SYNTHETIC ZEOLITES - STRUCTURE, CLASSIFICATION, CURRENT TRENDS IN ZEOLITE SYNTHESIS
REVIEW

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ABSTRACT

The synthesis of zeolites (molecular sieves) with a wide variety of engineered structures and properties requires profound theoretical and laboratory experiments. Recently, there is an increasing interest in the field of designing and preparation of synthetic zeolites in three main directions (by treatment of natural zeolites, which preserves their initial crystalline structure; by natural clay minerals; and by conventional hydrothermal synthesis).

An objective of this work is to review the current trends in zeolite synthesis as well as their structure and classification. Attention is given to the zeolite synthesis from industrial wastes, particularly from fly ash, and their role in solving environmental problems.

Key words: synthetic zeolites, structure, nomenclature, synthesis

INTRODUCTION

Zeolites are crystalline, micro porous, hydrated aluminosilicates that are built from an infinitely extending three dimensional network of [SiO₄]⁴⁻ and [AlO₄]⁵⁻ tetrahedra linked to each other by the sharing of oxygen atoms [1]. Generally, their structure can be considered as an inorganic polymer built from tetrahedral TO₄ units, where T is Si⁴⁺ or Al³⁺ ion. Each O atom is shared between two T atoms. The structure formula of zeolite is based on the crystallographic unit cell [2]:

\[ M_{x/n} [(AlO_2)_x(SiO_2)_y] \cdot wH_2O \]

where M is an alkali or alkaline earth cation, n is the valence of the cation, w is the number of water molecules per unit cell, x and y are the total number of tetrahedra per unit cell, and the ratio y/x usually has values of 1 to 5, though for the silica zeolite, y/x can be ranging from 10 to 100.

FRAMEWORK STRUCTURE OF ZEOLITE

The primary building unit for zeolites is the tetrahedron and the secondary building units (SBUs) are the geometric arrangements of tetrahedra [1]. The SBUs may be simple polyhedra such as cubes, hexagonal prisms, or cubo-octahedra [2]. The structures can be formed by repeating SBUs and according to them zeolites can be classified into eight groups. In fig.1,2 are presented components of the structure zeolite.

Figure 1. Chemical structure of zeolite [3]. Figure 2. Primary building unit of zeolite structure.

Zeolite open-structure framework consists of many channels and/or interconnected voids of discrete size (in the range 0.3-20 Å) which are occupied by cations and water molecules. Each AlO₄ tetrahedron in the framework bears a net negative charge which is balanced by a cation. Typically, these counter ions are elements from the IA and IIA groups of the periodic table. The cations can
reversibly be exchanged for other ions possessing the same sign charge when aqueous passed through channels and voids. This replacement results in the narrowing of the pore diameter of the zeolite channels. The water may be removed reversibly by the application of heat.

The SBU can be simple arrangements of tetrahedra such as four, six, eight, ten or more complicated membered ring. Other factors such as the location, size and coordination of the extra-framework cations can also influence the pore size. Some simple zeolite SBUs and their shorthand notations are given in Table 1.

<table>
<thead>
<tr>
<th>Number of linked tetrahedra</th>
<th>SBU created</th>
<th>Shorthand description</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>4 oxygen ring</td>
<td>S4R</td>
</tr>
<tr>
<td>5</td>
<td>5 oxygen ring</td>
<td>S5R</td>
</tr>
<tr>
<td>6</td>
<td>6 oxygen ring</td>
<td>S6R</td>
</tr>
<tr>
<td>8</td>
<td>8 oxygen ring</td>
<td>S8R</td>
</tr>
<tr>
<td>8</td>
<td>4-4 oxygen rings</td>
<td>D4R</td>
</tr>
<tr>
<td>12</td>
<td>6-6 oxygen rings</td>
<td>D6R</td>
</tr>
<tr>
<td>16</td>
<td>8-8 oxygen rings</td>
<td>D8R</td>
</tr>
</tbody>
</table>

(S = single, D = double, R = ring)

**NOMENKLATURE**

The wide variety of possible zeolite structures is due to the large number of ways in which the SBU can be linked to form various polyhedra. These polyhedra create networks of regular channels and cavities. One such polyhedron is the truncated octahedron; better known as the sodalite cage. Each sodalite cage consists of 24 linked tetrahedral which are further linked to form different zeolites with distinct framework topologies as depicted in Figure 3. The last one presents the general framework topologies of zeolites A/ZK4 and zeolites X/Y, and that of sodalite, Na₂Al₃Si₃O₁₂. The small face sharing β-cages characteristic of sodalite are linked through double four ring and six ring units in zeolites A/ZK4 and zeolites X/Y, respectively, to produce larger cages. Each type of zeolite has specific uniform pore size, for instance, 3.5-4.5 Å for zeolite LTA, 4.5-6.0 Å for ZSM-5 and 6.0-8.0 Å for zeolite X, Y type [2].

![Figure 3. Framework topologies of: a – Sodalite; b - Zeolite A/ZK-4; c - Zeolites X/Y](image)

Three-dimensional frameworks is given by a unique three-letter code. On the basis of crystallographic reports the Structure Commission (SC) of the International Zeolite Association

**Table 2. Typical oxide formula of some synthetic zeolites**

<table>
<thead>
<tr>
<th>Zeolites</th>
<th>Typical oxide formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolites A</td>
<td>Na₂O.Al₂O₃.2SiO₂.4,5H₂O</td>
</tr>
<tr>
<td>Zeolites N - A</td>
<td>(Na,TMA)₂O. Al₂O₃.4,8SiO₂.7H₂O</td>
</tr>
<tr>
<td>Zeolites H</td>
<td>K₂O.Al₂O₃.2SiO₂.4H₂O</td>
</tr>
<tr>
<td>Zeolites L</td>
<td>(K₂Na₂)O.Al₂O₃.6SiO₂.5H₂O</td>
</tr>
<tr>
<td>Zeolites X</td>
<td>Na₂O.Al₂O₃.2,5SiO₂.6H₂O</td>
</tr>
<tr>
<td>Zeolites Y</td>
<td>Na₂O.Al₂O₃.4,8SiO₂.8,9H₂O</td>
</tr>
<tr>
<td>Zeolites P</td>
<td>Na₂O.Al₂O₃.2 - 5SiO₂.5H₂O</td>
</tr>
<tr>
<td>Zeolites O</td>
<td>(Na₃,K₃,TMA₂)O.Al₂O₃.7SiO₂.3,5H₂O;TMA – (CH₃)₄N⁺</td>
</tr>
<tr>
<td>Zeolites Ω</td>
<td>(Na,TMA)₂O.Al₂O₃.7SiO₂.5H₂O; TMA – (CH₃)₄N⁺</td>
</tr>
<tr>
<td>Zeolites ZK-4</td>
<td>0,85Na₂O.0,15 (TMA)₂O. Al₂O₃.3,3SiO₂.6H₂O</td>
</tr>
</tbody>
</table>
Zeolites ZK-5 (R,Na2)O.Al2O3.4-6SiO2.6H2O (IZA) determines and assigns a three letter code to zeolite “topology” [4]. A convenient but arbitrary subdivision of phases in this range is given by Barrer. The International Zeolite Association (IZA) database shows that the number of structural types of unique microporous frameworks has been growing rapidly, from 27 in 1970 to 133 in 2001, whereas currently this number has reached 180 [4, 5]. In table 2 presented typical oxide formula of some of they synthetic zeolites.

**ZEOLITE SYNTHESIS**

Today, synthetic zeolites are used commercially more often than natural zeolites due to the purity of crystalline products and the uniformity of particle sizes. The sources for early synthesized zeolites were standard chemical reagents. Much of the study of basic zeolite science was done on natural zeolites. The main advantages of synthetic zeolites in comparison to naturally-occurring zeolites are that they can be engineered with a wide variety of chemical properties and pore sizes and that they have greater thermal stability. However, natural zeolites don’t show appropriate ion affinity, for example toward, Cu [6], Cs and Co [7], and Ur ions [8]. So, experiments aim to improve the ion exchange properties of the zeolites.

Conventional zeolite synthesis involves the hydrothermal crystallization of aluminosilicate gels (formed upon mixing an aluminate and silica solution in the presence of alkali hydroxides and/or organic bases), or solutions in a basic environment. The crystallization is in a closed hydrothermal system at increasing temperature, autogenous pressure and varying time (few hours to several days). The type of the zeolite is affected by the following factors [9-11]:

- Composition of the reaction mixture (silica to alumina ratio; OH⁻; inorganic cations).
  First, increasing the Si/Al ratio strongly affects physical properties of the zeolites. Second, OH⁻ modifies the nucleation time by influencing transport of silicates from the solid phase to solution. Third, inorganic cations act as structure directing agents and balance the framework charge. They affect the crystal purity and product yield.

- Nature of reactants and their pretreatments. The zeolite synthesis is carried out with inorganic as well as organic precursors. The inorganic precursors yielded more hydroxylated surfaces whereas the organic precursors easily incorporated the metals into the network.

- Temperature of the process. The rate of crystallization is directly proportional to temperature while the rate of nucleation is inversely proportional to temperature).

- Reaction time. Crystallization parameter must be adjusted to minimize the production of the other phases while also minimizing the time needed to obtain the desired crystalline phase.

- pH of the reaction mixture. The process of zeolitezation is carried out in alkaline medium (pH>10).

- Other factors. The synthesis can be carried out on a continuous or semi continuous mode, which enhances the capacity, making it compatible for industrial applications.

**CURRENT TRENDS IN ZEOLITE SYNTHESIS**

At present, the main problem in zeolite researchs is the availability and cost of raw material specifically the silica source. On the other hand, commercial silica (made of sand) which is available in gel, sol, fumed or amorphous solid is found to be variable in reactivity and selectivity. The preparation of synthetic zeolites from silica and alumina chemical sources is expensive. Yet, cheaper raw materials, such as clay minerals, natural zeolites, coal ashes, municipal solid waste incineration ashes and industrial slags, are utilized as starting materials for zeolite synthesis. The use of waste materials in zeolite synthesis contributes to the mitigation of environmental problems,
generally in the field of water purification, removing heavy metals or ammonium, and turns them into attractive and useful products.

Kaolin based zeolites. Kaolin is clay mineral which structure represent SiO$_4$ tetrahedral sheets joined to Al(O,OH)$_6$ octahedral sheets through shared oxygens. Zeolites prepared from natural kaolin are always contaminated with trace amount of iron, titanium, calcium, magnesium, etc. which are originally present in the natural kaolin. These elements may have some influence on the zeolite properties such as brightness, hardness, catalytic activity, electrical properties, etc. Presently, many researchers are working actively in various aspects on the synthesis of zeolite from kaolin. Clay minerals, such as kaolin [1, 12, 13], illite, smectite, interstratified illite-smectite [14], montmorillonite [15] and bentonite [12, 16] are widely used for synthesis of zeolites. The benefits of using kaolin as an aluminosilicate source in zeolite synthesis widely known [17, 18]. These authors have already studied the preparation of various zeolites from kaolin or other ashes and have made great progress in synthesis of 4A, mordenite, X, Y zeolites, etc. Kaolin is usually used after calcination at temperatures between 550-950 °C to obtain a more reactive phase metakaolin under chemical treatments, with the loss of structural water. Only a small part of AlO$_6$ octahedra is maintained, while the rest are transformed into much more reactive tetra- and penta-coordinated units [20]. The conditions of the kaolin calcination strongly influence the reactivity of the obtained solids. The best conditions for obtaining a very reactive metakaolin have been discussed by several authors who reported values between 600-800 °C [16, 21, 22].

Environmental impact. Globally, millions of tones of miscellaneous solid, liquid and gaseous waste materials, such as household, commercial, industrial, agricultural, radioactive and clinical wastes, are generated annually. It follows that for efficient use of the world’s resources recycling and reuse of waste is necessary. On the other hand, large daily output and the limited landfill capacity have resulted in social and environmental problems. Furthermore, the amount of these material is expected to increase dramatically in the near future and may cause major challenges and serious environmental problems.

Fly ash based zeolites. Various processes have been developed for synthesis of zeolite from fly ash, which have been reported by several patents and research articles. The processes developed include five different methodologies with variations in pretreatment steps, sodium aluminate addition, etc. as a function of structure development and exchange capacity [23].

Fly ash is an inorganic residue resulting from the combustion of coal in electricity generating plants, consisting mostly of SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$. As an industrial by-product fly ash is in the process of being beneficially used in several applications. Although the Si and Al concentrations are determined by the starting fly ash composition, the type and yield of synthesized zeolite strongly depended on alkaline condition and SiO$_2$/Al$_2$O$_3$ ratio of the starting fly ash. This ratio is important to predict whether the fly ash could successfully be converted into a specific zeolitic material by the adopted synthesis procedures [24]. On the other hand, it is necessary to clarify the influence of the silica–alumina composition for the zeolite formation because the fly ash composition seriously changes depending on the origin of coal sources, in order to synthesize a specific zeolite from any fly ash source [25].

CONCLUSION

Nowadays, ecological problems initiate studies of new materials, among which can find altered zeolites with new and unique properties gained by a chemical modification. An objective of the recent works is to further extend the possibilities of the method for the preparation of other types of zeolites and/or to further optimize synthesis of the existing ones. The methods have been modified in search for: 1) lowering the cost of the procedures yielding each type of zeolite; 2) protecting the environment.
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