1
Introduction

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1.1
Introduction

The past nearly six decades have seen a chronological progression in molecular sieve materials from the aluminosilicate zeolites to microporous silica polymorphs, microporous aluminophosphate-based polymorphs, metallosilicate and metallophosphate compositions, octahedral-tetrahedral frameworks, mesoporous molecular sieves and most recently hybrid metal organic frameworks (MOFs). A brief discussion of the historical progression is reviewed here. For a more detailed description prior to 2001 the reader is referred to [1]. The robustness of the field is evident from the fact that publications and patents are steadily increasing each year.

1.1.1
Molecular Sieves and Zeolites

Molecular sieves are porous solids with pores of the size of molecular dimensions, 0.3–2.0 nm in diameter. Examples include zeolites, carbons, glasses and oxides. Some are crystalline with a uniform pore size delineated by their crystal structure, for example, zeolites. Most molecular sieves in practice today are zeolites.

Zeolites are crystalline aluminosilicates of group IA and group IIA elements, such as sodium, potassium, magnesium and calcium [2]. Chemically, they are represented by the empirical formula:

$$M_{2/n}O \cdot Al_2O_3 \cdot y SiO_2 \cdot w H_2O$$

where y is 2–200, n is the cation valence and w represents the water contained in the voids of the zeolite. Structurally, zeolites are complex, crystalline inorganic polymers based on an infinitely extending three-dimensional, four-connected framework of AlO_4 and SiO_4 tetrahedra linked to each other by the sharing of oxygen ions. Each AlO_4 tetrahedron in the framework bears a net negative charge which is balanced by an extra-framework cation. The framework structure contains

Zeolites in Industrial Separation and Catalysis. Edited by Santi Kulprathipanja

ISBN: 978-3-527-32505-4

intracrystalline channels or interconnected voids that are occupied by the cations and water molecules. The cations are mobile and ordinarily undergo ion exchange. The water may be removed reversibly, generally by the application of heat, which leaves intact a crystalline host structure permeated by the micropores and voids which may amount to 50% of the crystals by volume. The intracrystalline channels or voids can be one-, two- or three-dimensional. The preferred type has two or three dimensions to facilitate intracrystalline diffusion in adsorption and catalytic applications.

In most zeolite structures the primary structural units, the AlO_4 or SiO_4 tetrahedra, are assembled into secondary building units which may be simple polyhedra, such as cubes, hexagonal prisms or cubo-octahedra. The final framework structure consists of assemblages of the secondary units (see Chapter 2). More than 70 novel, distinct framework structures of zeolites are known. They exhibit pore sizes from 0.3 to 1.0 nm and pore volumes from about 0.10 to 0.35 cm^3/g. Typical zeolite pore sizes include: (i) small pore zeolites with eight-ring pores, free diameters of 0.30–0.45 nm (e.g., zeolite A), (ii) medium pore zeolites with 10-ring pores, 0.45–0.60 nm in free diameter (ZSM-5), (iii) large pore zeolites with 12-ring pores of 0.6–0.8 nm (e.g., zeolites X, Y) and (iv) extra-large pore zeolites with 14-ring pores (e.g., UTD-1).

The zeolite framework should be viewed as somewhat flexible, with the size and shape of the framework and pore responding to changes in temperature and guest species. For example, ZSM-5 with sorbed neopentane has a near-circular pore of 0.62 nm, but with substituted aromatics as the guest species the pore assumes an elliptical shape, 0.45 to 0.70 nm in diameter.

Some of the more important zeolite types, most of which have been used in commercial applications, include the zeolite minerals mordenite, chabazite, erionite and clinoptilolite, the synthetic zeolite types A, X, Y, L, “Zeolon” mordenite, ZSM-5, beta and MCM-22 and the zeolites F and W.

1.1.2
Nomenclature

There is no systematic nomenclature developed for molecular sieve materials. The discoverer of a synthetic species based on a characteristic X-ray powder diffraction pattern and chemical composition typically assigns trivial symbols. The early synthetic materials discovered by Milton, Breck and coworkers at Union Carbide used the modern Latin alphabet, for example, zeolites A, B, X, Y, L. The use of the Greek alphabet was initiated by Mobil and Union Carbide with the zeolites alpha, beta, omega. Many of the synthetic zeolites which have the structural topology of mineral zeolite species were assigned the name of the mineral, for example, synthetic mordenite, chabazite, erionite and offretite.The molecular sieve literature is replete with acronyms: ZSM-5, -11, ZK-4 (Mobil), EU-1, FU-1, NU-1 (ICI), LZ-210, AlPO, SAPO, MeAPO, etc. (Union Carbide, UOP) and ECR-1 (Exxon). The one publication on nomenclature by IUPAC in 1979 is limited to the then-known zeolite-type materials [3].

The *Atlas of Zeolite Structure Types* [4], published and frequently updated by the IZA Structure Commission, assigns a three-letter code to be used for a known framework topology irrespective of composition. Illustrative codes are LTA for Linde zeolite A, FAU for molecular sieves with a faujasite topology (e.g., zeolites X, Y), MOR for the mordenite topology, MFI for the ZSM-5 and silicalite topologies and AFI for the aluminophosphate $AlPO_4$-5 topology. The acceptance of a newly determined structure of a zeolite or molecular sieve for inclusion in the official *Atlas* is reviewed and must be approved by the IZA Structure Commission. The IZA Structure Commission was given authority at the Seventh International Zeolite Conference (Tokyo, 1986) to approve and/or assign the three-letter structure code for new framework topologies.

The definition and usage of the term "zeolite" has evolved and changed, especially over the past decade, to include non-aluminosilicate compositions and structures. Beginning with the second revised edition of the *Atlas* [5], the term "zeolite and zeolite-like materials" is introduced to try and capture the range of materials of interest. The inclusion of a structure in the *Atlas* is limited to three-dimensional, tetrahedral oxide networks with a framework density less than about 21 T-atoms per 1000 $Å^3$ irrespective of framework composition. Similarly the term zeolite has been broadened in the mineralogy literature to include tetrahedral framework compositions with T-elements other than Al and Si but where classic zeolite properties are exhibited (e.g., structures containing open cavities in the form of channels and cages, reversible hydration–dehydration characteristics [6]). Very recently as a sign of the times the term "nanoporous" materials has been applied to zeolites and related molecular sieves [7].

1.1.3
Early History

The history of zeolites began in 1756 when the Swedish mineralogist Cronstedt discovered the first zeolite mineral, stilbite [8]. He recognized zeolites as a new class of minerals consisting of hydrated aluminosilicates of the alkali and alkaline earths. Because the crystals exhibited intumescence when heated in a blowpipe flame, Cronstedt called the mineral a "zeolite" (derived from two Greek words, *zeo* and *lithos*, meaning "to boil" and "a stone"). From 1777 through about the 1800s various authors described the properties of zeolite minerals, including adsorption properties and reversible cation exchange and dehydration. St. Claire Deville reported the first hydrothermal synthesis of a zeolite, levynite, in 1862 [9]. In 1896 Friedel developed the idea that the structure of dehydrated zeolites consists of open spongy frameworks after observing that various liquids such as alcohol, benzene and chloroform were occluded by dehydrated zeolites [10]. Grandjean in 1909 observed that dehydrated chabazite adsorbs ammonia, air, hydrogen and other molecules [11], and in 1925 Weigel and Steinhoff reported the first molecular sieve effect [12]. They noted that dehydrated chabazite crystals rapidly adsorbed water, methyl alcohol, ethyl alcohol and formic acid but essentially excluded acetone, ether or benzene. In 1927 Leonard described the first use of X-ray diffraction for identification in mineral synthesis [13]. Taylor and Pauling described the first single crystal structures of zeolite minerals in 1930 [14, 15]. In 1932 McBain established the term “molecular sieve” to define porous solid materials that act as sieves on a molecular scale [16].

Thus, by the mid-1930s the literature described the ion exchange, adsorption, molecular sieving and structural properties of zeolite minerals as well as a number of reported syntheses of zeolites. The early synthetic work remains unsubstantiated because of incomplete characterization and the difficulty of experimental reproducibility.

Richard M. Barrer began his pioneering work in zeolite adsorption and synthesis in the mid-1930s to 1940s. He presented the first classification of the then-known zeolites based on molecular size considerations in 1945 [17] and in 1948 reported the first definitive synthesis of zeolites, including the synthetic analog of the zeolite mineral mordenite [18] and a novel synthetic zeolite [19] much later identified as the KFI framework. Barrer’s work in the mid- to late 1940s inspired Robert M. Milton of the Linde Division of Union Carbide Corporation to initiate studies in zeolite synthesis in search of new approaches for separation and purification of air. Between 1949 and 1954 Milton and coworker Donald W. Breck discovered a number of commercially significant zeolites, types A, X and Y. In 1954 Union Carbide commercialized synthetic zeolites as a new class of industrial materials for separation and purification. The earliest applications were the drying of refrigerant gas and natural gas. In 1955 T.B. Reed and D.W. Breck reported the structure of the synthetic zeolite A [20]. In 1959 Union Carbide marketed the “ISOSIV” process for normal–isoparaffin separation, representing the first major bulk separation process using true molecular sieving selectivity. Also in 1959 a zeolite Y-based catalyst was marketed by Carbide as an isomerization catalyst [21].

In 1962 Mobil Oil introduced the use of synthetic zeolite X as a hydrocarbon cracking catalyst. In 1969 Grace described the first modification chemistry based on steaming zeolite Y to form an “ultrastable” Y. In 1967–1969 Mobil Oil reported the synthesis of the high silica zeolites beta and ZSM-5. In 1974 Henkel introduced zeolite A in detergents as a replacement for the environmentally suspect phosphates. By 2008 industry-wide approximately 367 000 t of zeolite Y were in use in catalytic cracking [22]. In 1977 Union Carbide introduced zeolites for ion-exchange separations.

1.1.4
Natural Zeolites

For 200 years following their discovery by Cronstedt, zeolite minerals (or natural zeolites) were known to occur typically as minor constituents in vugs or cavities in basaltic and volcanic rock. Such occurrences precluded their being obtained in mineable quantities for commercial use. From the late 1950s to 1962 major geologic discoveries revealed the widespread occurrence of a number of natural zeolites in sedimentary deposits throughout the western United States. The discoveries resulted from the use of X-ray diffraction to examine very fine-grained (1–5 μm) sedimentary rock. Some zeolites occur in large, nearly mono-mineralic deposits suitable for mining. Those that have been commercialized for adsorbent applications include chabazite, erionite, mordenite and clinoptilolite [23].

Mordenite and clinoptilolite are used in small volume in adsorbent applications including air separation and in drying and purification [24]. Natural zeolites have also found use in bulk applications as fillers in paper, in pozzolanic cements and concrete, in fertilizer and soil conditioners and as dietary supplements in animal husbandry.

1.2
History of Molecular Sieve Materials

The theme of research on molecular sieve materials over the past nearly 60 years has been a quest for new structures and compositions. The major discoveries and advances in molecular sieve materials during that period are summarized in Table 1.1.

The history of commercially significant molecular sieve materials from 1954 to 2001 was reviewed in detail by one of us (E.M.F., ref [1]) Highlights from that review and the subsequent history are presented here. The reader is referred to Chapter 2 for the structures of the materials and to Chapter 3 and ref [25] for a detailed discussion on zeolite synthesis.

Table 1.1 Evolution of molecular sieve materials.

Time of initial discovery	Composition
Late 1940s to early 1950s	Low Si/Al ratio zeolites
Mid-1950s to late 1960s	High Si/Al ratio zeolites
Early 1970s	SiO_2 molecular sieves
Late 1970s	$AlPO_4$ molecular sieves
Late 1970s to early 1980s	SAPO and MeAPO molecular sieves
Late 1970s	Metallo-silicates, aluminosilicates
Early to mid-1980s	$AlPO_4$-based molecular sieves
Early to mid-1990s	Metallophosphates Mesoporous molecular sieves Octahedral–tetrahedral frameworks
Late 1990s	Metal organic frameworks
2000s	UZM aluminosilicate zeolites, Si/Al = 2–30 Germanosilicate zeolites SiO_2 molecular sieves in fluoride media

1.2.1
Aluminosilicate Zeolites and Silica Molecular Sieves

The early evolution of aluminosilicate zeolites, in the 1950s to 1970s, is summarized in Table 1.2, based on increasing framework Si/Al composition. The four somewhat arbitrary categories are: (i) “low”, (ii) “intermediate”, (iii) “high” silica zeolites and (iv) “silica” molecular sieves.

The transition in properties accompanying the increase in the framework Si/Al are generalized here but should only be viewed as trends. The thermal stability increases from about 700 °C in the low silica zeolites to 1300 °C in the silica molecular sieves. The surface selectivity, which is highly hydrophilic in the low silica zeolites, is hydrophobic in the high silica zeolites and the silica molecular sieves. The acidity tends to increase in strength with increasing Si/Al ratio. As the Si/Al ratio increases, the cation concentration and ion exchange capacity (proportional to the aluminum content) decreases. The structures of the low silica zeolites are predominantly formed with four, six and eight rings of tetrahedra. In the intermediate silica zeolites we see the onset of five rings in mordenite and omega zeolite. In the high silica zeolite structures and the silica molecular sieves we find a predominance of five rings of tetrahedra, for example, silicalite.

The low silica zeolites represented by zeolites A and X are aluminum-saturated, have the highest cation concentration and give optimum adsorption properties in terms of capacity, pore size and three-dimensional channel systems. They represent highly heterogeneous surfaces with a strongly hydrophilic surface selectivity. The intermediate Si/Al zeolites (Si/Al of 2–5) consist of the natural zeolites erionite, chabazite, clinoptilolite and mordenite, and the synthetic zeolites Y, mordenite, omega and L. These materials are still hydrophilic in this Si/Al range.

The high silica zeolites with Si/Al of 10–100 can be generated by either thermochemical framework modification of hydrophilic zeolites or by direct synthesis. In

Table 1.2 The early evolution of aluminosilicate molecular sieve materials.

Composition and examples
“Low” Si/Al zeolites (1 to 1.5): A, X
“Intermediate” Si/Al zeolites (~2 to 5): A. Natural zeolites: erionite, clinoptilolite, mordenite B. Synthetic zeolites: Y, L, large pore mordenite, omega
“High” Si/Al zeolites (~10 to 100): A. By thermochemical framework modification: Highly siliceous variants of Y, mordenite, erionite B. By direct synthesis: ZSM-5, beta
Silica molecular sieves (Si/Al > 100): Silicalite

the modification route stabilized, siliceous variants of Y, mordenite, erionite and over a half-dozen other zeolites have been prepared by steaming and acid extraction. These materials are reported to be hydrophobic and organophilic and represent a range of pore sizes from 0.4 to 0.8 nm. A very large number of high-silica zeolites prepared by direct synthesis have now been reported, including beta, ZSM-5, -11, -12, -21, -34, NU-1, FU-1 and ferrisilicate and borosilicate analogs of the aluminosilicate structures. Typical of the reported silica molecular sieves are silicalite, fluoride silicalite, silicalite-2 and TEA-silicate. ZSM-5 and silicalite have achieved commercial significance.

In summary, when we compare the properties of the low and intermediate zeolites with those of the high silica zeolites and silica molecular sieves, we find that their resulting properties allow the low and intermediate zeolites to remove water from organics and to carry out separations and catalysis on dry streams. In contrast, the hydrophobic high silica zeolites and silica molecular sieves can remove and recover organics from water streams and carry out separations and catalysis in the presence of water.

1.2.2
The Materials Explosion Since the 1980s

Overall the period since the 1980s can be described as a period of explosion in the discovery of new compositions and structures of molecular sieves. This can perhaps be seen most vividly by comparing the numbers of structure types contained in the various editions of the *Atlas of Zeolite Structure Types* [4]. The first edition (1978) contained 38 structure types, the second edition (1987) 64, the third edition (1992) 85 and the most recent edition (2007) 176. Thus 112 new structure types have been discovered since 1978. However, the reader should be cautioned that a significant number of the structure types included in the *Atlas* are not truly microporous or molecular sieve materials (i.e., they are not stable for the removal of as-synthesized guest species, typically water or organic templates) and therefore cannot reversibly adsorb molecules or carry out catalytic reactions. Unfortunately, the *Atlas* gives only limited information on the stability of the structures described.

1.2.2.1 **The 1980s**

In the 1980s there was extensive work carried out on the synthesis and applications of ZSM-5 and a proliferating number of other members of the high silica zeolite family. In 1982 microporous crystalline aluminophosphate molecular sieves were described by Wilson *et al.* [26] at Union Carbide, and additional members of the aluminophosphate-based molecular sieve family, for example, SAPO, MeAPO, MeAPSO, ElAPO and ElAPSO, were subsequently disclosed by 1986 [27]. Considerable effort in synthesizing metallosilicate molecular sieves was reported when the metals iron, gallium, titanium, germanium and others were incorporated during synthesis into silica or aluminosilicate frameworks, typically with the ZSM-5 (MFI) topology [28]. Additional crystalline microporous silica molecular sieves and related clathrasil structures were reported.

The 1980s saw major developments in secondary synthesis and modification chemistry of zeolites. Silicon-enriched frameworks of over a dozen zeolites were described using methods of: (i) thermochemical modification (prolonged steaming) with or without subsequent acid extraction, (ii) mild aqueous ammonium fluorosilicate chemistry, (iii) high-temperature treatment with silicon tetrachloride and (iv) low-temperature treatment with fluorine gas. Similarly, framework metal substitution using mild aqueous ammonium fluorometallate chemistry was reported to incorporate iron, titanium, chromium and tin into zeolite frameworks by secondary synthesis techniques.

Aluminophosphate-Based Molecular Sieves In 1982 a major discovery of a new class of aluminophosphate molecular sieves was reported by Wilson *et al.* [26]. By 1986 some 13 elements were reported to be incorporated into the aluminophosphate frameworks: Li, Be, B, Mg, Si, Ti, Mn, Fe, Co, Zn, Ga, Ge and As [27]. These new generations of molecular sieve materials, designated $AlPO_4$-based molecular sieves, comprise more than 24 structures and 200 compositions.

The >24 structures of $AlPO_4$-based molecular sieves reported to date include zeolite topological analogs and a large number of novel structures. The major structures are shown in Table 1.3. They include 15 novel structures as well as seven structures with framework topologies related to those found in the zeolites

Table 1.3 Typical structures in $AlPO_4$-based molecular sieves.

Species	Structure type	Pore size, nm	Saturation H_2O pore volume, cm^3/g	Species	Structure type	Pore size, nm	Saturation H_2O pore volume, cm^3/g
Very large pore				Small pore			
VPI-5	Novel	1.25	0.35	14	Novel	0.4	0.19
8	Novel	0.9	0.24	17	ERI	0.43	0.28
				18	Novel	0.43	0.35
				26	Novel	0.43	0.23
Large pore				33	Novel	0.4	0.23
5	Novel	0.8	0.31	34, 44, 47	CHA	0.43	0.3
36	Novel	0.8	0.31	35	LEV	0.43	0.3
37	FAU	0.8	0.35	39	Novel	0.4	0.23
40	Novel	0.7	0.33	42	LTA	0.43	0.3
46	Novel	0.7	0.28	43	GIS	0.43	0.3
				52	Novel	0.43	0.3
				56	Novel	0.43	0.3
				Very small pore			
Intermediate				16	Novel	0.3	0.3
11	Novel	0.6	0.16	20	SOD	0.3	0.24
31	Novel	0.65	0.17	25	Novel	0.3	0.17
41	Novel	0.6	0.22	28	Novel	0.3	0.21

CHA (-34, -44, -47), ERI (-17), GIS (-43), LEV (-35), LTA (-42), FAU (-37) and SOD (-20). Also shown is the pore size and saturation water pore volume for each structure type. The structures include the first very large pore molecular sieve, VPI-5, with an 18-ring one-dimensional channel with a free pore opening of 1.25 nm [29], large pore (0.7–0.8 nm), intermediate pore (0.6 nm), small pore (0.4 nm) and very small pore (0.3 nm) materials. Saturation water pore volumes vary from 0.16 to 0.35 cm^3/g, comparable to the pore volume range observed in zeolites (see Chapter 2 for detailed structures).

The addition of another element to the aluminophosphate reactants, for example, Si, metal ions Mg, Co, Mn, Fe, as well as other elements, led to the silicoaluminophosphate family "SAPO", the metalloaluminophosphate family "MeAPO" and other elements, the "ElAPO" family, where the added element is incorporated into the hypothetical $AlPO_4$ framework.

The aluminophospahate molecular sieve product composition expressed in terms of oxide ratios is:

$$x\mathrm{R} \cdot \mathrm{Al_2O_3} \cdot 1.0 \pm 0.2\ \mathrm{P_2O_5} \cdot y\mathrm{H_2O}$$

where R is an amine or quaternary ammonium ion. The $AlPO_4$ molecular sieve as synthesized must be calcined at 400–600 °C to remove the R and water, yielding a microporous aluminophosphate molecular sieve.

The characteristics of aluminophosphate molecular sieves include a univariant framework composition with $Al/P = 1$, a high degree of structural diversity and a wide range of pore sizes and volumes, exceeding the pore sizes known previously in zeolite molecular sieves with the VPI-5 18-membered ring material. They are neutral frameworks and therefore have nil ion-exchange capacity or acidic catalytic properties. Their surface selectivity is mildly hydrophilic. They exhibit excellent thermal and hydrothermal stability, up to 1000 °C (thermal) and 600 °C (steam).

The silicoaluminophosphate (SAPO) family [30] includes over 16 microporous structures, eight of which were never before observed in zeolites. The SAPO family includes a silicon analog of the 18-ring VPI-5, Si-VPI-5 [31], a number of large-pore 12-ring structures including the important SAPO-37 (FAU), medium-pore structures with pore sizes of 0.6–0.65 nm and small-pore structures with pore sizes of 0.4–0.43 nm, including SAPO-34 (CHA). The SAPOs exhibit both structural and compositional diversity.

The SAPO anhydrous composition can be expressed as $0\text{–}0.3\mathrm{R}(\mathrm{Si}_x\mathrm{Al}_y\mathrm{P}_z)\mathrm{O}_2$, where x, y and z are the mole fraction of the respective framework elements. The mole fraction of silicon, x, typically varies from 0.02 to 0.20 depending on synthesis conditions and structure type. Martens *et al.* have reported compositions with the SAPO-5 structure with x up to 0.8 [32]. Van Nordstrand *et al.* have reported the synthesis of a pure silica analog of the SAPO-5 structure, SSZ-24 [33].

The introduction of silicon into hypothetical phosphorus sites produces negatively charged frameworks with cation-exchange properties and weak to mild acidic catalytic properties. Again, as in the case of the aluminophosphate molecular sieves, they exhibit excellent thermal and hydrothermal stability.

In the metal aluminophosphate (MeAPO) family the framework composition contains metal, aluminum and phosphorus [27]. The metal (Me) species include the divalent forms of Co, Fe, Mg, Mn and Zn and trivalent Fe. As in the case of SAPO, the MeAPOs exhibit both structural diversity and even more extensive compositional variation. Seventeen microporous structures have been reported, 11 of these never before observed in zeolites. Structure types crystallized in the MeAPO family include framework topologies related to the zeolites, for example, -34 (CHA) and -35 (LEV), and to the $AlPO_4$s, e.g., -5 and -11, as well as novel structures, e.g., -36 (0.8 nm pore) and -39 (0.4 nm pore). The MeAPOs represent the first demonstrated incorporation of divalent elements into microporous frameworks.

The spectrum of adsorption pore sizes and pore volumes and the hydrophilic surface selectivity of the MeAPOs are similar to those described for the SAPOs. The observed catalytic properties vary from weakly to strongly acidic and are both metal- and structure-dependent. The thermal and hydrothermal stability of the MeAPO materials is somewhat less than that of the $AlPO_4$ and SAPO molecular sieves.

The MeAPO molecular sieves exhibit a wide range of compositions within the general formula $0–0.3R(Me_xAl_yP_z)O_2$. The value of x, the mole fraction of Me, typically varies from 0.01 to 0.25. Using the same mechanistic concepts described for SAPO, the MeAPOs can be considered as hypothetical $AlPO_4$ frameworks that have undergone substitution. In the MeAPOs the metal appears to substitute exclusively for aluminum resulting in a negative (Me^{2+}) or neutral (Me^{3+}) framework charge. Like SAPO, the negatively charged MeAPO frameworks possess ion-exchange properties and Bronsted acid sites.

The MeAPSO family further extends the structural diversity and compositional variation found in the SAPO and MeAPO molecular sieves. These quaternary frameworks have Me, Al, P and Si as framework species [27]. The MeAPSO structure types include framework topologies observed in the binary $AlPO_4$ and ternary (SAPO, MeAPO) compositional systems and the novel structure -46 with a 0.7 nm pore. The structure of -46 has been determined [34].

Quinary and senary framework compositions have been synthesized containing aluminum, phosphorus and silicon, with additional combinations of divalent (Me) metals. In the ElAPO and ElAPSO compositions the additional elements Li, Be, B, Ga, Ge, As and Ti have been incorporated into the $AlPO_4$ framework [27].

Most of the catalytic interest in the $AlPO_4$-based molecular sieves have centered on the SAPOs which have weak to moderate Bronsted acidity, and two have been commercialized: SAPO-11 in lube oil dewaxing by Chevron and SAPO-34 in methanol-to-olefins conversion by UOP/Norsk Hydro. Spurred on by the success of TS-1 in oxidation catalysis, there is renewed interest in Ti, Co, V, Mn and Cr substituted $AlPO_4$-based materials. For a review of recent developments in the $AlPO_4$-based molecular sieves see [35].

Metallosilicate Molecular Sieves A large number of metallosilicate molecular sieves have been reported, particularly in the patent literature. Those claimed include silicates containing incorporated tetrahedral iron, boron, chromium, arsenic, gallium, germanium and titanium. Most of the earlier work has been reported with structures of the MFI type. Others include metallosilicate analogs of ZSM-11, -12, THETA-1, ZSM-34 and beta. The early metallosilicate molecular sieves are reviewed in detail by Szostak [28]. More recently crystalline microporous frameworks have been reported with compositions of beryllosilicate, such as nabesite [36], lovdarite [37] and OSB-1 [38]. Zinc silicates with significant framework Zn include VPI-7 [39], VPI-8 [40], VPI-9 [41] and CIT-6 [42]. There has also been a dramatic increase in new frameworks prepared by incorporating Ge into silicate and aluminosilicate frameworks (see below). Fe and Ga incorporation has so far produced the same structure types as Al incorporation. In contrast, framework incorporation of B, Be, Ge and Zn in metallosilicate compositions can yield novel structures difficult or impossible to obtain with Al. To date only B, Be, Ga, Ge, Fe, Ti and Zn have been sufficiently characterized to confirm structural incorporation. The titanium-silicalite composition, TS-1, has achieved commercialization in selective oxidation processes and iron-silicalite in ethylbenzene synthesis.

Other Framework Compositions Crystalline microporous frameworks have been reported with compositions of: beryllophosphate [43], aluminoborate [44], aluminoarsenate [45], galloarsenate [46], gallophosphate [47], antimonosilicate [48] and germanosilicate [49].

Harvey *et al.* [43] reported the synthesis of alkali beryllophosphate molecular sieves with the RHO, GIS, EDI and ANA structure topologies and a novel structure, BPH. Simultaneously, the first beryllophosphate mineral species were reported: tiptopite [with the cancrinite (CAN) topology] by Peacor *et al.* [50] and pahasapaite (with the RHO topology) by Rouse *et al.* [51].

In the late 1980s Bedard *et al.* reported the discovery of microporous metal sulfides, based on germanium (IV) and Sn (IV) sulfide frameworks [52]. The microporous sulfides are synthesized hydrothermally in the presence of alkylammonium templating agents. The GeS_4-based compositions include one or more framework-incorporated metals: Mn, Fe, Co, Ni, Cu, Zn, Cd and Ga. Over a dozen novel structures were reported which have no analogs in the microporous oxides. Ozin *et al.* have extended this work to a large number of microporous sulfides and selenides [53]. It should be noted that the microporous sulfides and selenides are prone to structure collapse upon calcination to remove the template species.

1.2.2.2 **The 1990s**

The explosion in the discovery of new compositions and structures observed in the 1980s continued through the 1990s. Some three dozen or more novel tetrahedral structures were synthesized in the 1990s, based on aluminosilicate, silica, metallosilicate and metallophosphate frameworks. Three are especially noteworthy. The gallophosphate cloverite (-CLO) has the first 20-ring pore (0.4×1.32 nm in diameter) and the lowest observed framework density (number of T-atoms per 1000 $Å^3$): 11.1 [54]. The cloverite structure contains the D4R and alpha cages reminiscent of the aluminum-rich zeolite Type A (LTA), combined with the rpa cage found in the aluminophosphate structures. It is an interrupted framework structure and thus has somewhat limited thermal stability. The siliceous zeolite UTD-1(DON) contains a 14-ring pore (0.75 × 1.0 nm in diameter) and is the first aluminosilicate with a pore size larger than a 12-ring [55]. CIT-5 (CFI), a second 14-R structure with a pure silica composition and a 0.8 nm pore, was reported by Wagner *et al.* [56].

Stucky *et al.* discovered a generalized method for preparing a large number of metallo-aluminophosphate and metallo-gallophosphate frameworks containing transition metals. The method utilizes amine SDAs and high concentrations of transition metal and phosphate in mixed solvents, typically alcohol and water. Two of the novel structures (UCSB-6, UCSB-10) have multi-dimensional 12-ring channels connecting large cages. In addition numerous zeolite structure analogs were also observed [57]. Unfortunately, the high framework charge reduces structural stability when template removal is attempted.

Gier *et al.* reported zinc and beryllium phosphates and arsenates with the X (FAU), ABW and SOD structures reminiscent of the early aluminum-rich synthetic zeolite chemistry. The synthesis of $ZnPO_4$-X (FAU) is especially spectacular. Crystallization occurs almost instantaneously at 0 °C [58]. Concurrent with ease of synthesis, the structure is thermally unstable.

Table 1.4 lists some of the major new structures reported in the 1990s. Interestingly, as organic SDAs tended to dominate discovery of new frameworks, there were no new aluminum-rich synthetic zeolites reported in either the 1980s or the 1990s. The new aluminosilicate structures were all high silica or pure silica in composition. It awaited the 2000s for new aluminosilicate zeolite materials with low to medium Si/Al to be reported (see below).

Not to be outdone by humankind there were a number of new zeolite minerals discovered in nature during the 1990s. The zeolite mineral boggsite (BOG) has a novel framework topology with three-dimensional pores combining 10Rs and 12Rs, and it has not yet been reproduced synthetically [61]. Tschernichite is an aluminum-rich mineral analog of the synthetic zeolite beta [62]. Gottardiite is a new mineral analog of synthetic zeolite Nu-87 [63]. The zeolite mineral terranovaite (TER) has a novel structure with pentasil chains and a two-dimensional 10R channel [64]. Mutinaite is a high-silica zeolite mineral analog of ZSM-5 with the

Table 1.4 Major new synthetic structures of the 190s.

Species	Structure type	Pore size, nm	Ring size	Reference
MCM-22, 49	MWW	0.6	10	[59]
UTD-1	DON	1.0	14	[55]
CIT-5	CFI	0.8	14	[56]
EMC-2	EMT	0.7	12	[60]
Cloverite	–CLO	1.3	20	[54]

highest silica content of all known zeolite minerals (Si/Al = 7.7) [65]. The structure of the zeolite mineral perlialite was reported [66] to have the same topology as that of the synthetic zeolite L (LTL), some 35 years after the synthesis of zeolite L.

Tschortnerite (TSC) surely is the most remarkable novel zeolite mineral discovered [67]. Its unique framework topology contains five different cages: D-6Rs, D-8Rs, sodalite cages, truncated cubo-octahedra and a unique 96-membered cage. Cu-containing clusters are encapsulated within the truncated cubo-octahedra. The pore structure is three-dimensional with 8R channels, and the framework density of 12.2 is among the lowest known for zeolites. The framework is alumina-rich with Si/Al = 1, unusual for zeolite minerals.

Two major new classes of molecular sieve type materials were reported in the 1990s: (i) microporous frameworks based on mixed octahedral-tetrahedral frameworks in contrast to the previously described tetrahedral frameworks and (ii) mesoporous molecular sieves with pore sizes ranging from about 2 nm to greater than 10 nm.

Octahedral–Tetrahedral Frameworks The microporous materials described heretofore were all based on tetrahedral frameworks. Microporous titanosilicate materials with mixed octahedral–tetrahedral frameworks were reported in the 1990s. The framework linkage is through TiO_6 octahedra and SiO_4 tetrahedra. Chapman and Roe described the titanosilicate GTS-1, a structural analog of the mineral pharmacosiderite, with a three-dimensional channel system and 8-R pores [68]. Kuznicki and coworkers reported the synthesis of the titanosilicates ETS-4 and ETS-10 [69]. Their respective pore sizes are 0.4 and 0.8 nm. ETS-4 is the synthetic analog of the rare titanosilicate mineral zorite. The novel structure ETS-10 contains a three-dimensional 12-R pore system and shows a high degree of disorder (ref. [61]). ETS-10 has achieved commercial status in adsorption applications.

Mesoporous Molecular Sieves A major advance in molecular sieve materials was reported in 1992 by researchers at Mobil. Kresge *et al.* and Beck *et al.* described a new family of mesoporous silicate and aluminosilicate materials, designated M41S [70]. The members of the family include: MCM-41 (with a one-dimensional hexagonal arrangement of uniform open channels 0.2–10 nm in diameter), a cubic structure MCM-48 (with a three-dimensional channel system with pore sizes ~0.3–10 nm) and a number of lamellar structures. The order in the structure is derived from the channel arrangement. The silica or aluminosilicate wall outlining the channel is disordered and exhibits properties much like amorphous silica or silica–alumina.

Within the same time-frame and independently, Inagaki and coworkers reported a mesoporous material designated FSM-16, prepared by hydrothermal treatment of the layered sodium silicate kanemite, $NaHSi_2O_5.3H_2O$ [71]. Chen *et al.* substantiated that FSM-16 and MCM-41 bear a strong resemblance to each other, both with narrow mesopore distributions and similar physicochemical properties, but with FSM-16 having higher thermal and hydrothermal stability due to the higher degree of condensation in the silicate walls [72].

Both mesoporous materials are synthesized hydrothermally with a surfactant liquid crystal as the template (see synthesis section below). They exhibit very high surface areas and pore volumes, of the order of 1000 m^2/g and 1.5 cm^3/g, respectively.

Since this initial work there has been a plethora of literature on mesoporous molecular sieves. In addition to the silica and aluminosilicate frameworks similar mesoporous structures of metal oxides now include the oxides of Fe, Ti, V, Sb, Zr, Mn, W and others. Templates have been expanded to include nonionic, neutral surfactants and block copolymers. Pore sizes have broadened to the macroscopic size, in excess of 40 nm in diameter. A recent detailed review of the mesoporous molecular sieves is given in ref [73]. Vartuli and Degnan have reported a Mobil M41S mesoporous-based catalyst in commercial use, but to date the application has not been publicly identified.[74].

In a *tour de force* of detective work, Di Renzo *et al*. uncovered an obscure United States patent filed in 1969 and issued in 1971 to Chiola *et al*., describing a low-density silica. Reproduction of that patent resulted in a product having all of the properties of MCM-41 [75].

1.2.2.3 **The New Millennium**

Recent developments in zeolite synthesis and new materials include: (i) the use of combinatorial methodologies, microwave heating, multiple templates or SDAs and concentrated fluoride media in synthesis, (ii) synthesis using the charge density mismatch (CDM) concept, (iii) synthesis in ionothermal media, (iv) synthesis with complex "designer" templates or SDAs, (v) synthesis of nanozeolites, (vi) zeolite membranes and thin films (vii) and germanosilicate zeolites [76]. Several of these developments are discussed here.

A major return to the early lower Si/Al aluminosilicate zeolites of Milton and Breck was undertaken in the early part of this century. A novel synthetic strategy denominated the charge density mismatch (CDM) technique was pioneered by Lewis and coworkers at UOP. The method features the initial formation of a CDM aluminosilicate reaction mixture characterized by the mismatch between the charge density on the organoammonium structure-directing agent (SDA) and the charge density on the aluminosilicate network that is expected to form. For example, with a large SDA (low charge density) in an aluminosilicate reaction mixture with a low Si/Al ratio (high charge density), the crystallization of a zeolite is difficult or impossible, even with variation of hydroxide levels and crystallization temperature. Crystallization can be induced by the controlled addition of supplemental SDAs that have charge densities that are more suitably matched to that of the desired low ratio aluminosilicate network (e.g., alkali metal SDAs). Advantages of this approach are greater control over the crystallization process and reliable cooperation of multiple templates. The approach is demonstrated in the TEA-TMA template system, in which the new zeolites UZM-4, UZM-5 and UZM-9 are synthesized. with Si/Al of 2–5 [77]. The UZM family contains structures related to previously known topologies, such as UZM-4 (BPH) [78], UZM-9 (LTA) [78] and UZM-12 (ERI) [79], as well as new framework types such as UZM-5 (UFI) [80].

A broad range of high silica and pure silica molecular sieves have been synthesized by employing hydrothermal synthesis in fluoride media at low H_2O concentration, near neutral pH and alkali-free [81]. The significant new pure silica zeolite, ITQ-29, a structural analog of zeolite A (LTA) was reported by Corma at al [82]. Unlike the highly hydrophilic zeolite A, the ITQ-29 is hydrophobic.

The structure directing tendency of framework elements (e.g., Ge or Be) has also been successfully harnessed to prepare novel structures. In germanosilicates the smaller Ge–O–Ge and Ge–O–Si bond angles stabilize D4R building blocks improving the chances of preparing structures with three-dimensional channel systems. The novel zeolites IM-12 [83] and ITQ-15 [84] were all synthesized using organic SDAs and in some cases F in the media. They can be singled out for the special contribution of the Ge to the formation of secondary building units critical to structure formation. These silicogermanates have the UTL framework type which contains a unique two-dimensional channel system with channels bounded by 14-membered rings intersecting 12-membered ring channels. Structure analysis of both the IM-12 and ITQ-15 indicate that the Ge atoms are localized in the D4R units. Two recent beryllosilicate structures, OSB-1 and OSB-2, feature a high concentration of three rings and very low framework density [38]. These are made without the benefit of organic SDAs or fluoride. Thermal stability is very low.

The number of newly described metal organic frameworks (MOFs) exploded in the past decade. Since the MOFs are not strictly zeolites that family of materials is not discussed here. The reader is referred to several current reviews of the field [85].

1.3
Synthesis

The method developed by Milton in the late 1940s, involves the hydrothermal crystallization of reactive alkali metal aluminosilicate gels at high pH and low temperatures and pressures, typically 100 °C and ambient pressure. Milton, Breck and coworkers synthesis work led to over 20 zeolitic materials with low to intermediate Si/Al ratios (1–5) [86]. Chapter 3 and references [1] and [25] provide more detailed discussion of synthesis.

The advent of the addition of a quaternary ammonium cation as template or structure directing agent (SDA) to the alkaline gel by Barrer and coworkers, and Mobil Oil coworkers, led to the SiO_2 enriched zeolite A in the case of Barrer and to the high silica zeolites, Beta and ZSM-5, by the Mobil group. The latter synthesis temperature typically is 100–200 °C, higher than Milton's original work.

The addition of fluoride to the reactive gel led to more perfect and larger crystals of known molecular sieve structures as well as new structures and compositions. The fluoride ion also is reported to serve as a template or SDA in some cases. Fluoride addition extends the synthesis regime into the acidic pH region. Synthesis in fluoride media is discussed in greater detail in references [25] and [87].

The synthesis of the $AlPO_4$-based molecular sieves is similar to that of the high silica zeolites and silica molecular sieves, utilizing hydrothermal crystallization of reactive aluminophosphate gels, an amine or quaternary ammonium cation as a "template" or structure directing agent, and typical crystallization temperatures of 100–200 °C. In general they do not contain alkali or alkaline earth cations, unlike most zeolites, and the pH is typically slightly acidic to slightly basic.

In a further modification, the mesoporous materials are synthesized hydrothermally with a surfactant liquid crystal as the template.

Overall Milton's concept of hydrothermal crystallization of reactive gels has been followed with various additions and modifications for most of the molecular sieve, zeolite, and zeotype materials synthesis since the late 1940s.

1.4
Applications

Applications of zeolites and molecular sieves in the past several decades showed a growth in petroleum refining applications with emphasis on resid cracking and octane enhancement. ZSM-5 was commercialized as an octane enhancement additive in fluid catalytic cracking (FCC) where Si-enriched Y zeolites serve as the major catalytic component in high-octane FCC catalysts. The use of zeolite catalysts in the production of organic (fine) chemicals appeared as a major new direction. Zeolites in detergents as a replacement for phosphates became the single largest volume use for synthetic zeolites worldwide [22]. Zeolite ion exchange products, both synthetic and natural, were used extensively in nuclear waste cleanup after the Three Mile Island and Chernobyl nuclear accidents. New applications emerged for zeolite powders in two potentially major areas, odor removal and as plastic additives.

In adsorption and separation applications there has been a major growth in the use of pressure swing adsorption for the production of oxygen, nitrogen and hydrogen. Processes for the purification of gasoline oxygenate additives were introduced. Recent environmentally driven applications have arisen using the hydrophobic molecular sieves, highly siliceous Y zeolite and silicalite, for the removal and recovery of volatile organic compounds (VOC) that offer promise for significant market growth.

An exciting new scientific direction emerged in the 1980s and 1990s for exploring molecular sieves as advanced solid state materials. In a 1989 review, Ozin *et al.* [88] speculated "that zeolites (molecular sieves) as microporous molecular electronic materials with nanometer dimension window, channel and cavity architecture represent a 'new frontier' of solid state chemistry with great opportunities for innovative research and development". The applications described or envisioned included: molecular electronics, "quantum" dots/chains, zeolite electrodes, batteries, non-linear optical materials and chemical sensors. More recently there have been significant research reports on the use of zeolites as low k dielectric materials for microprocessors [89].

Zeolites have also been used as raw materials for ceramic compositions relevant to the electronic industry. Bedard *et al.* reported the high-temperature processing of zeolite B (P) to form cordierite ceramic compositions [90].

1.5
Markets

Since their introduction as a new class of industrial materials in 1954, the annual market for synthetic zeolites and molecular sieves has grown immensely, to 1.8×10^6 t worldwide in 2008 [22]. The major application areas are as adsorbents, catalysts and ion-exchange materials. The largest single market by volume (72%) is the detergent application, where zeolite A (and recently Type P) functions as an ion exchanger. In 2008, 1.27×10^6 t were estimated to be consumed in that application. Although the second largest volume use is as catalysts (17%), this is the largest value market for zeolites, about 55% of the total. Fluid catalytic cracking (FCC) catalysts, containing primarily silica-enriched forms of zeolite Y, represent more than 95% of total zeolite catalyst consumption, with smaller volumes used in hydrocracking and chemical and petrochemical synthesis. Catalyst consumption in 2008 is estimated at 303 000 t [22]. Adsorption applications are varied and include: drying and purification of natural gas, petrochemical streams (e.g., ethylene, propylene, refrigerants, insulated windows), bulk separations (e.g., xylenes, normal paraffins) and in air separation to produce oxygen by pressure swing adsorption (PSA) or vacuum pressure swing adsorption (VPSA) processes. Adsorbent consumption in 2008 is estimated at 180 000 t [22] (10% of the total by volume).

World production of natural zeolites was estimated at about 3.0×10^6 t in 2008 [22]. China and Cuba consume the largest quantity of natural zeolites, largely to enhance the strength of cement [22].

The price of zeolites varies considerably depending on the application. The typical price of catalysts in the United States varies from about US$ 3–4/kg for FCC to about US$ 20/kg for specialty catalysts, adsorbents from about US$ 5–9/kg, up to tens of dollars per kilogram for specialty adsorbents and about US$ 2/kg for detergents. Natural zeolites in bulk applications sell for US$ 0.04–0.25/kg and in industrial adsorbent applications for US$ 1.50–3.50/kg [22].

1.6
The Future

1.6.1
Materials

As noted previously there has been an explosive and accelerating increase in the discovery of new compositions and structural topologies. Based on the very high activity in this area in the past quarter of a century, we can expect a continuation of the proliferation of new molecular sieve compositions and structures. Further advances can also be expected in novel compositions derived from modification and secondary synthesis chemistry. When we consider the very large number of structures and compositions now reported in the molecular sieve area (176 in the sixth edition of the *Atlas*) and compare that with the number of commercial molecular sieves, approximately 12–15, what is the probability of future commercialization of a new material? There are many factors affecting the achievement of commercial status: (i) unique and advantageous properties of the material compared to present commercial products, (ii) market need, (iii) market size, (iv) cost of development and marketing and (v) cost and degree of difficulty in manufacturing. As a result it is likely, based on historical experience, that no more than a few of the prolific number of new molecular sieve materials of the past 25 years will achieve commercial status in the new millennium.

1.6.2
Applications

Molecular sieve adsorbents will continue to be used in the now-practiced separation and purification applications throughout the chemical process industry. New directions in the past 20 years include environmental and biopharmaceutical applications which have only recently received attention. Future trends in catalysis include: (i) a continuing accelerated discovery of new catalytic materials, (ii) an expanded use in petroleum refining particularly in the area of high octane gasoline, in the development of reformulated gasoline, the processing of heavy crudes and in the production of diesel, (iii) commercial development in conversion of alternate resources to motor fuels and base chemicals such as bio- and green fuels and (iv) as routes to organic chemical intermediates or end-products.

The large application of zeolites as ion exchangers in detergents leveled off in demand in North America, Western Europe and Japan in the late 1990s, but should continue to grow during the 2000s, particularly in Asia, Australia and Latin America [22]. The other applications of zeolites as ion exchangers in the nuclear industry, in radioactive waste storage and cleanup and in metals removal and recovery will probably remain a relatively small fraction of the worldwide market for molecular sieve materials.

Among the new application areas that could become large volume applications are the use of molecular sieves as functional powders, in odor removal, as plastic additives and in composites. The use of zeolites in solid-state applications is highly speculative. If ever practically realized that application would most probably represent a relatively small volume of the total zeolite consumption.

1.7
History of International Conferences and Organizations

In 1957 the first informal molecular sieve conference was held at Pennsylvania State University in the United States. In 1967 the first of a series of international molecular sieve conferences chaired by Professor R.M. Barrer was held in London. Subsequently, international meetings have been held every few years – 1970 in Worcester, 1973 in Zurich, 1977 in Chicago, 1980 in Naples, 1983 in Reno, 1986 in Tokyo, 1989 in Amsterdam, 1992 in Montreal, 1994 in Garmisch-Partenkirchen, 1996 in Seoul, 1998 in Baltimore, 2001 in Montpellier, 2004 in Capetown – and the most recent International Zeolite Conference was 2008 in Beijing.

An international molecular sieve organization was first formed in 1970 in conjunction with the Worcester Conference, called the International Molecular Sieve Conference (IMSC), and formalized with a constitution at the Zurich Conference in 1973. Its responsibility was to continue the organizational implementation of future international molecular sieve conferences on a regular basis. In 1977 at the Chicago Conference the name of the organization was changed to the International Zeolite Association (IZA) and its scope and purpose expanded to "promote and encourage all aspects of the science and technology of zeolitic materials", as well as organizing "International Zeolite Conferences" on a regular basis. The term zeolite in the new organization "is to be understood in its broadest sense to include both natural and synthetic zeolites as well as molecular sieves and other materials having related properties and/or structures" [91]. International Zeolite Association regional affiliates have been established and include: the British Zeolite Association (BZA, 1978), the Japan Association of Zeolites, (JAZ, 1986) and regional zeolite associations in France, Italy, Hungary, The Netherlands and Germany (late 1980s, early 1990s). In addition there are nearly a dozen other unaffiliated zeolite associations throughout the world (http://iza-online.org).

The IZA has several established Commissions. The Structure Commission formed in 1977 has published four editions of the *Atlas of Zeolite Structure Types* (1978, 1987, 1992, 1996) and two subsequent editions in the *Atlas of Zeolite Framework Types* (2001, 2007). An up-to-date version is maintained on the World Wide Web at the IZA Structure Commission web site (http://www.iza-structure.org). Subsequently commissions were established in catalysis (1998), synthesis (1992), ordered mesoporous materials (2001) and natural zeolites (2001). The synthesis commission published a volume, "*Verified Syntheses of Zeolitic Materials*", in 1998, with a second revised edition in 2001 (http://www.iza-structure.org).

In 1995, a Federation of European Zeolite Associations (FEZA) was formed and presently includes Zeolite Association members from the United Kingdom, Bulgaria, The Netherlands, France, Germany, Hungary, Italy, Romania, Spain, Poland, Georgia, the Czech Republic, Portugal and Slovakia. FEZA sponsors several workshops in Europe each year covering various aspects of zeolite science and holds International FEZA Conferences every three years (Hungary in 1999, Italy in 2002, Czech Republic in 2005, France in 2008; http://feza-online.org).

Other related organizations include the International Committee on Natural Zeolites (ICNC) and the International Mesostructured Materials Association (IMMA; (http://www.iza-structure.org).

1.8
Historical Epilog

Key factors in the growth of molecular sieve science and technology include: (i) the pioneering work of Barrer, (ii)the key discoveries of Milton and Breck and associates at Union Carbide, (iii) the rapid commercialization of the new synthetic zeolites and their applications by Union Carbide (1949–1954), (iv) the major development at Union Carbide in adsorption process design and engineering technology [92] major discoveries in hydrocarbon conversion catalysts at Union Carbide, Exxon, Mobil Oil, Shell and other industrial laboratories, (v) the discovery and commercialization of sedimentary zeolite mineral deposits in the United States in the 1960s and, last but not least, (vi) the dedication and contribution of so many high quality scientists and engineers. It is estimated that by the beginning of the twenty-first century there were over 20 000 such scientists and engineers in industry and academia dedicating a significant portion of their work to zeolite and molecular sieve science and technology.

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