

Zeolite Synthesis

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Developed from a symposium sponsored
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Foreword

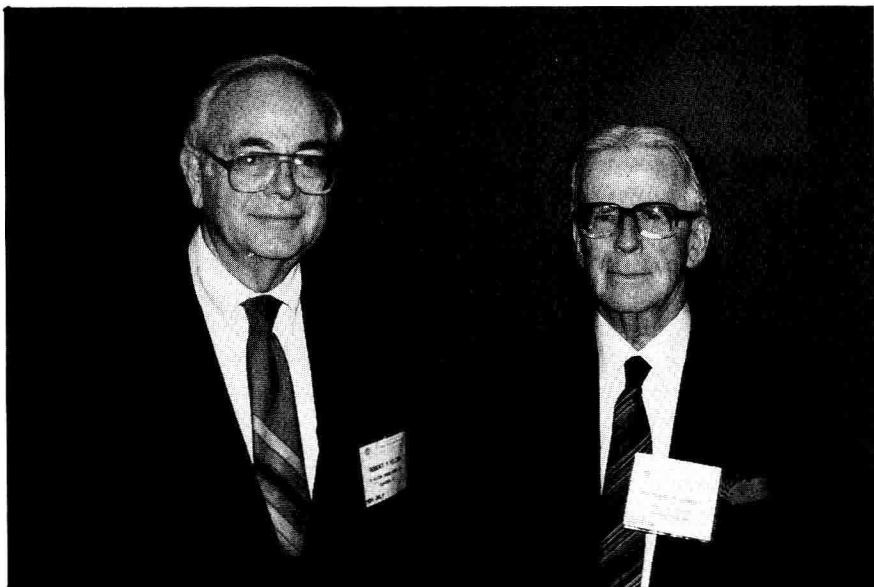
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Preface

THE FIRST ZEOLITE, STILBITE, WAS DISCOVERED IN 1756 by Baron Cronstedt, a Swedish mineralogist. He named these types of minerals *zeolites* from the Greek words *zeo* (boil) and *lithos* (stone), because when gently heated, the stones evolved water vapor. Because of the multiplicity of properties possessed by natural zeolites, it is not surprising that extensive attempts at their synthesis began so long ago. In fact, efforts to achieve the hydrothermal synthesis of analogs of natural zeolites date back to 1845, although the elevated temperatures and pressures employed and the lack of proper identification techniques precluded a high degree of success for more than a century. The bulk of successful work began in the 1940s when X-ray diffraction provided easy product identification and R. M. Barrer developed the gel synthesis. This approach was based on starting with very reactive components in closed systems and employing temperature and crystallization conditions that were more typical of the synthesis of organic compounds than of mineral formation. *Zeolite Synthesis*, and the symposium on which it is based, is a review of the progress that, to date, has been made toward understanding the various aspects of this field on a molecular level.

By 1959, under the leadership of R. M. Milton, the Linde Division of Union Carbide had successfully synthesized nearly all the commercially important zeolites. The first chapter of this volume is a personal account by Milton of how Union Carbide pioneered the synthetic molecular sieve zeolite business. In the synthesis area, results have indeed been impressive. Of the 35 now-recognized naturally occurring zeolites, 24 have been duplicated in the laboratory. In the process, more than 200 new synthetic phases have been discovered, including VPI-5, ZSM-5, and ALPO, a new family of molecular sieves. Today, ZSM-5 is considered to be one of the most important catalytic materials to be found since the cracking properties of faujasite were established in the early 1960s by Plank and Rosinsky. Aluminophosphates, such as ALPO, SAPO, and MEAPO, equip the chemist with an almost endless supply of crystalline molecular sieves with unique composition and structural characteristics. Synthesis of VPI-5, the first 18-membered ring molecular sieve, suggests that many more new and technologically important molecular sieves (some of which exist already as models) await to be synthesized.

Until fairly recently, zeolite synthesis has been mainly an empirical science in which a large number of experiments were used to systematically change synthesis parameters in the hope of obtaining new phases and crystal composition. Good luck and the execution of the right "mistakes" were thought by many to be essential to the synthesis and discovery of new zeolites. This Edisonian approach to zeolite synthesis is now being gradually replaced by methods based on the use of new characterization techniques that will provide a better understanding of gel chemistry, zeolite nucleation, crystal growth, crystallization kinetics, and structure-directing phenomena.



The two founders of zeolite synthesis technology, R. M. Barrer (right) and R. M. Milton (left), September 22, 1988, Los Angeles, CA (photo by Mario L. Occelli).

A great part of the success of the symposium on zeolite synthesis can be attributed to the generous contributions from several industrial sponsors and to the support of the Division of Colloid and Surface Chemistry of the American Chemical Society and of the International Zeolite Association. A special acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support provided during the early stages of this project.

We would also like to thank D. E. W. Vaughan, E. M. Flanigen, T. Inui, D. Bibby, and G. Volyocsik for helping to chair the symposium, and to express our gratitude to the many colleagues who acted as technical referees. Mario L. Occelli is particularly grateful to Unocal for permission to participate in and complete this project, and to G. Smith for her invaluable secretarial help.

Finally, we would like to thank the authors of *Zeolite Synthesis* for the time and effort they gave to presenting their research at the symposium and preparing the manuscripts for this book.

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Chapter 1

Molecular Sieve Science and Technology

A Historical Perspective

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Union Carbide pioneered the synthetic molecular sieve zeolite business, initiating research in 1948, entering the market in 1954, and turning a profit on an annual basis beginning in 1960 with an up-front cost of a little over \$7 million. Based on this effort, Union Carbide dominated the field of synthetic molecular sieves for many years. This state-of-the-art volume on zeolite synthesis represents a giant step from 1949, when I first began hydrothermal synthesis studies on zeolites at Union Carbide. Although this chapter is not intended to provide a thorough, historical perspective, it should give readers a view of the atmosphere and the people contributing to the initial development of the field of zeolite synthesis.

The work leading to Union Carbide's success began in 1948 after I had been at Linde's Tonawanda Research Laboratory for nearly two years. Management asked me to investigate physical adsorption as a potentially useful methodology in the purification and separation of air. At that time the only group working actively in zeolites was R. M. Barrer's group abroad. This introduction represents a condensed history of Union Carbide's work on molecular sieve zeolites from discovery to commercial success.

New Zeolite Synthesis Methodology

In the fall of 1948, I was measuring the adsorption characteristics of numerous commercial adsorbents and of the natural zeolite, chabazite. Several uses for silica gel in air separation plants were identified. But the more we learned about chabazite, the more intrigued I became by its potential as a commercial adsorbent as well as its possible use in air purification and separation. I envisioned, as others had before me [1-5], major new separation processes based on a series of different pore size zeolites. The stumbling blocks were that (1) chabazite was the only known zeolite with seemingly practical adsorption

¹NOTE: Retired from Union Carbide Corporation, 39 Old Ridgebury Road, Danbury, CT 06817

characteristics, (2) large deposits of the mineral had never been found, and (3) although many had tried, no one had succeeded in synthesizing chabazite [6]. I requested and received permission for a limited exploratory zeolite synthesis program in mid 1949.

We started hydrothermal syntheses in September 1949, using relatively insoluble forms of silica and alumina in mildly alkaline solutions (pH 8-11) containing calcium, magnesium, and sodium cations at temperatures of 200°-300°C. Reaction periods varied from a few days to a week. In some experiments there was no reaction; in others we made analcime or small pore mordenite. These had been made by others under similar conditions and neither was considered a commercially useful adsorbent [7, 8].

Our first change in synthesis procedures was to repeat some of the earlier experiments while applying a hydrostatic pressure of about 2,000 psig. This additional pressure had no apparent effect on zeolite crystallization.

By October 1949, I started experimenting with crystallization at 100°C, reasoning that the higher water content zeolites with larger pore volumes and, presumably, larger pore sizes, would be more likely to crystallize at temperatures lower than 200°-300°C. In nature the anhydrous aluminosilicates were formed at relatively high temperatures, and the hydrous ones were believed to have been formed later as the earth's surface cooled. Not surprisingly, when we first tried low temperature synthesis with relatively insoluble silica and alumina in mildly alkaline solutions, there was no reaction in reasonable time periods.

This was solved by using soluble forms of silica and alumina under highly alkaline conditions. We dissolved sodium aluminate in water, or dissolved alumina trihydrate in hot sodium hydroxide solutions and then mixed the aluminate solution with sodium silicate solutions. On mixing a gel usually formed. The gel was stirred thoroughly and placed in metal or glass containers, which were sealed and immersed in a 100°C water bath. The results were dramatic. Within a few hours, hydrated solid species usually settled out of the mother liquor and in most cases these were crystalline zeolites. The relative amounts of sodium oxide, alumina, silica, and water in the initial gel were key variables in determining what materials were formed. Temperature, gel stirring, and gel aging were also important variables.

Following crystallization, the solid was separated from the mother liquor by filtration, washed with distilled water, and air dried in an oven at 100°C to remove loosely bound water. Samples of the dried powder were sent routinely to the x-ray laboratory. The fact that we could obtain a strip chart recording of the x-ray powder pattern within 30 minutes was an important factor in the pace of our work. Adsorption evaluations were facilitated by use of multiple, quartz spring, McBain-Bakr balances connected in parallel. As many as 16 adsorbent samples could be evaluated simultaneously.

By year end 1949 we had developed not only a new and widely applicable method for synthesizing zeolites but had discovered the A zeolite, the B zeolite later shown to be gismondite, the C zeolite later identified as basic sodalite, and a crystalline impurity named X [9-10].

I first identified the 'X' zeolite by its x-ray peaks as an impurity in the B zeolite in 1949 at about a 20% concentration. We next saw it in February 1950 at about a 50% concentration with the B zeolite when N. R. Mumbach brought in the x-ray pattern from his first attempt to scale up the synthesis of B. By mid 1950, I had discovered how to routinely make pure zeolite X [11]. Chabazite was synthesized in late 1950, and by mid 1951 I had made three new

zeolites in the potassium-aluminosilicate system [12-14]. Adsorption properties of A and X had been determined including the discovery that the pore size could be reduced or enlarged by appropriate ion exchange with potassium, calcium, or magnesium ions. Both A and X had proven stable at 500°C. [15,16]. By mid 1953 we had made a total of 20 crystalline zeolites, including erionite, gmelinite, and 14 with no known natural counterparts [15].

Crystal Structure

In mid 1951 two young scientists joined the laboratory staff, Drs. T. B. Reed, a crystallographer, and D. W. Breck, an inorganic chemist. Reed had hoped to work with me on molecular sieves. In the applicant interview, I had challenged him to determine the detailed structures of the A and X zeolites from powder x-ray data, pore size and volume information, and ion exchange properties. He was assigned, however, to a different project in another group.

Dr. Breck was assigned to my molecular sieve group. He quickly appreciated the value of knowing the crystal structures of A and X if we were to fully understand their unique properties. Early in 1952 Reed and Breck decided to work together on the A and X structures. Progress was slow. Their studies were conducted frequently during lunch hour and in the evenings, since Reed had another full time assignment and Breck was busy with continuing zeolite synthesis and characterization studies.

By March 1954 they achieved their final structure for the A zeolite, verifying it shortly thereafter with single crystal x-ray data on a 30 micron A crystal that Breck and Nancy A. Acara had recently grown [17]. By mid 1954, they also completed the structures of X and faujasite [18], with help from single crystal x-ray data on faujasite. This was completed two to six years before these structures were described by others [19-21]. Interestingly, a manuscript by Breck et al. on the synthesis, structure, and properties of X was rejected by the *Journal of Physical Chemistry* in 1958 on the basis of insufficient reader interest.

These were remarkable accomplishments considering the size of the unit cells and the complexity of the structures. I remember posing the problem to Dr. Linus Pauling when he visited our laboratory in the mid fifties. Some 25 years earlier he had published on the structure of the zeolite natrolite and several feldspathoids [22]. He assured me that it was a waste of time to even try to determine the detailed structure of zeolites from powder x-ray data.

X, Y, Faujasite

In August 1952 Breck located the powder x-ray data for mineral faujasite and realized that it was very similar to that of the X zeolite. We obtained about 50 mg. of faujasite and studied it carefully. The x-ray pattern was indeed very similar to that of X. The adsorption capacity was somewhat lower but similar. The silica/alumina ratio was 4.7 compared to 2.5 for X. The cations in faujasite were calcium, magnesium, and barium, not sodium as in X. It was clear that X and faujasite were isostructural but with different compositions. Further similarities and differences could not be studied at that time due to the limited supply of faujasite.

In mid 1954 Breck proposed that it should be possible to synthesize the X structure with silica/alumina ratios as high as 4.7, found in faujasite, and possibly higher. He further hypothesized that the higher ratio materials, with lower aluminum and exchangeable cation content, would be more stable to acid attack

and to heat in the presence of water vapor than the 2.5 ratio X. If true, this could be a valuable property as X had limited stability to the high temperature burn-off of carbon deposits necessary in regeneration of petroleum cracking catalysts and to acid containing gases such as cracker gases.

N. A. Acara, Breck's synthesis assistant, collected samples of X made over the past few years and sent some of them in for chemical analysis. Heretofore most lots of X had never been analyzed. Those that had, always gave silica/alumina ratios very close to 2.5 with none higher than about 2.7. This analysis of old lots of X showed some lots with ratios as high as 2.83 and 2.92. With this background, Breck and Acara soon learned how to routinely synthesize X with ratios between 3.0 and 4.0. Later analyses of additional old lots of X showed ratios of 3.05, 3.47, and 3.48. We had made high silica X before but had not recognized it.

Beginning in 1956, E. M. Flanigen learned how to make X with silica/alumina ratios between 4.0 and 5.7. Now with a full range of ratios from 2.5 to 5.7, we were able to study systematically the variation in properties with alumina content. Breck's original hypothesis proved to be correct. The high silica forms were more stable to acid attack and to high temperatures in the presence of water vapor than the low silica forms [23].

Since X had been defined in our patent applications as having silica/alumina ratios between 2.0 and 3.0, and because there was a significant change in properties at a ratio of 3.0, the isostructural zeolites with ratios above 3.0 and up to 6.0 were named and patented as zeolite Y. The Y zeolite was not introduced into the market place until we had time to file appropriate patents and evaluate it as a catalyst [24].

Patents

Scientists do not usually get deeply involved in the intricacies of patent coverage, but it was essential in the case of the A and X zeolites because they involved concepts and science totally new to Union Carbide patent lawyers. During 1952 and 1953 I spent probably 20% of my time on patent matters.

The first lawyer assigned to molecular sieves planned to base protection on the process of manufacture. Since we could not possibly cover all practical methods of making A and X, we asked for composition of matter coverage, with process claims only to protect our actual manufacturing methods, and broad use claims covering as many applications as possible, so as to minimize the possibility of restrictive use claims by others.

Carbide's patent department had reservations because in their experience, composition of matter claims had to be drawn very narrowly to be valid and as such were frequently easy to circumvent. We convinced them that the unique properties that make A and X useful are singular results of their specific chemical composition and the arrangement of atoms in the crystal lattice of the zeolites. To our knowledge, the use of powder x-ray data as a finger print to uniquely identify a specific crystal structure was a new concept in patent protection.

When the first drafts of the patent applications came back from our patent department for checking, it was clear that major changes were needed. After several unsuccessful attempts to revise the original drafts, I had to rewrite both applications. At about that time a young patent lawyer, J. B. Browning, replaced the original attorney. He was quick to comprehend the significance of