First, the use of advanced scattering and diffraction techniques to probe the earliest stages of zeolite formation resulted in the importance of the colloidal component of the synthesis sol becoming generally appreciated for the first time. Second, molecular modeling progressed from a specialist interest to a technique which had significant things to say to both theoreticians and experimentalists alike. The final years of the decade also furnished a remarkable development in the field of mineral zeolites: structural equivalents of several high-silica zeolites were found to occur among natural deposits in the USA and in Antarctica.

A. Mesoporous Materials: Genesis in Japan and the USA

Although the chemistry of alkylammonium-clay intercalation complexes had been studied for many years,[242] a new step was taken in 1990 when the initial intercalates formed by the single-layered polysilicate kanemite were subjected to hydrothermal treatment followed by calcination.[243] The procedure achieved at least partial condensation to form three-dimensional networks having pores of 2−4 nm in diameter and surface areas of ca. 900 m^2 g^{-1}. In a subsequent report,[244] optimization of the reaction conditions led to a highly ordered mesoporous product having a hexagonal unit cell and a hexagonal honeycomb structure clearly visible by TEM. However, by that time the remarkable papers by the Mobil workers had appeared[5,6] (as well as the first patents[245−247]) revealing a host of data on a new family of mesoporous materials, designated M41S, where the hexagonal MCM-41 bore many resemblances to the Japanese material (subsequently designated FSM-16).

In a further twist to the story, Di Renzo et al.[248] have drawn attention to a procedure for the preparation of low-density silica described in a patent[249] filed in 1969 by Chiola, Ritska, and Vanderpool (Sylvania Electric Products Inc.). Reproduction of the reported synthesis led[248] to a material essentially identical to MCM-41, although many of the characteristic properties were unrecognized in the original disclosure. Following the extensive Mobil discoveries, subsequent progress has been widespread and rapid.[9,10,250]

B. Advances in Microscopy

The improvements in electronics and the vast increase in computing power of the 1990s had a huge impact on the speed and power of the physical techniques used in the characterization of microporous and mesoporous materials. The implications of this for mechanistic studies and theoretical modeling are described below, but one specific area of materials characterization which must be singled out is that of microscopy. High-resolution electron microscopy (HREM) had not only established itself as a major contributor to structure solution (e.g., for ETS-10[240]) but could now be used to test the probable extent of template−framework interaction as well as domain structure in potentially twinned crystals (e.g., for ZSM-12[251]). In addition, the emerging science of electron crystallography could now be used for ab initio structure solution.[252] For a research area in which well-formed crystals larger than a few micrometers in size could be difficult or impossible to obtain, this was a most welcome advance.

In a completely separate development, the advent of a new family of scanning probe microscopies was revealing surface detail at a resolution previously unattainable.[253] The matching of surface features with framework structural units and parameters provides new insights into crystal growth mechanisms.[254] Figure 14 shows the topography of the [010] face of a 15 μm silicalite crystal, obtained by atomic force microscopy (AFM). The step height is 1.0 nm, which corresponds to the thickness of the basic structural (pentasil) chain (the full *b*-axis repeat distance being 1.99 nm).

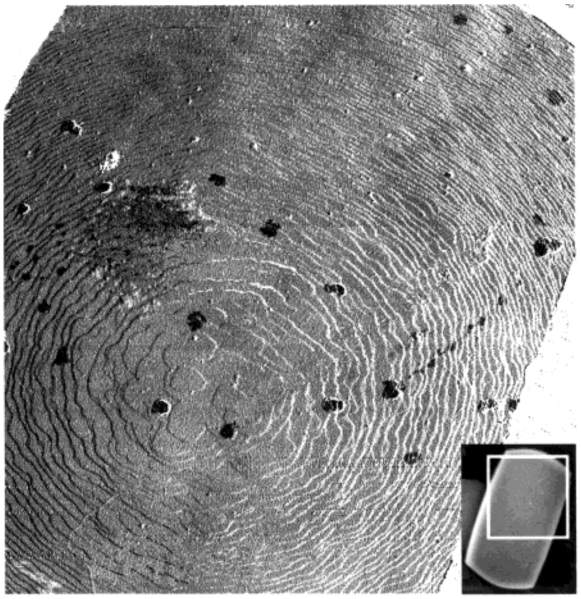

Figure 14. AFM microscopy. Regular growth terraces observed on the [010] face of a silicalite-1 crystal (inset, length 15 μm) recorded as a phase image (TappingMode) on a Digital Instruments Nanoscope III instrument. The terrace height is 1.0 nm, which corresponds to the thickness of a pentasil chain. (We thank Drs J. R. Agger and N. Hanif of the UMIST Centre for Microporous Materials for this image.)

C. The Earliest Stages of Zeolite Formation: Information from Scattering and Diffraction Studies

To make meaningful observations of events occurring in aqueous media at very small length scales, two conditions have to be satisfied. First, the equipment used has to be capable of sufficient sensitivity and resolution to afford good-quality data, and second, the systems studied have to be carefully chosen so that the results are likely to be chemically significant. Early work in this area suffered from deficiencies on both counts. However, in due course, improved facilities for small-angle X-ray and neutron scattering (SAXS and SANS) became available in addition to the realization[255] that much of what was being observed related to the equilibration processes taking place in silicate and aluminosilicate sols and was only indirectly related to zeolite formation. In addition, effective, laser-sourced commercially available equipment for dynamic light scattering (DLS), alternatively known as photon correlation spectroscopy (PCS), established a good laboratory method for the measurement of particle size in colloidal sols.

Most of the information in the above areas comes from a small number of research groups, and the majority of investigations are based on the TPA−silicalite system. There is considerable divergence in the detail of the current results from this work and it will be interesting to see how significant these differences will remain. However, there is also a broad undercurrent of agreement. Thus, de Moor et al.[256] have studied the clear solution hydrothermal synthesis of TPA−silicalite in situ using a combination of X-ray scattering techniques and electron microscopy. This has provided access to information on a continuous range of length scales spanning over 4 orders of magnitude (0.17−6000 nm). They observe as precursors to the crystalline product both 2.8 and 10 nm particles (designated “primary units” and “aggregates”) and suggest that the formation of the aggregates is an essential step in the nucleation process with reaction-controlled inclusion of the 2.8 nm units at the crystal surface providing the crystal growth step. Watson et al.[257] were led to the broadly similar conclusion of an aggregation assembly process from 4.3 nm primary particles which were interpreted as representing cylindrical primary nuclei 2 × 2 unit cells in cross section. In a subsequent study, the same group detected particles with a radius of gyration of 2.8 nm in a sol that was aged at room temperature for six months.[258]

Although some DLS work was included in the studies mentioned above, the most detailed use of this technique has been by Schoeman and colleagues.[259,260] In particular, an in situ study of TPA−silicalite crystallization at 70 °C[261] clearly showed the presence of a persisting background population of 3.3 nm particles from which, at around 10 h reaction time, a new population of growing particles could be distinguished (Figure 15). This new population, which could be identified as crystalline silicalite, grew as a nonlinear function of time up to an average particle size of ca. 20 nm, after which a linear growth at a rate of 0.72 nm h^{-1} was recorded. Below 9.5 h,

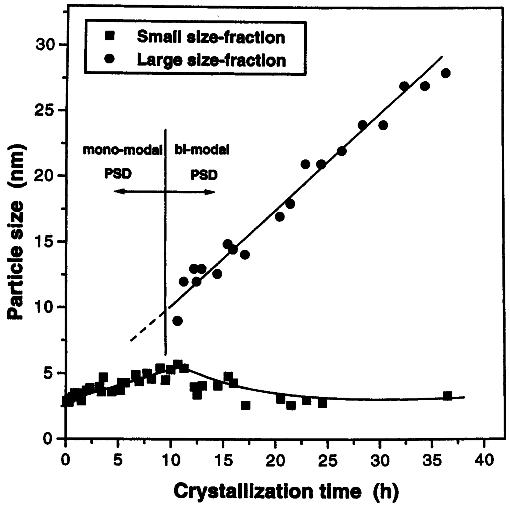

Figure 15. The initial stage of TPA–silicalite-1 synthesis: an in situ light-scattering study at 70 °C by B. J. Schoeman (1997). The particle size distributions measured before 9.5 h are monomodal. At later times, two distinct particle populations can be resolved. (Reprinted from ref 261, Copyright 1997, with permission from Elsevier Science.)

the two populations could not be distinguished so that it cannot be said whether they are completely independent. If the two groups of particles are unconnected, this would represent the case of homogeneous nucleation in which the initially observed 3.3 nm particles comprised the reservoir of silica in the system and formed the nutrient for the independently nucleated crystalline product. However, the more likely scenario is that the two populations are linked and this was the interpretation favored by Schoeman.[261] Deconvolution of the intensity data up to 10 h indicated that the larger sized silicalite particles had their origin in the smaller subcolloidal particles and furthermore that (from FTIR, FTR, and N_2-sorption studies) some of the subcolloidal particles may possess a short-range structure. In this view, the crystalline product nucleates heterogeneously on the (initially) amorphous subcolloidal particles which additionally constitute the principal reservoir of nutrient silica in the system. This topic will be discussed in more detail below (sections VI.D and VI.E).

D. Emergence of the Colloid

An important result from the scattering studies outlined above was the more general realization of the importance of the colloidal component in zeolite synthesis. As noted earlier (section V.C), many previous investigations of zeolite synthesis tended to concentrate on spectroscopic methods, in particular, solution-phase NMR measurements. This placed undue emphasis on the lower molecular weight species in true solution, often in solutions whose compositions were unrepresentative of zeolite synthesis. Where the importance of the colloidal phase (which in many high-silica zeolite syntheses constitutes most or all of the nutrient reservoir) was stressed, the evidence presented was deduced from crystal growth studies, microscopy, and investigations by chemical methods. Even so, it was possible to demonstrate clearly that, for clear sol syntheses of MFI materials, (i) the invisible colloidal component comprised the principal reservoir of amorphous nutrient in the system and was converted into the crystalline product via a near-constant concentration of true solution species and (ii) the crystalline product was almost certainly nucleated heterogeneously upon colloidal gel particles.[262,263] However, advances in high-resolution transmission electron microscopy (HRTEM) now provided the opportunity for more direct confirmation of the role of the colloid. Mintova and co-workers[264,265] have used HRTEM in conjunction with in situ DLS to examine the formation and growth of zeolites A and Y from clear sols. Single zeolite A crystals were observed[264] to nucleate in amorphous gel particles of 40–80 nm in size within 3 days at room temperature. The embedded zeolite A nanocrystals grew at room temperature, consuming the gel particles and forming a colloidal suspension of 40–80 nm crystals. A similar picture was found at 100 °C for the zeolite Y studies,[265] confirming nucleation and initial growth within the amorphous colloidal particles, with solution mass transfer as the dominant mechanism for further crystal growth at prolonged reaction times.

E. Recent Studies on Synthesis Mechanism

1. An Important Study of ZSM-5 Synthesis Mechanism

In a very significant paper, Chang and Bell[266] studied the formation of ZSM-5 from Al-free precursor gels at 90–95 °C using XRD, ^{29}Si MAS NMR spectroscopy, and ion exchange. The NMR results suggested that major changes in gel structure occur during the early stages of reaction. This was confirmed by the demonstration of ion sieve effects suggesting that, in the tetrapropylammonium (TPA) system, embryonic structures with Si/TPA = 20–24 are formed rapidly upon heating. These first-formed units, approximating to channel intersections and each containing essentially one TPA^+ cation, are initially randomly connected but in time become ordered (“annealed”) through repeated cleavage and recombination of siloxane bonds, mediated by hydroxide ion. The hydrophobic effect and the isomorphism between water and silicate structure are invoked to provide a possible mechanism for ZSM-5 nucleation with the following steps: (a) formation of clathrate-like water structure around the template, (b) isomorphous substitution of silicate for water in these cages (which resemble ZSM-5 channel intersections), and (c) progressive ordering of these entities into the final crystal structure.

2. Passive vs Invasive Techniques

The zeolite synthesis medium is a very complex reaction system. Like a living organism, its features are prone to change if disturbed by invasive examination procedures. The most reliable study techniques are likely to be those which can be carried out in situ during the synthesis reaction itself (e.g., spectroscopy, diffraction/scattering, microscopy), and some examples of these have been discussed earlier. Invasive techniques have been used to different

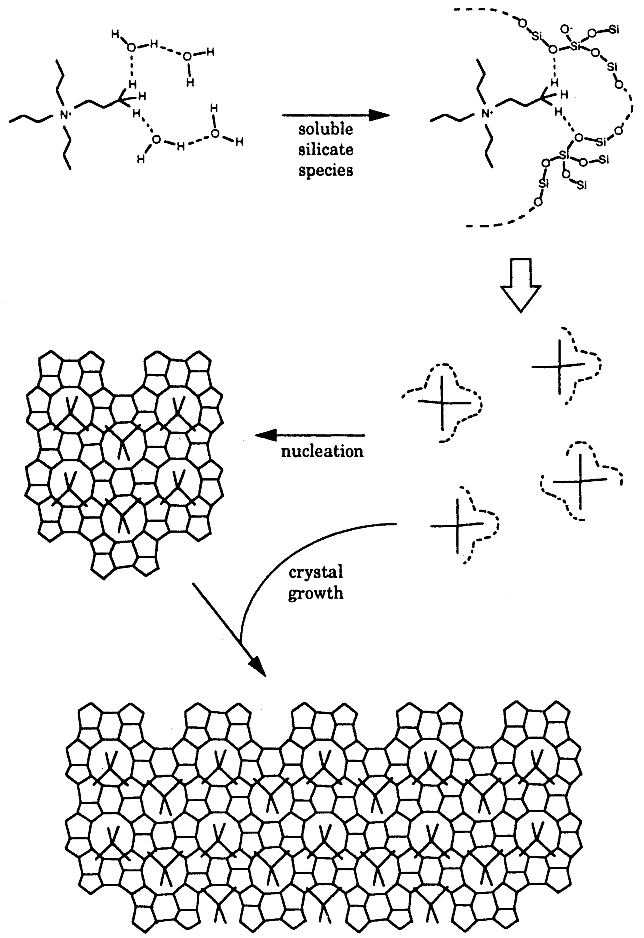

Figure 16. Mechanism of structure direction and crystal growth in the synthesis of TPA–Si-ZSM-5 as envisaged by Burkett and Davis. This view highlights the interactions between TPA and silicate within inorganic–organic composite precursor species (upper portion of diagram). (Reprinted with permission from ref 267. Copyright 1994 American Chemical Society.)

extents in two recent investigations of the formation of a zeolite templated by an organic molecule, both of which take as their example the case of TPA–MFI formation.

In the first series of papers[267–269] Burkett and Davis build upon the work of Chang and Bell[266] mentioned above to examine the role of TPA as structure-directing agent in silicalite synthesis, primarily by MAS NMR spectroscopy. ^{1}H-^{29}Si CP MAS NMR results provide direct evidence for the existence of preorganized inorganic–organic composite structures during the synthesis, in which the TPA molecules adopt a conformation similar to that which they have in the zeolite product. The initial formation of the inorganic–organic composite is initiated by overlap of the hydrophobic hydration spheres of the inorganic and organic components, with subsequent release of ordered water to establish favorable van der Waals interactions. Thereafter, aggregation of these composite species is responsible for nucleation. Crystal growth occurs through diffusion of the same species to the surface of the growing crystallites to give a layer-by-layer growth mechanism. These ideas are illustrated in Figure 16.

The above authors sought to obtain further evidence for the proposed inorganic–organic composite

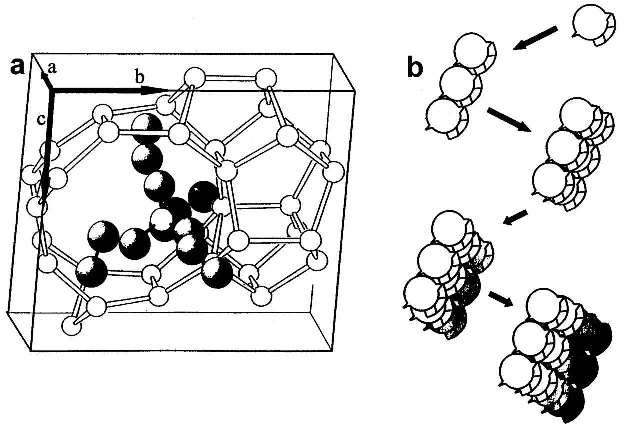

Figure 17. The "nanoslab" hypothesis of the Leuven research group: (a) the precursor unit containing one TPA cation and (b) schematic representation of nanoslab formation by aggregation of precursor units, as determined by XRS and GPC. (Reprinted with permission from ref 273. Copyright 1999 American Chemical Society.)

species through trimethylsilylation studies carried out on the unheated synthesis mixture but the results were equivocal. However, in a series of papers by the Leuven group,[270–274] this type of procedure constitutes the main framework of their studies. In part, the work is a continuation of the characterization of the zeolite precursor material identified by Schoeman[261] and mentioned earlier (section VI.C) and concentrates on the early stages of MFI (and MEL) formation. The silica species in an aged clear sol (which crystallizes silicalite upon heating) were extracted (80% efficiency) using a sequence of acidification, salting out, phase transfer into organic solvent, and freeze-drying. The resulting powder was characterized by a wide variety of methods leading to the identification of constituent "nanoslabs" having dimensions 1.3 × 4.0 × 4.0 nm and having the MFI structure with nine intersections per particle, each constituent unit containing a TPA cation (Figure 17a). Aggregation of precursor units leads to larger particles measuring up to 15.6 × 8 × 8 nm and ultimately to the crystalline colloidal MFI-type material which forms the final product of the synthesis (Figure 17b). More recent work (section VIII.B) includes the use of more direct investigative methods.

3. Aluminosilicate Solutions: How Al Enters the Silicate Equilibration Chain

In a unique paper, Harris and co-workers have made an important contribution to our understanding of aluminosilicate solutions.[275] A chemical method was earlier used to show how aluminate ions enter into the complex chain of silicate equilibria, so that during ZSM-5 synthesis the aluminate gradually "disappears" into an increasingly kinetically inert network.[263] However, the present spectroscopic study provides far more detailed evidence for this evolutionary process. As a first step, HMBTP silicate solutions were prepared, where HMBTP is the octahydrohexamethyl benzotripyrrolium cation used in the synthesis of ZSM-18.[276] Aluminate solutions were then added and the evolving aluminosilicate species studied as a function of time by ^{27}Al NMR (including two-dimensional EXSY) spectroscopy. Aluminosilicate anions with Al bound to 1−4 Si atoms through oxygen linkages were observed, assignment being complicated by the existence of chemical exchange processes. Most of the anions did not reach dynamic equilibrium rapidly at 25 °C, the more highly connected aluminum sites being the most stable.

4. Mechanistic Information from Product Framework Ordering

While most investigations of synthesis mechanism have been based on the monitoring of changes occurring in the reaction medium, a few have relied upon information obtained solely from the isolated crystalline products. Notable among these is the ^{29}Si MAS NMR study by Melchior et al. of metal ordering in the framework of directly synthesized faujasites having Si/Al ratios in the range 1.3−5.3.[277] Following a detailed analysis of the local environment fine structure in the spectra, it is found that the relative populations of discreet local environments (differing in the number and types of first- and second-shell Al substituents) are a function of composition. Arguing from the constraints imposed by both connectivity and Loewenstein's rule (forbidding Al−O−Al linkages), the authors find stronger pair avoidance within, rather than between, different D6R subunits and infer from this the crystallization pathway

$$4R \rightarrow D6R \rightarrow FAU$$

In this view, the single four-ring (4R) is seen as the secondary building unit which leads to the double six-ring (or hexagonal prism) D6R. This latter unit (described also as a "triple four-ring") is regarded as the immediate precursor to the FAU lattice.

F. Vapor Phase Synthesis

In 1990, Xu et al. reported the first examples of a zeolite synthesis in which some of the reaction components were supplied from the vapor phase.[278] In these cases, a preprepared damp or dried sodium aluminosilicate gel was suspended above liquid in an autoclave and subjected to the mixed vapor of ethylenediamine, triethylamine, and water at elevated temperature and pressure. Under these conditions, ZSM-5 crystallized in 5−7 days at 453−473 °K. Subsequent work by several groups has provided many more examples of this type of process, which is described variously as the dry gel conversion (DGC) or vapor phase transport (VPT) technique and has recently been reviewed.[68] A useful distinction can be made between the amine vapor procedure of the original report by Xu et al. [278] and methods in which only steam is supplied from the gas phase. The latter method is designated "steam-assisted conversion" (SAC) by Matsukata and co-workers.[68] These vapor-assisted techniques can be very useful, for example, (i) in preventing loss of soluble components to a bulk liquid phase or (ii) in affording reaction products, such as fully siliceous zeolite β, which are not normally obtainable by the more traditional wet gel route from similar starting materials.[68] However, hydrothermal zeolite syntheses from "dry" starting materials had been established previously.[279,280] These compositions had the appearance of free-flowing powders although they contained 20−44% water by weight. Clearly, their thermal conversion to zeolites must involve conditions closely related to those applying in the SAC methods noted above. In terms of reaction mechanism, there is no reason to view these syntheses as fundamentally different from those having a more accessible liquid phase.[12]

All of the above vapor-assisted syntheses can be regarded as involving hydrated, or at least solvated, reaction components. However, it seems probable that the reaction system described by Althoff and co-workers[281] is genuinely "dry". In this case, ZSM-5 is synthesized at 180 °C from amorphous $SiO_2.Al_2O_3$ precursors (dried at 650 °C) in the presence of dried NH_4F and TPABr. The synthesis is believed to involve a vapor phase mass transfer process with SiF_4 as the mobile species. As noted earlier (section V.G.3), there is an interesting general similarity between the rather restricted range of zeolite products (principally pentasils and clathrasils) obtained from nonaqueous syntheses[217−222] and those from the least hydrous of the vapor phase conversions.[68,281−283] This suggests that in the absence, or near-absence, of water itself, some mechanistic pathways remain open whereas others are essentially inaccessible.

G. Tschernichite and the Antarctic Zeolites

We have noted earlier (section IV.C.3) the interplay between synthetic and natural zeolites in which sometimes a mineral material has anticipated the structure of a subsequently discovered synthetic product and sometimes the reverse. What is perhaps the most remarkable of these dialogues has occurred quite recently. Since most naturally occurring zeolites have quite low Si:Al ratios (<5) and the majority of high-silica zeolites can presently be made only by using organic templates, it was tacitly assumed that these siliceous materials would not be found as natural minerals. This misapprehension was dispelled in 1991 by the recognition[284,285] that a specimen from Goble Creek, Oregon, originally found in 1972 and suspected to be apophyllite, was in fact a new mineral zeolite having the same topology as the first high-silica zeolite ever synthesized, zeolite β. Named tschernichite after its discoverer, tiny deposits of this extremely rare mineral were subsequently also found at Mount Adamson in Antarctica. Both locations also yielded boggsite, a further new, and so far unsynthesized, zeolite containing five-membered T-atom rings. Further investigations at the Mount Adamson site led to the identification of three more new pentasil zeolite minerals: gottardiite (the natural counterpart of the synthetic phase NU-87), mutinaite (ZSM-5), and terranovaite, which at present has no synthetic analogue.[286] All the mineral structural equivalents of known high-silica zeolites differ from their synthetic counterparts in two important respects: (i) their Si:Al ratios are much lower (the highest being gottardiite at 6.2), and (ii) their associated cation sets are rich in calcium. This suggests both that their compositional range is larger than had been thought and also that organic templates are probably unnecessary for their synthesis. These observations offer a fascinating challenge to the synthetic chemist.

H. Template–Framework Relationships

The role of structure-directing agents in the synthesis of zeolitic materials has been mentioned above in association with advances in electron microscopy, and it was noted earlier how the appearance of two reviews in the 1980s[22,27] served to focus attention on this topic. In view of the large number of new microporous structures discovered since that time, nearly all of which were prepared in the laboratory using organic templating agents, several groups began systematic studies on template−framework relationships. Of these, the work of Gies and Marler stands out,[287,288] as do the studies carried out by both Zones and Davis, often in collaboration.[289,290] Their work relates systematic changes in the structure, size, shape, and chemical nature of both neutral and charged template molecules to the type, geometry and structure of the products obtained by clathrating synthesis. Such work is directly related to the advances in theoretical studies and molecular modeling described below.

One particular area which became the focus of much attention was the successful strategy of using bulky organic molecules as templates in the quest for novel large-pore structures. Using this approach, the first zeolitic materials containing 14-ring channels were both first reported in this decade. The microporous silica UTD-1 (DON framework type)[291−293] was synthesized using a permethylated bis-cyclopentadienyl "sandwich" complex of cobalt, and the similarly siliceous CIT-5 (CFI structure type)[294,295] was made using a polycyclic amine in the presence of lithium.

Experimental determination of the location of template molecules by single-crystal X-ray diffraction has proved a landmark in helping to establish template−framework relationships. However, this approach is often difficult to use because of the problem in producing crystals of a suitable size for analysis. The first determination of this kind established the location of the tetrapropylammonium ions in fluoride−silicalite (at the channel intersections).[212,296] More recently, advances in the development of powder techniques have allowed the location of templates for microcrystalline samples.[297] Also, the size of crystal from which a full structure determination can be accomplished using synchrotron radiation continues to diminish.[298] These methods, although not routine, have played an important role in providing detailed coordinates against which theoretical molecular modeling techniques may be validated.

VII. Up To and beyond the Year 2000: (I) Modelling Studies Related To Zeolite Synthesis

Molecular modeling methods have centered on the study of three key aspects of zeolite synthesis:
(a) The determination of the location and energies of the templating agents occluded within zeolite structures during synthesis.
(b) The detailed investigation of small framework fragments, their geometries, and solvation energies.
(c) The enumeration of framework structures.

A. Calculations on Occluded Templates

1. Early Developments Using Molecular Mechanics-Based Approaches

Calculations that have been performed in the first category of simulations have normally been based on a molecular mechanics-type approach. This method treats a molecule (or lattice) as a simple ball and spring model and applies the classical laws of physics to the system under investigation. The first reported example of this type of calculation to appear in the literature studied the dynamics of the tetramethylammonium (TMA) ion occluded in a β-cage of sodalite.[299] In this study, molecular dynamics was used to show that the TMA ion has a considerable degree of rotational freedom within the cage. This movement was attributed to the high degree of flexibility of the zeolite lattice during the simulation run.

Schmitt and Kennedy[300] successfully employed the molecular mechanics methodology to rationally design and screen new template molecules for the zeolite ZSM-18 (MEI).[276] Their work used modeling to predict the geometries for a range of candidate templates. These molecules were then screened by inspecting the van der Waals' overlap produced when the optimized template was docked into the zeolite's cage. The derivation of new templates for this framework was a notable success because prior to this study there was only one template known to synthesize ZSM-18. Moreover, the best template derived from this work had the benefit that it could be more easily removed from the framework, resulting in reduced loss of crystallinity in the product on calcination. Moini et al.[301] successfully exploited molecular graphics capabilities to dock "by eye" optimized templates into the side-pockets of the EUO structure. This demonstrated the excellent void filling properties exhibited by organic structuring agents that successfully template this framework.

2. Application of Monte Carlo Protocols

The development of automated docking procedures based on a Monte Carlo approach represented a significant advance in methodology. This method, initially developed to help interpret the distribution of products in catalytic reactions,[302] uses a Monte Carlo approach to dock the guest molecule at a random location within the host framework. The energy of the template at this location is then determined, and the resulting configuration is accepted only if the resulting energy falls below a specified threshold value. Once the specified number of templates has been docked using this approach, an energy minimization routine is then used to optimize the location of the guest molecules inside the framework. The inclusion of a simulated annealing protocol[303] is a useful additional step in the procedure, particularly when several template molecules are included inside the simulation box.

Lewis et al.[304] used the Monte Carlo docking methodology to investigate the relationship between template molecules and their products for a range of quaternary alkylammonium ions. This study showed that low-energy configurations for template molecules can be obtained that are in excellent agreement with experimental observations. In addition, it was found that the relative nonbonded energy between template and framework could be used as a measure of the efficacy with which a selected template could form a particular framework. These nonbonded energies essentially reflect the “goodness of fit” for a template within the zeolite cavity, supporting the lock and key analogy first developed by Lok and co-workers.[22]

Theoretical work on tetraalkylammonium templates has recently been extended by Shen and co-workers. An initial energy minimization study,[305] using full periodic boundary conditions, suggested that tetrapropylammonium (TPA) cations should be more effective at stabilizing the ZSM-11 (MEL) lattice than tetrabutylammonium cations (TBA), an observation clearly at odds with the experimental result. Further work[306] demonstrated the need to include the entropic component of the Gibbs free energy in calculations of this type in order to rationalize the synthesis of ZSM-11 by TBA ions.

Other examples of the use of the Monte Carlo methodology include the work of Harris et al.,[307] who showed that the nonbonded energies obtained from this type of calculation could be related to crystallization time for a range of templates that successfully synthesize nonasil (NON). Increasing nonbonded energies were found to correlate with a reduction in the observed crystallization time. A combined Monte Carlo-simulated annealing (MC-SA) approach was employed by Stevens and colleagues[303] to show that binding energies for the dibenzyldimethylammonium (DBDM) template are very similar in three different frameworks that this particular template can synthesize: BEA, EUO, and MTW. Furthermore, despite the vastly different topologies of their respective channel systems, the DBDM molecule is an excellent fit in all three frameworks, adopting a different stacking arrangement in each case (Figure 18).

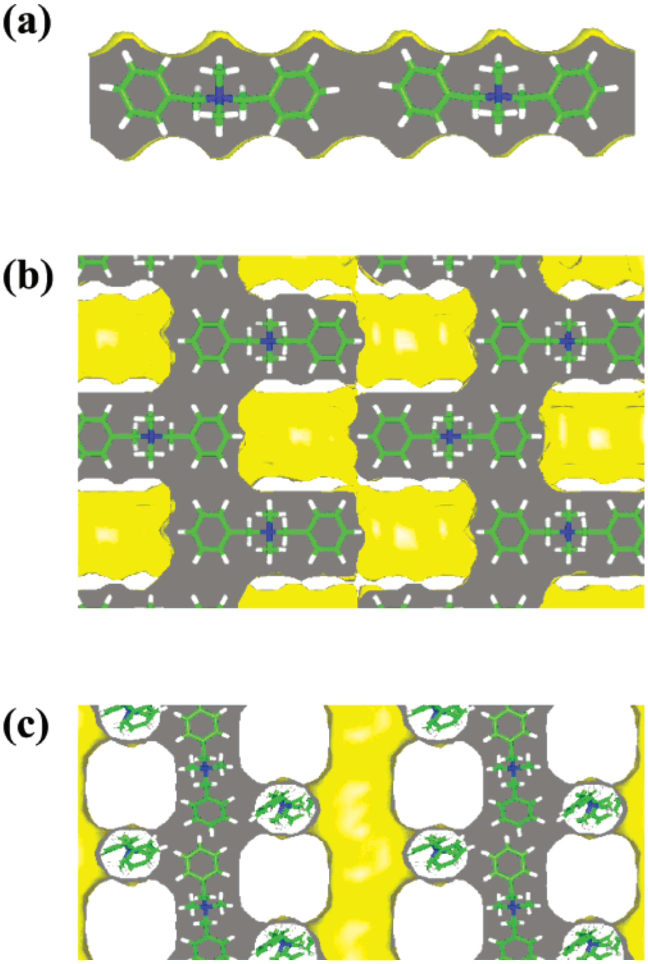

Figure 18. Template versatility: the location and different stacking arrangements of the dibenzyldimethylammonium template in (a) ZSM-12 (MTW), (b) EU-1 (EUO), and (c) β (BEA) as determined via MC-SA calculations. The zeolite frameworks have one-, two-, and three-dimensional channel systems, respectively, and the template molecule achieves an excellent fit in each case.

3. Synergy of Theory and Experiment

An extensive modeling and experimental investigation by Rollman et al.[308,309] of the relationship between the structure of small amines and the zeolite product they produce yielded several interesting conclusions. The modeling confirmed a pore stabilization role for both amines that are structure specific and those which are not structure specific. Even though differences in energies for different amine–framework combinations were found to be small, the results consistently reflected the experimental observations, again highlighting the potential of this type of modeling work to screen candidate template molecules.

The successful application of strategic design methods has also been elegantly demonstrated by the work of Zones and his team in their discovery of new frameworks.[310] Their approach is based on understanding the role and interaction of the organic structure-directing agent in the gel chemistry and the final crystalline product in terms of host–guest relationship. The size and shape of rigid, bulky cyclic, and polycyclic organic amines have been specifically designed so that these templates are too large, or have the wrong geometries, to synthesize common default products. This has led to the discovery of several new zeolite-type structures. Recent examples include SSZ-35, SSZ-36, and SSZ-39.[290]

Chatterjee and Iwasaki[311] have developed a promising method for determining the best template for synthesising a particular framework based on the hard and soft bases (HASB) principle. This approach involves the use of density functional theory (DFT) to calculate reactivity indices for template molecules and fragments of the target framework. Not only can these indices be compared in order to rank potential templates, but the approach can also be used to pinpoint interaction sites between the template molecule and zeolite framework. In this study, the authors have demonstrated the success of the approach with reference to the ZSM-5 structure. If successful for other frameworks, this methodology will be of great value in rational design.

In a study which indirectly provides clues to the interaction between template and surrounding structure, Sastre et al.[312] have used a modeling approach based on interatomic potentials to predict the location of the aluminum and acid sites within the zeolite framework. This method highlights the importance of the structure directing agent in determining the distribution of the aluminum in the framework, and the success of the approach is demonstrated by the good agreement obtained between the predicted and experimental IR spectrum for ITQ-7.

4. Shape Similarity amd Cooperative Templating

Strong geometric matching is a commonly observed feature in framework-template calculations. Boyett and co-workers[313] have exploited this by using shape analysis tools to study the geometries of over 200 template molecules and to relate the shapes of templates to the products they form. Overlapping regions of shape-space are found to contain molecules that synthesize the same structure. The work also highlights the fact that templates with different individual spatial characteristics can form the same product when they 'pack' together to produce the same overall shape; a phenomenon which might be called cooperative templating and which may find wider application in the future. In addition, shape analysis is a useful screening tool for assessing possible products (desired or undesired) from among known frameworks.

5. Structure Blocking

Most modeling studies have centered upon the relationship between template molecules and the framework structures that they successfully synthesize and also have focused on models in which the template is fully occluded inside the zeolite product. However, a recent investigation by Cox et al.[56] has investigated the phenomenon of structure blocking, whereby the addition of low levels of an organic molecule can be used to prevent the formation of a particular framework. In this study, the ability of low levels of the hexamethonium ion $(CH_3)_3N^+(CH_2)_6N^+(CH_3)_3$ to block the formation of ZSM-5 from a standard inorganic preparation mixture for this structure has been probed. The modeling work again used a MC-SA approach to dock the hexamethonium molecule inside the ZSM-5 framework, but also extended the methodology to investigate how hexamethonium binds to the growing surface of the structure. The effectiveness of the hexamethonium structure to block ZSM-5 formation is attributed to two characteristic features of the molecule. First, the $-(CH_2)_6$ chain is too short to span the intersections in the sinusoidal part (Figure 19) of the channel system, and second, the binding energy for the molecule on this part of the growing surface is highly favorable. Thus, the molecule can sterically hinder the genesis of subsequent layers of the growing structure, hence blocking its formation.

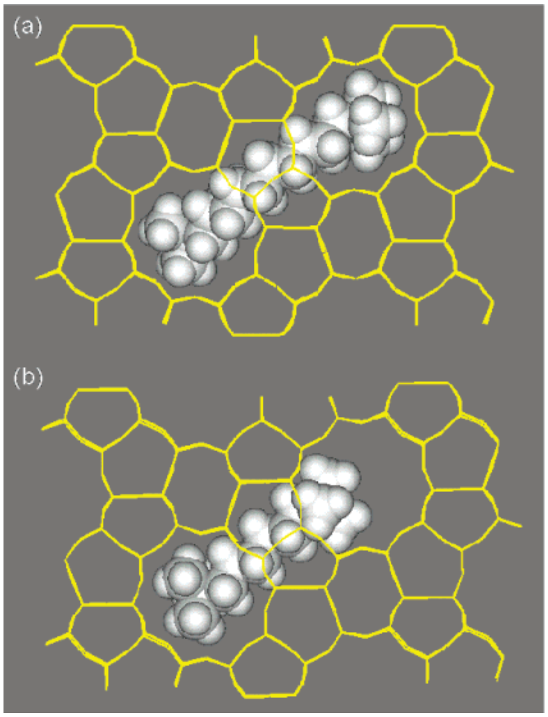

Figure 19. The location of (a) decamethonium $(CH_3)_3N^+(CH_2)_{10}N^+(CH_3)_3$ and (b) hexamethonium $(CH_3)_3N^+(CH_2)_6N^+(CH_3)_3$ cations in the sinusoidal channel of ZSM-5. Decamethonium, which templates the formation of ZSM-5, perfectly bridges the channel intersections. Hexamethonium, which blocks its formation, leaves bulky $-(CH_3)_3$ groups inside the narrow part of the channel.

6. Low Void Filling

Forbes and Rees[314,315] used a combined experimental/simulation approach to investigate the formation of ZSM-5 and Theta-1 using the diethanolamine template. The model proposed suggests that void-filling is near-complete in Theta-1, with template–framework interactions stabilized by van der Waals forces. In contrast, for ZSM-5 lower void-filling is compensated by increased electrostatic interactions. The model successfully predicts the SiO_2/Al_2O_3 ratio required for each framework and the approach developed shows the promise of theoretical modeling in helping to understand the conditions under which frameworks are able to form when void filling by the template is low.

7. Quantum Mechanical Methods

The use of quantum mechanical (QM) methods to study template-zeolite pairs has the advantage that electronic effects will be treated more rigorously than those based on molecular mechanics approaches such as those discussed so far (indeed many of the above studies have used no charges on the framework or template). However, QM methods have the disadvantage that they are significantly more CPU-intensive; a problem for periodic zeolite structures that often contain several hundreds of atoms in the unit cell. Chatterjee and Vetrivel[316] have shown that semiempirical QM methods can be successfully used to determine the interaction energy and electron distribution for several different templates within a cluster of the ZSM-5 framework. Calculations of this type show promise and will be of significant interest in the future, in particular, when the full zeolite framework is incorporated into high-level QM methodologies.

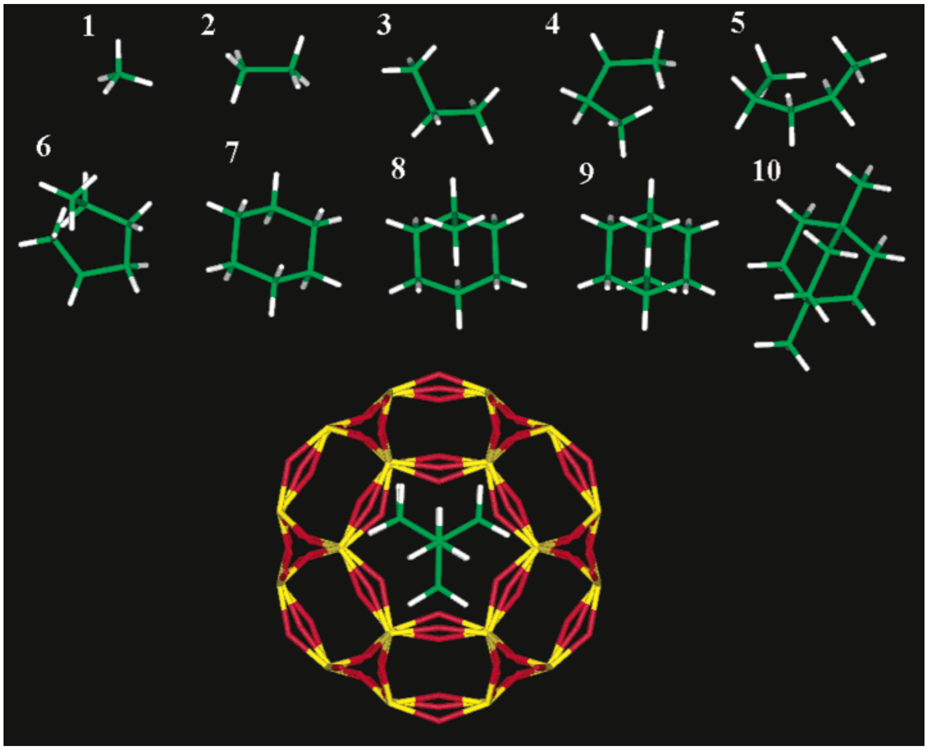

Figure 20. The successive steps (1−10) in building a theoretical template for the LEV framework from a fragment database using the de novo technique. The energy-minimized location of the final molecule (10) in the LEV framework, highlighting the excellent shape/symmetry relationship, is shown below.

8. De Novo Design

An important advance in the design of new candidate molecules for target frameworks has been the modification of the de novo methodology used in drug design work. In this method[317] a template molecule is “grown” computationally inside the host framework by the successive addition of fragments from a library database to an initial seed molecule (Figure 20). A computational function is applied which aims to maximize the packing efficiency of the template. Symmetry operators are used to create images in equivalent pore space to ensure that template-template interactions are appropriately considered. The success of this approach[318] has been demonstrated by the design of a template for DAF-5 (a CoAPO material). One of the templates designed using the de novo method, 4-piperidinopiperidine, was successfully used to prepare pure samples of DAF-5 with short crystallization times. Previous attempts at this synthesis using templates that were not derived using the de novo approach had proved unsuccessful.

B. Modeling Crystallization: Cluster Calculations

While the studies considered so far have yielded a unique insight into the relationship between zeolite-template pairs, the use of computational methods to investigate the mechanism of crystallization and growth has remained more difficult. However, recent studies demonstrate the potential that modeling has to offer in these areas also. As discussed earlier (section V.C), ^{29}Si NMR has proved to be an effective tool in identifying the gross structural features of silica fragments in solutions akin to synthesis mixtures. However, it is difficult to study the properties of individual fragment types via experimental methods. Several computational studies have used different levels of theory to investigate the structure, energies, and reactions for a wide-range of silica clusters. Recent work has focused on high-level Hartree−Fock[319−321] and density functional theory[322,323] calculations. Systematic analysis of these data offers the possibility of the development of kinetic models that will describe the initial step in growth mechanisms.

Catlow et al.[55,60] have developed these approaches to investigate interactions between solvated fragments of zeolite structures and template molecules. This work demonstrates that calculations of this type can provide a powerful tool for investigating the mechanism of zeolite synthesis. The results show[60] that the organic template plays an important role in stabilizing clusters of framework material, preserving their structure under the influence of water. In addition, charge interactions between the template and framework fragment serve to bind these components together for sufficiently long periods to allow further condensation to take place. In this study, the 1-aminoadamantane molecule is shown to influence the spatial orientation of a surrounding silica fragment so that it resembles geometries observed in one of the zeolite products formed by this template. These approaches may ultimately enable us to make predictions about possible framework products for a given template molecule.

Theoretical methods for investigating nucleation processes have recently been extended by the work of Wu and Deem.[324] A Monte Carlo methodology has been developed that models a silicate solution on the atomic scale in the absence of a structure directing agent. This study has yielded a valuable insight into fundamental aspects of the nucleation process such as an estimation of the nucleation barrier and the critical cluster size.

The advances in modeling methodologies outlined above offer the hope that an appropriate template for a zeolite framework that has been specifically tailored for a particular reaction may be successfully designed and synthesized. Modeling studies of catalytic reactions and sorption by zeolites (see, for example, refs 302 and 325) suggest that candidate frameworks for a given application could be screened in this way. However, suitable target frameworks need to be derived if the advances in modeling template−framework interactions are to be used in the quest for 'designer zeolites' of this type.

C. Enumeration of Framework Structures

Enumeration of zeolite structures is a considerable challenge because an infinite number of hypothetical three-dimensional four-connected networks can be formed. However, there are currently only around 120 distinct tetrahedral frameworks recognized for zeolites and related materials, suggesting that the key to this area lies not simply in being able to generate structures systematically but additionally in the effective assessment of the chemical and topological viability of the networks so created.

Much of the basic description of three-dimensional network structures was first undertaken by Wells.[326,327] Smith and co-workers have described a large number of hypothetical structures (see for example ref 328). One notable achievement of this work was the prediction of the net including 18-rings that was subsequently identified in the aluminophosphate VPI-5[148,151] (section V.A). Of the many classification methods for zeolite frameworks, one of the most powerful and predictive is that first introduced by Akporiaye and Price.[329] This provides a simple description of a large fraction of the known frameworks in terms of a corrugated three-connected net and uses mathematical stacking operators to act on these sheets to produce the next sheet in the sequence until the unit cell is fully described. This method has proved successful in helping to solve the structure of several new materials, including NU-87 and NU-86.[330] It also allows the generation of hypothetical framework structures, using sheets and operators that are observed in known systems to propagate a host of new framework types. Computational energy minimization methods have been used to assess the viability of some of the derived hypothetical structures, and several have been reported.[329]

Treacy et al.[331] have used a computational approach to derive systematically all hypothetical structures for a given number of unique tetrahedral atoms and the appropriate crystallographic space group. Results have been presented for one unique tetrahedral atom in each of the 230 different crystallographic space groups. More than 6400 structures were generated using this approach, and their viability was assessed using a simulated annealing protocol. Around 3% of these structures refined to reasonable conformations, several of which are described by the authors. However, the approach is restricted to consideration of small numbers of unique atoms because of the large numbers of potential structures that are generated. In a related study, O'Keeffe and co-workers[332−334] have used empirical computer search algorithms to derive new structures. By moving a point in small amounts throughout the asymmetric unit of the unit cell of all the cubic, hexagonal, tetragonal, and orthorhombic space groups in turn, they were able to generate all the equivalent points in the unit cell by the application of the appropriate symmetry operators. This approach proved highly successful in generating a large number of novel structures.

One important new development in the enumeration of hypothetical structures is the recent work by Klinowski et al.,[335,336] who have demonstrated that mathematical tiling theory offers a systematic and exhaustive means of enumerating structures. Many of the structures identified using this approach have not been revealed using other enumeration methods, particularly for frameworks where two or more symmetrically inequivalent types of tetrahedral vertexes are present.

VIII. Up To and beyond the Year 2000: (II) New Ideas and Current Trends in Experimental and Background Work

The preceding discussion (section VII) offers a perspective on the major advances which have been made in computer modeling studies related to zeolite synthesis, most of them within the last 10 years. To complement this, the present section considers the spectrum of contemporary experimental studies and related background theory, both to illustrate areas of growing interest and also in an attempt to identify topics which may be seen as landmark issues in the future. It is also a truism to remark on the increasingly close synergy which will undoubtedly develop between modeling and laboratory approaches. In the first instance, we describe several studies, some still in progress, which have continued to sharpen our perceptions on different aspects of the energetics, kinetics and mechanism of zeolite synthesis. Mention is then made of progress brought about through advances in experimental techniques. Finally, there is a short survey of the field of new materials in relation to hydrothermal synthesis.

A. New Insights into Zeolite Synthesis

1. Precursors and Small Particles

In what has developed into a major study, the Leuven "nanoslab" hypothesis (see section VI.E.2) continues to unfold. Most recently,[337,338] direct investigative methods (TEM, ^{29}Si NMR, SAXS) have been used on the precursor sols to substantiate the original idea of discrete nanoslab building units which combine by self-assembly to form tablets and MFI-type zeolite crystals. Specific silicate oligomers (particularly a pentacyclic dodecamer) were identified as intermediates in nanoslab evolution. However, other workers dispute such a “structural fragment condensation” theory, as can be seen from a recent exchange of views.[339,340]

The above work, and indeed many related studies on the early stages of zeolite synthesis (see sections VI.C and VI.D), owes much to research carried out in the early 1990s, when both Verduijn[341,342] and Schoeman and co-workers[343,344] reported the synthesis of colloidal zeolite suspensions. The distinction of these materials lies in their very small particle size (usually <150 nm), the narrowness of their particle size distributions (often monodisperse), and, especially, the fact that the sols are composed of discrete particles (usually single crystals) rather than aggregates. Since product crystal size is commensurate with the dimensions of colloidal precursors, the system represents a convenient vehicle for investigations of crystal nucleation and growth.[259−261,270,271] Using a two-stage, varying-temperature synthesis, Sterte and co-workers charted the development of the crystal population as a function of T_1 and T_2 ($T_1 < T_2$), where the reaction mixture was first maintained at the lower temperature before final heating at T_2. By observing the time at T_1 beyond which there was no further increase in the crystal numbers at the end of the two-stage synthesis, the nucleation rate at T_1 could be estimated. Measurements were carried out on silicalite[345−347] and faujasite[348,349] under a variety of conditions. A mechanistic probe into the nucleation and growth of colloidal silicalite crystals has also been obtained by exploiting the differences between microwave and thermal heating (see below, section VIII.B.1).

2. Background Studies: Equilibria and Kinetics

Early work by the Mulhouse group sought to establish rules for zeolite solid−solution equilibria and solubility relationships.[170−172] In further papers,[174,175] the same workers showed that the silicate oligomer distributions in silicate solutions could be calculated to reasonable agreement with experiment from known or estimated equilibrium constants. While many of the same concepts occur in the equilibrium model of Lowe,[158] very little further extension of these ideas occurred until quite recently. However, in an important series of papers, Šefčík and McCormick review the thermochemistry of aqueous silicate solutions,[350] discuss what is meant by the solubility of zeolite A,[351] and extend the modeling of solution equilibria to the prediction of zeolite crystallization diagrams.[352] (The latter are phase diagrams, usually in the form of triangular plots, relating the occurrence of crystallized products to the proportion of major compositional components, e.g., $Na_2O-SiO_2-Al_2O_3$). There is emphasis throughout on a meaningful and physically relevant approach and altogether this is an impressive body of work. In the same context, mention must be made of the series of studies published by Lechert and his group. Over a number of years, expressions have been developed which relate the Si/Al ratios of product zeolites to elements of the synthesis batch composition, particularly the excess alkalinity [(Na−Al)/Si].[353−355] Although the relationships derived are semiempirical, they are the product of much thought and experience. The generality of their applicability (covering at least seven types of aluminous zeolites) and the agreement with experiment are impressive, strongly suggesting that the findings reflect a basis of fundamental, if as yet incompletely understood, theory. Two further relevant contributions also merit mention here. Swaddle has recently presented a very useful review of silicate complexes of Al(III) in aqueous systems[356] and—for a mineralogist’s rather different perspective—Chipera and Apps have summarized current views on the geochemical stability of natural zeolites.[357]

The recent renaissance in solution equilibria studies has been reinforced by an important series of publications on zeolite thermochemistry from Navrotsky and collaborators. Early papers in this series were concerned with calorimetric studies of zeolite or zeotype structure−stability or composition−stability relationships (see e.g., ref 358). However, more recent reports have dealt with in situ calorimetric studies of zeolite synthesis for faujasite[359,360] and silicalite[361] (the latter once again using one of the Schoeman colloidal silicalite preparations[261]). In the former case, the sensitivity of the method enabled detection of the crystalline phase before the mass fraction was high enough for observation by XRD, NMR, or IR methods. Also, a change in the Arrhenius activation energy for crystallization from 66 ± 2.3 to 72 ± 0.8 kJ/mol could be seen, corresponding to the increase in Si/Al ratio in the solution, as the crystallization proceeded from 5% to 75% completion. This supports the established trend (section IV.D) of decreasing reaction rate with increase in Si/Al ratio.[136,137] For the clear “solution” TPA-MFI synthesis, the results are discussed on the basis of a crystal growth mechanism involving orderly aggregation of pre-assembled primary 3 nm particles.

Finally, two recent papers discuss the thermochemistry of pure-silica zeolites[362] and the thermodynamics of their synthesis.[363] The range of enthalpies of transition observed is quite narrow at only 6.8−14.4 kJ/mol above that of quartz. Correspondingly, Gibbs free energy changes for the crystallization of microporous silica phases from amorphous silica are estimated for quaternary ammonium complexes of zeolites ZSM-5 and β to be in the range -4.9 to -8.5 kJ/mol SiO_2. No single thermodynamic factor dominated the overall Gibbs free energies, and the small energetic differences were taken to suggest that kinetic factors were of major importance in molecular sieve preparation. (Interestingly, a similar inference was drawn from values calculated on the basis of the Lowe equilibrium model for zeolite synthesis.[31,158] If figures of 2.5×10^{-3} and 1.8×10^{-4} mol dm^{-3}, representative values for the true solubility of amorphous and crystalline silica,[158] are inserted into the supersaturation (ΔG) equation from Table 3, a free energy change of -6.5 kJ/mol SiO_2 at 25 °C is obtained. However, at that time (1983) there were no supporting data with which to corroborate this conclusion!) In a further paper, attention is drawn to the relationship between energetics and zeolite internal surface areas.[364] A linear relationship was found between formation enthalpy and internal surface areas for α-quartz, α-cristobalite, and 17 zeolitic frameworks. In this context, it is instructive to remember the work of Pope[365] in which he pointed out that the energetics of zeolite nucleation may be greatly modified from that of dense phases because of the presence of the large internal surface area.

On a broader front, a useful overview of the nucleation and crystallization of solids from solution has been given by Schüth.[366] Models for the layer-by-layer growth of microporous materials are discussed by Anderson and co-workers in the context of results from atomic force microscopy and high-resolution electron microscopy.[367,368] The question of the balance between homogeneous and heterogeneous events in zeolite synthesis (viz. Figure 5) has been a feature of recent work by Serrano, van Grieken, and colleagues, and they present a thoughtful account of this research area in a recent review.[71]

3. Aluminum Distribution

The possibility of obtaining mechanistic information from product framework ordering in a faujasite system has been discussed above (section VI.E.4). Similarly, the distribution of aluminum among the tetrahedral sites in high-silica zeolites, although difficult to determine, is a potential source of information on the assembly mechanism of the structure. By using visible spectroscopy to monitor the distribution of bare divalent Co(II) ions exchanged into different samples of ZSM-5, workers at the Heyrovský Institute in Prague were able to deduce that the Al atoms were not randomly distributed but were sited at locations affected by both the Si/Al composition and the synthesis procedure.[369] Using MAS NMR techniques (CPMAS and REDOR), Shantz and co-workers showed that the methylene protons of the benzyltrimethylammonium structure-directing agent (SDA) are preferentially located near the Si atoms adjacent to the framework aluminum, suggesting a direct association between the latter and the charge center of the SDA.[370] In a novel approach by the Valencia team, calculations based on interatomic potentials were used to predict the Al distribution in ITQ-7.[312] By including the structure directing agent in the calculations, the authors showed the importance of the SDA in influencing the distribution of the Al atoms in the framework. Moreover, good agreement was found between predicted and experimental IR frequencies for the H−ITQ-7 bridged hydroxyls associated with the presence of Al, demonstrating the validity of the modeling approach used.

4. Zeolite Films and Membranes

Much of the effort on the preparation of zeolite membranes has necessarily been directed toward improving the fabrication of defect-free polycrystalline films. The importance of controlling the preparative chemistry has been noted earlier (section V.E) and recent investigations continue to provide an oblique insight into the more general topic of crystallization mechanism. Several studies establish correlations between synthesis conditions and crystal orientation and morphology,[371−373] and the conversion of gel particles to oriented crystals has been described in terms of a solid-state transformation.[374] As part of an extensive research program on zeolite films, Li et al. have described the preparation of Al-zoned MFI films.[375] In the attempted growth of one layer upon another, continuous growth with no discontinuity was achieved between dissimilar layers when ZSM-5 was grown upon silicalite but not vice-versa. The difference was ascribed to competition for discharge of supersaturation between nucleation and growth processes: continued growth upon silicalite was more favorable than nucleation of new ZSM-5 crystals, whereas nucleation in the TPA−silicalite-1 synthesis solution/film interface exceeded the rate of growth of the ZSM-5 (high-alumina) exposed crystal faces.

B. Progress in Experimental Techniques

1. Microwave Dielectric Heating

Following the first report of the application of microwave dielectric heating to zeolite synthesis,[376] this method has been used increasingly in the synthesis of porous materials.[62] The technique offers the potential for convenient and often rapid sample preparation, usually affording products of high crystallinity. There is also the possibility of (genuine) selectivity. In the microwave synthesis of zeolite Y, crystallization of undesired phases is suppressed,[377] even at an unusually high synthesis temperature (150 °C).[378] Such selectivity is largely attributable to the high heating rates attainable in microwave syntheses and their effect upon the rival rates of nucleation and growth of competing phases (in this case, zeolites Y and P). Similarly, in colloidal silicalite synthesis, the different rates of temperature rise achievable by microwave and thermal heating made it possible to distinguish between the crystal population nucleated during the heating process and that arising from proto-nuclei generated during the room-temperature aging of the precursor sols.[379] A very rapid (3 min) microwave crystallization of ZSM-5 probably reflected a contribution from the interfacial superheating of nanocrystal seeds.[111] However, under near-equilibrium conditions, there was no significant difference between the crystal linear growth rates in thermally and microwave heated reactions, the growing crystals acting in this case as a form of internal thermometer.[380]

2. Increasing Use of Fluoride Media

When first introduced,[125] the fluoride route was probably seen as a useful alternative to the more usual hydroxide-based synthesis. However, as its application spread from high to low pH systems and further to non-aluminosilicate syntheses,[36,39,41,45] results began to appear which were not achievable by the hydroxide route.[53,67] In part, this may be through access to new regions of synthetic chemistry, but a further important element is the incorporation of fluoride ion into the product. In some cases, it is not known whether this is an adventitious or an essential element of the synthesis but some materials, e.g., the 20-T-ring gallophosphate cloverite,[381] have never (so far) been made in the absence of fluoride. The unambiguous location of fluoride by diffraction or MAS NMR methods has shown that the F^- ion appears always to be occluded in small cages within the zeolite framework, usually close to a 4-T-ring window.[67] Fluoride ion could therefore be considered as a structure-director[382] and has been shown from NMR studies to interact strongly with framework silicon atoms.[383,384] In terms of the solution chemistry, Lindner and Lechert have studied the influence of fluoride ion on the crystallization kinetics of zeolite Y.[385] On comparing $Al(OH)_4^-$ and $AlF(OH)_3^-$ as potential growth species, their incorporation into the growing crystals was identified as the rate-determining step of zeolite NaY crystallization in this system.

3. Combinatorial Synthesis

It was inevitable that the current activity in high-throughput (combinatorial) techniques would find interesting outlets in the synthesis and catalytic evaluation of zeolites. The first report relating to the hydrothermal synthesis of zeolites was that by Akporiaye and co-workers, who used a 10 × 10-chamber Teflon block to obtain ternary and quaternary crystallization diagrams for single and mixed cation systems at 100 °C.[386] Current progress has recently been discussed in the context of new materials discovery by Holmgren and co-workers[387] and by Newsam et al.[388] who consider key experimental and computational issues together with bottlenecks to productivity. The technique would seem well suited to the development of zeolite membranes and a 21-well combinatorial assembly for this purpose has recently been described.[389]

4. High-Pressure Methods

Rather unexpectedly, there has recently been a return to the mineralogists' technique of synthesis at very high (kilobar) pressures. Ghobarkar et al.[390,391] have reported the synthesis of a variety of natural zeolite counterparts from synthetic glasses and distilled water at temperatures of 170−270 °C and a reaction time of 60 days. In some cases, a direct effect of pressure was observed. For example, bikitaite could not be synthesized under these conditions at 1 kbar pressure but was obtained successfully at 2 kbar.

5. Salt-Solution Transformations

Since the very early work of Barrer (see section II), there has been little utilization of the salt-solution transformation reaction (unless the fluoride route is seen as a special example). In this method, an existing zeolite is treated hydrothermally in a solution of a metal salt. Barrer[77−79] used concentrated neutral solutions of barium chloride or bromide to convert analcime into new zeolites "P" (from $BaCl_2$) and "Q" (from $BaBr_2$), both materials subsequently being found to have the KFI structure.[80−82] Recently, Davis and co-workers[392,393] have used more dilute (0.1−1.0 N) alkaline earth halide solutions to convert zeolites Y, P1, and L into a variety of natural zeolite analogues, principally harmotome, heulandite, brewsterite, gmelinite, epistilbite, and yugawaralite. The phase obtained depended mainly on the solution composition and the Si/Al ratio of the starting zeolite. To date, the route has not yielded any further new or previously unsynthesized phases.

C. New Materials

1. Burgeoning Silica Polymorphs

In addition to the yearly growth in the number of known synthetic zeolites, there has also been an increase in the proportion which can be made in (essentially) pure silica form. Of some two dozen structural types of zeolitic silica polymorph now recognized, one-third have been prepared since 1995. Particularly significant in this area has been the work of Camblor and co-workers[67] using the fluoride route (q. v. section VIII.B.2 above). Employing low H_2O/SiO_2 ratios in a key modification of the standard procedure,[53] the new phases produced are of unusually low density. For example, silica−chabazite is the least dense silica polymorph known, with a void fraction of 46%. Significantly, the usual (tetraethylammonium hydroxide) route to zeolite β will not crystallize a pure silica version under normal preparative conditions, but will do so by the steam-assisted-conversion method (section VI.F) in which a dried gel is heated in a steam atmosphere.[68] The effect of water content on the synthesis of silica molecular sieves thus extends beyond the chemistry of the fluoride route.

2. Labile Layer Structures

The bonding density in different directions within a crystal structure will affect many of its fundamental properties, including linear growth rates and observed morphology.[394] In cases where such bonding is highly anisotropic, unusual behavior may result. The first example of a zeolite formed by calcination of a layer-structured precursor appears to be that of NU-6.[395] More detail is available in the case of "PREFER", where the transformation of this two-dimensional aluminosilicate into the zeolite ferrierite on calcination at 550 °C has been carefully studied.[396,397] The precursor appears to consist of ferrierite-type sheets in the *bc* plane, separated by molecules of the bulky template (4-amino-2,2,6,6-tetramethylpiperidine). On burning out the occluded organic molecule, the ferrierite layers progressively link together in the *a*-direction as new T−O−T linkages are formed by condensation reactions. However, it is also possible to modify this process. PREFER and related materials can be delaminated and re-assembled in a number of ways to give a series of high surface area derivatives with catalytically active sites accessible to bulky reactants. Examples from the Valencia school are ITQ-2,[398] ITQ-6, and ITQ-36.[399] Similar relationships characterize the Mobil MCM-22 family[400,401] (Figure 21) which already form the basis for a new and commercially operating process for the manufacture of ethyl benzene.[402] It should be noted that although the 2D → 3D transformation has been established for this 2-stage synthetic route, layered intermediates detected in the course of normal hydrothermal preparations may be

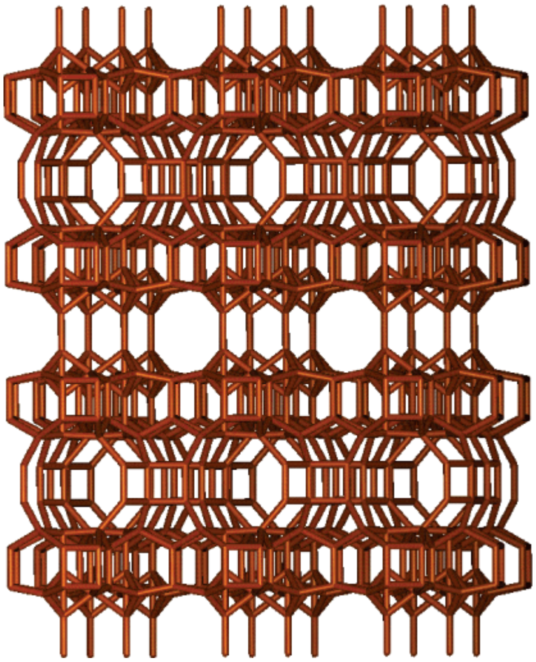

Figure 21. The futuristic tower-like structure of MCM-22 (structure code MWW), clearly showing the layers of strong and weak bonding density (for further details, see ref 404).

only indirectly involved (as nutrient-storing transients) in the course of the synthesis.[403]

3. Zeotypes at the Cutting Edge

There have been notable recent advances in zeolite synthesis and in the generation of new structures. The use of a wider range of organic (and organometallic) templates, many of them very specifically designed, has generated numerous new zeolites, several having previously unknown structural elements or ring sizes.[404] However, it has been with the zeolite analogues (zeotypes) that some of the most surprising and novel findings have arisen.[65,72] In structural terms, ring sizes larger than 12-T atoms were first seen in metallophosphate systems: VPI-5 (Al−P) 18-ring, cloverite (Ga−P) 20-ring, JDF-20 (Al−P) 20-ring.[72] This trend has continued, recently revealing the largest ring size so far observed: ND-1 (Zn−P) 24-ring.[405] Aluminophosphates were also the first to demonstrate coordination numbers greater than four in microporous frameworks. [238] Other hyper-tetrahedral frameworks are now well-established, such as the ETS- and AM- titanosilicate families (which have four-coordinate silicon and five- and/or six-coordinate titanium sites[241]) and the octahedral molecular sieves (OMS) based on manganese.[406,407] The differences seem likely to extend from structure into the preparative chemistry. Some of these materials (notably the zinc phosphates) can be made very rapidly under very mild conditions,[408−411] suggesting a more nearly ionic assembly route. In line with this, a recent review of metallophosphate formation discusses a synthesis mechanism in which significant elements of the structure exist in solution as identifiable building blocks before being “clipped” together to from the precipitated product.[412]

A further demonstration of the augmented chemical and structural flexibility afforded by the substitution of heteroatoms into aluminosilicate structures is given by recent discoveries concerning zeolite β. Up to now, synthetic zeolite β (and its natural counterpart tschernichite) have been found to contain a random stacking of two polymorphs, designated A and B. A further polymorph, C, was predicted but not found.[413] However, Corma et al. have synthesized a new family of β structures (ITQ-16) formed by polymorphs A, B, and C, in which the proportion of polymorph C can be controlled by changing the organic structure directing agent and/or the germanium content of the synthesis gel.[414] Furthermore, in the presence of Ge, pure polymorph C (ITQ-17) can be synthesized.[415,416]

4. Hierarchical Pore Structures

Materials which combine different levels of porosity into a single, highly ramified network have a number of potential advantages, e.g., improved overall mass transport characteristics. Two synthetic strategies can be distinguished. The first type of approach seeks to impose a larger-scale periodic order upon a microporous material, for example, by growing zeolite crystals on a porous substrate or by controlled packing of zeolite nanocrystals. Two groups of workers have used synthetic techniques allied to biomineralization to build composites based on diatom skeletons.[417−420] At one extreme, conditions are chosen such that the 20 μm diatoms act as supports for a polycrystalline zeolite overgrowth. In contrast, the diatom support may be partly or wholly consumed in the synthesis (i.e., as a reagent) to leave a polycrystalline zeolite pseudomorph. In both cases, the resulting materials contain a hierarchy of pores ranging from macropores to zeolitic micropores and the approach can be extended to other biostructures such as wood.[421] An alternative possibility relies on the “templating” effect of latex spheres, which are afterward removed, usually by calcination. The interstices may be infiltrated with a zeolite synthesis mixture to give a foamlike structure having regular 250 nm voids with microporous polycrystalline zeolite walls.[422] In a different procedure, the interstices are permeated with a ready-formed dispersion of zeolite nanocrystals to give eventually a structure consisting of micropores arranged into periodic, interconnected networks of submicron macropores.[423]

The second type of general approach takes a mesoporous structure as its starting point and seeks to address two interlinked problems which reduce the potential catalytic utility of aluminous mesostructures such as Al−MCM-41, e.g., for the cracking of large hydrocarbons. The pore walls of most mesoporous materials are amorphous and usually of inadequate thickness to contain sufficient domains of crystalline (i.e., zeolite-like) structure to form the basis of strong acid sites. They are also of poor hydrothermal stability. Attempts to overcome this usually employ some sort of compromise strategy in which elements of zeolite synthesis are included in the type of surfactant−silicate composition used in mesoporous materials synthesis. In some cases, an existing mesoporous assembly is subjected to zeolitisation.[424,425] In others, there is the reverse situation in which zeolite nanocrystals[426] or embryonic or partially crystallized zeolite synthesis mixtures[427,428] form the basis of subsequent surfactant-ordered assembly reactions. From the perspective of zeolite synthesis, a particularly interesting example of the latter strategy has recently been described by Liu and Pinnavaia.[429] "Seeds" of faujasite, ZSM-5 and β zeolites were prepared after the fashion of "nucleating broths" (often employed to assist the inception of crystallization), in that a suitable, alkali-based reaction mixture was subjected to a limited hydrothermal treatment, insufficient to produce detectable XRD crystallinity. These seed mixtures were then incorporated into the synthesis of mesostructured cellular foams (MCF)[430] and large pore hexagonal mesostructures of the SBA-15[431] type. Although no acidity data are given, the well-characterized products (pore sizes 80−130 nm) showed good steam stability (20% steam, 800 °C, 2h). Significantly, the syntheses of the mesostructures required conditions of acidic pH (from below pH 2 up to pH 6.5), the authors noting that "protozeolitic nanoclusters clearly persist under acidic conditions and can be incorporated into the final mesostructures" (q.v. section V.F).

Finally, two interesting and unusual approaches to hierarchically structured pore systems are noted. In one form of "confined space synthesis", zeolite nanocrystals are grown within the restriction of a porous carbon.[432] However, an alternative outcome lies in the growth of larger crystals which engulf the carbon particles. Calcination of the resulting composite leads to crystals containing mesopores vacated by removal of the carbon.[433] In a completely different procedure, a bimodal molecular sieve was formed on heating an MCM-41 synthesis mixture containing a relatively large amount of sodium oxide and alumina. The product was a composite material consisting of zeolite Y with an overgrowth of MCM-41. In the cracking of vacuum gas oil, this material showed a higher conversion of heavy products compared to a conventional ultrastable-Y catalyst.[434]

IX. Conclusion

We have seen how the practice of hydrothermal zeolite synthesis became a science following the pioneering work of Barrer and Milton over 50 years ago. Since that time, the subject has developed through a continuous evolution of ideas, directed, as is often the case, by a combination of deductive reasoning and chance discovery. One major theme has been the drive to obtain new structures and compositions of matter which might provide key materials for use in ion exchange, sorptive separation, and selective catalysis. In this way, whole new families of zeolite-like materials have been revealed. However, many of these discoveries have been the result of inspired intuition, serendipity, or the careful pursuit of small, unexplained observations rather than the application of any fundamental theory. This has led researchers to struggle with the physical chemistry of these complex multiphase systems in an effort to find out just how such porous crystals (or pseudo-crystals) are formed. During the course of this review, we have discussed a selection of the diagrammatic representations which have been used to describe the process of zeolite synthesis. In conclusion, it is interesting to consider the evolution in the perception of zeolite synthesis mechanism which is revealed by these illustrations (Figures 3, 5, 9, 12, 16, and 17).

From the outset, it was clear to key protagonists that zeolite synthesis was a reaction-crystallization process in which amorphous reactants were converted to the crystalline product through the agency of hydroxyl ion, which acted as a type of catalyst by breaking and remaking Si,Al−O−Si,Al bonds. The earliest picture (Figure 3, Breck,[99] 1964) starts from the concept of an aqueous aluminosilicate gel with its associated cations. This hydrous polymer is depolymerized by hydroxide ions into unspecified units which are ordered by the hydrated cations into basic polyhedral building blocks. These then link to form the overall zeolite framework. Zhdanov's treatment (based on the supporting analytical work)[15] (1971) enabled him to come a little closer to the chemistry connecting the amorphous, crystalline, and solution phases (Figure 9). He proposed that the solid and liquid phases are connected by a solubility equilibrium (a concept quantified by Lowe in his equilibrium model of 1983[158]). The amorphous solid phase was seen as the nutrient reservoir from which a wide variety of solution phase species could be generated. Condensation reactions gave rise to building units (four- and six-membered rings) with which growth from solution on to crystal nuclei (also formed in condensation reactions) occurred until the amorphous phase had completely dissolved. It was thus accepted that both the solid phase and the solution played a part in the overall transformation. The major source of confusion lay in the extent to which the amorphous solid-phase functioned as an active participant in the crystallization process as opposed to playing only a passive role as nutrient reservoir. Despite considerable further work and discussion,[71] this question is even now not completely resolved.

On the basis of investigations using a wide variety of techniques, Gabelica and co-workers put forward (initially in 1981) a pragmatic view of the ZSM-5 synthesis mechanism.[193] To account for their experimental observations, and in particular for the different radial aluminum distributions found in the product crystals, they proposed two pathways for ZSM-5 formation (Figure 12). For syntheses of type A (typified by high values for the alkalinity, concentration and TPA/Na ratio), the suggested reaction mechanism bears many resemblances to the solution-mediated scheme of Zhdanov (Figure 9). However, in type B syntheses (where concentrations, base levels and the TPA/Na ratio are lower), the crystals are perceived to nucleate and grow within the hydrous silica−alumina gel in a process described as a solid hydrogel phase transformation. Following the polemic discussed in section III.A, the two extreme views of solution-mediated crystallization versus gel reconstruction are shown in the Caullet-Guth diagram of 1986 (Figure 5).[29] The Breck visualization could be interpreted in either of the ways depicted in Figure 5, depending on whether the dissolution of the gel is considered to be total or partial, although the author himself was in no doubt that some solution participation was essential. The type A and type B classification of Gabelica et al.[196] appears to correspond to the Caullet-Guth dichotomy—but it is unclear whether the solution phase is considered to permeate the gel (which was certainly regarded by the original authors as containing TPA cations throughout).

It is probably best to acknowledge that there are some instances in hydrothermal zeolite synthesis which approximate to a classical solution-mediated crystallization, whereas other cases appear, at least at first sight, to involve some type of solid-to-solid phase transition. However, it is demonstrated elsewhere that these apparent differences can be reconciled if we accept a role for solution-phase chemistry in the latter process also.[12] The devil is indeed in the detail. A conceptual breakthrough has occurred in the past few years with the recognition of the importance of the colloidal phase in zeolite synthesis.[256−265] Most of the liquid phases present in synthesis mixtures are not true solutions but sols, with a well-defined amorphous phase which happens to be invisible to the naked eye. The source of at least some of the confusion over the separate roles of the solid and solution components is then immediately apparent with the realization that both amorphous and crystalline material can be present as nanoparticles in the liquid phase.

Building on ideas put forward by Chang and Bell,[266] the pathway (Figure 16) proposed by Burkett and Davis[267] specifically considers the assembling role of the TPA template, showing how the original hydration sphere of the cation is replaced by an organized assembly of solution-derived silicate anions. Nucleation is envisaged as taking place through aggregation of the inorganic−organic composite species, while crystal growth occurs by further accretion of the same units. The scheme of Kirschhock et al.[273] (Figure 17) has the same essential features, in that there is emphasis on a primary building block based on the TPA−silicate unitary assembly, followed by propagation of the structure by an aggregation process.

While there has been an understandable emphasis on the role of organic templates in zeolite synthesis, it is advisable to keep their importance in perspective. The earliest authors were concerned only with rationalizing the synthesis of inorganic, aluminous zeolites. When first introduced,[90−92] alkylammonium compounds were considered principally as bulky cations which slightly modified the reaction products (raising the Si/Al ratio) but had no major impact upon the chemistry of synthesis. With the discovery of organic-templated high-silica zeolites,[95,110] this view changed and increasing emphasis was placed upon the structuring function of the organic template (an extension of the ordering role envisaged earlier for alkali metal cations).[16,18,22,27] More recently, spectroscopic and microscopic techniques have provided more detail on the nature of the inorganic−organic precursor complexes,[256−274,337−340] while much of the work on molecular modeling has concentrated on the interactions between organic templates and zeolite frameworks.[299−318] However, it is certain that ZSM-5 and some other high-silica zeolites can be synthesized without the use of organic compounds,[116−124] and it is also very likely that the recently discovered group of mineral analogues[284−286] were formed in nature by inorganic routes.

As in many areas of science, zeolite and zeotype synthesis has witnessed several intriguing resonances between the laboratory and the natural world and between observations made at different points in time. Instances have been given both of synthetic analogues of known natural materials (e.g., zeolites X and Y ≡ faujasite, section II) and, more remarkably, of cases where newly discovered minerals have been found to be isostructural with phases previously manifest only in the laboratory (e.g., mazzite ≡ ZSM-4/zeolite omega, tschernichite ≡ zeolite β, sections IV.C.3 and VI.G.) Developments in characterization techniques have also sometimes led to the reassessment of earlier reports. In an interesting link between zeolites and zeotypes, two phosphate-containing zeolites having the zeolite A structure (LTA) and designated ZK-21 and ZK-22[435−437] were originally (1971) believed to contain the phosphate occluded in the sodalite cages rather than as a framework constituent. However, following the introduction of MAS NMR spectroscopy, these materials were reexamined in 1990[108] and also compared with the isostructural silico-aluminophosphate SAPO-42 which had been reported in 1984.[438,439] Significant framework substitution by phosphorus, as well as phosphate occluded in the sodalite cage, was found in samples of all three materials. Even the first (1988) 18-T-ring structure, VPI-5 (section V.A), was found to have a historical pre-echo, when in 1990 it was shown[440,441] that a related material (H1[442]) was present among a group of aluminum phosphate hydrates synthesized by d'Yvoire in 1961.[443]

It has been the intention of this present survey to show in outline how our ideas on the nature of hydrothermal zeolite synthesis have developed from the earliest days up to the present time (2002). Mention has been made of the main discoveries of new materials. Advances in structure determination and in the characterization of products and reaction mixtures have shaped our perception of the nature of zeolite synthesis compositions. New ideas have sought to explain how the product crystals nucleate and grow, while major advances in modeling techniques have provided new common ground between theory and experiment. Particular attention has been focused on a number of classic papers which are believed to have been especially important or influential. Certainly, they show the debt we owe to certain key individuals, particularly in the early days when information was harder to come by. It is interesting that some of the most important ideas did not immediately lead to a burst of new work but, like the crystals themselves, required a certain induction period before real growth was evident. Some key examples of this would be the use of organic templates, the exploitation of the fluoride route, and, indeed, the recognition of high-silica zeolites as significantly different from materials such as A or X. It is also apparent that some of the main developments have come about not through aluminosilicate zeolites themselves but in the spin-off field of zeotypes, a trend which shows no sign of abatement.

The general features of hydrothermal zeolite synthesis are now well-known and it seems likely that soon many of the long-standing conundrums will be resolved. Computer modeling techniques will perhaps become sufficiently powerful that the chemical engineering type of reaction model can be combined with theoretical procedures having a molecular basis. In addition to increasing our understanding of the synthesis process, this may also lead to a predictive tool with the ability to anticipate the optimum synthesis conditions for a novel zeolite framework that has been designed for a specific application. Scattering techniques will continue to illuminate the colloidal phase in the same way that NMR and vibrational spectroscopy have done for true solution species. In situ electron microscopy and scanning probe microscopies should enable the intimate details of the crystal growth step to be revealed, although a key point—the nature of the species which carry mass to the growing crystal—may continue to resist resolution for a while. However, such details will be necessary if ever we are to appreciate the whole picture.

X. Acknowledgments

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XI. Appendix I—The 1960 Breck and Flanigen Paper: A Lost Landmark in the Historical Development of the Mechanism of Zeolite Synthesis

At the ACS Inorganic Chemistry Meeting in Cleveland, Ohio in April 1960, Edith Flanigen and Donald Breck presented a remarkable paper entitled “Crystalline Zeolites, V. Growth of Zeolite Crystals from Gels”. In this report[96,97] the authors sought to elucidate (1) the formation of the aluminosilicate gel or reaction mixture and (2) the nucleation and growth of zeolite crystals from the reaction mixture. In what was almost certainly the first study of its type, the authors used XRD measurements to follow the crystallization with time of zeolite Na−A (at 100 °C) and Na−X (at 50 °C and 100 °C). They showed the now-familiar S-shaped growth curves and described an induction period followed by a sudden rapid growth. The induction period for zeolite X was 60 h at 50 °C compared to 3 h at 100 °C. From an Arrhenius plot of crystallization time for zeolite X from 25 °C (840 h) to 120 °C (1.5h), they calculated an apparent activation energy of 15 kcal/mol, while a similar procedure for zeolite A gave 11 kcal/mol. Changes in the solid phase of the gels during crystallization were studied by electron microscopy. The morphological changes observed[98] were interpreted as a successive ordering of the gel as crystallization proceeds, leading to a conclusion that crystal growth takes place predominantly in the solid phase. (Notably, the final micrograph in this series (“Plate 8”) clearly shows layered growth steps on the (100) face of zeolite A, the steps averaging about 50 Å in height.[98])

The above work was subsequently summarized as part of an educational article for the New England Association of Chemistry Teachers.[99] In this review, Breck gave what is believed to be the first schematic representation of zeolite formation (Figure 2). The gel structure is depolymerized by hydroxide ions. Rearrangement of the aluminosilicate and silicate anions present in the hydrous gel is brought about by the hydrated cation species present. Tetrahedra regroup about hydrated sodium ions to form the basic polyhedral units (24-hedra). These then link to form the massive, ordered cystal structure of the zeolite. A very similar scheme appeared later in Breck’s book (p. 341).[1]

In light of subsequent events, it is regrettable that the Cleveland paper was not published in full. Sections from it did appear in later publications.[1,99,100] However, at the time, only the Abstract appeared in print.[96] The final paragraph of the Abstract has been quoted in full or in part several times (e.g., refs 101 and 102). The complete version of this paragraph reads:

> “A mechanism of crystal growth is proposed; extensive heterogeneous nucleation occurs during formation of the highly supersaturated gels. Crystal growth in the solid phase then proceeds by a series of depolymerization−polymerization reactions, catalyzed by excess hydroxyl ion. There is no significant solution of the solid phase during crystallization.”

The final section of the original paper,[97] which is presumably what the attendees of the ACS Meeting originally heard, runs as follows (reference numbers having been translated into those of the present review):

> “These observations lead logically to the following suggested mechanism for the nucleation and growth of zeolite crystals from ‘gels’. First, a large number of nuclei form during gelation from highly supersaturated solutions. These nuclei undoubtedly are of several types. This spontaneous nucleation leads to a criticality of gelation conditions. The nuclei of the crystallites do not necessarily represent a unit cell but may consist of more preliminary building units of polyhedra as suggested by Barrer.[103] An example might be the hexagonal prism of 12 oxygen tetrahedra found in the X zeolite structure. Crystal growth is preceded by an induction period which apparently is related to the growth of the nuclei to a critical

size, followed by rapid growth to small and uniform size crystals.

"Growth of the crystal proceeds through a type of polymerization and de-polymerization process which involves both the solid and liquid phases. The solid phase, however, appears to play the predominant role. The hydroxyl ion behaves as a type of catalyst by breaking and remaking Si,Al−O−Si,Al bonds but does not lead to a significant dissolution of the solid phase of the gel. The growth steps clearly evident in Plate 8[98] indicate that the species in solution contribute to the growth.

"The formation of crystalline zeolite phases from reactive alumino-silicate gels apparently represents an unusual system for crystal growth. It differs considerably in complexity and mechanism from the more classical crystallization methods."

XII. Note Added after ASAP Posting

Several typesetting errors in the original version of this paper, originally posted ASAP on 2/21/2003, most notably in the equation in section V.B and the final quotation in the Appendix, have been corrected. The correct version was posted 3/12/2003.

XIII. References

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