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Progress in zeolite synthesis promotes advanced applications

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Dedicated to Dr. Michael Stöcker on the occasion of his retirement as Editor-in-Chief of Microporous and Mesoporous Materials.

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ABSTRACT

This article outlines the importance of zeolite synthesis and their unique physicochemical characteristics promoting advanced applications. The main strategies for preparation of zeolites including organic-template assisted, organic-template free and alternative procedures are considered for synthesis of crystallites offering control and fine-tuning of their properties. Besides, rational design of zeolites with pre-determined structure, porosity, size, morphology, and composition are more viable by studying carefully the chemical and physical parameters controlling the zeolite synthesis and understanding the crystallization mechanism. Finally, a particular attention to the preparation of zeolites with nanosized dimensions and their utilization in innovative applications including photovoltaic, medicine and holographic sensors are presented.

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1. Introduction

The well-defined porous structure of zeolites makes them true shape-selective molecular sieves with wide ranging applications in catalysis, ion exchange and adsorption processes [1,2]. Besides the different pore size and shape, the hydrophilic/hydrophobic nature of zeolites renders them as useful selective sorbents and hosts for guest molecules (organic or inorganic) that are stable in gas and liquid phase. In order to control the synthesis process and to obtain zeolites with predetermined properties, significant efforts have been dedicated to the fundamental understanding of the zeolite crystallization process and the influence of numerous variables and their impact on the physicochemical properties of the final product [3,4]. Amongst the number of factors controlling the synthesis of zeolites, the most important to be considered are divided in two groups-chemical and physical parameters (Fig. 1).

1.1. Parameters governing zeolite synthesis

The chemistry of the initial precursor mixture (gel/suspension) used for the synthesis of zeolites, more precisely the type of the initial sources, molar ratios, type of solvents, templates, additives and presence of seeds are of significant importance [5–7]. Under variation of these parameters, the initial precursor mixtures can appear as dry solid, dense (viscous) gel, liquid gel, milky suspension, or water clear suspension prior hydrothermal treatment [8–11]. Almost immediate polymerization and depolymerization processes are occurred, and a possible precipitation can follow. The next step involves hydrothermal synthesis of zeolites that are usually performed in closed reacting systems. The high super-saturation within the precursor mixture leads to spontaneous nucleation and controlled crystallization process under low temperature hydrothermal conditions (bellow 200 °C). The initial aluminosilicate precursor under the combined action of mineralizing (OH^-, F^-) and structure-directing agents (SDAs) is transformed into crystalline zeolite (Fig. 2). The SDAs could be alkali metal cations (Na^+, K^+, Li^+, etc.) or positively charged organic molecules, usually tetraalkylammonium cations (TAA^+). The generally accepted scheme includes the arrangement of SiO_4^- and AlO_4^- tetrahedra around charged templating species, *i.e.* hydrated alkali metal cations or organic molecules (Fig. 2).

Although all the chemical parameters listed above are strictly specified in the preparation of the initial precursor mixtures, still a large number of variables can influence the crystallization of zeolites. Since the zeolites are metastable phases, a fast transformation from less stable to more stable zeolites can occur under very small changes in the synthesis procedure. Therefore, very specific precursor materials have to be used in order to stimulate the formation of a certain zeolite phase. For example, the dissolution

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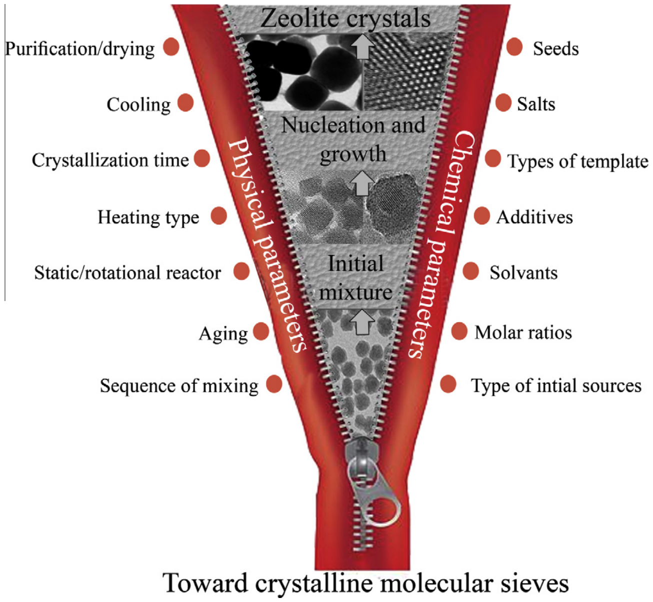

Fig. 1. Main parameters governing zeolite synthesis.

degree of silica or alumina sources has a major influence on the formation of precursor species with different Si/Al ratio and size that will be easily converted into target zeolite phase. In contrast, the viscous gels prepared by mixing of slow or not completely dissolved initial materials would result in inhomogeneous reactions that would generate a mixture of several crystalline phases or inter-grown crystallites. Recent experiments have demonstrated the possibility to capture highly metastable zeolite (EMT-type) via tuning the chemical composition of the precursor suspension. By exploring the very early stages of zeolite formation, it is possible to favor kinetically the nucleation of desired zeolite and thus to avoid the use of organic structure directing agents [12,13].

As mentioned above, organic structure directing agents are commonly employed to form and stabilize the framework of molecular sieves [14,15]. Many organic templates have been designed and used to obtain new framework types or to extend the composition of a known zeolite beyond the limits imposed by the nature. The chemical nature, shape and size of the organic templates are believed to influence the framework structure by stabilizing intermediate species during the nucleation. Further, the organic molecules provide an energetic stabilization to a given structure and therefore, it has a structure directing effect due to a thermodynamic effect by which the structure would minimize the energy of the inorganic-organic system, and ultimately the zeolite will be formed. Hence, the development of organic molecules that are used to direct zeolite crystallization is a major approach to novel synthesis of microporous materials.

The incorporation of organic template controls and stabilizes to some extent the pore structure of the zeolite through electrostatic interactions between the framework and the occluded organics. However, the organic templates are not as specific as anticipated since the same organic template can be used for synthesis of several zeolite phases [16]. Another recent example is the preparation of 11 different structures as B-rich, pure-Si and aluminosilicates using 16 imidazolium SDAs [17,18]. Besides, organic-template-assisted zeolites require a series of post synthesis treatments (purification, extraction or calcination) to discharge the templates occluded in the pores of the zeolites. In general, the removal of template has undesired effects on the crystalline structures such as partial or complete collapse of the pore structure and framework and partial release of the aluminium from the framework. Moreover, the production cost and the environmental regulations for chemical production are more restrictive, and therefore the combustion of organic templates becomes a much-undesired approach nowadays. Therefore a special attention on the development of recyclable SDAs has been paid [19,20]. One approach is based on the fragmentation and recovery of organic templates and successive use in more synthesis cycles (Fig. 3a). The other approach is based on the reuse of non-reacted SDAs after low temperature synthesis (bellow 100 °C), which results in significant decrease of the consumption of initial materials and mainly SDAs and ultimate decrease of pollution and product price (Fig. 3b). Another approach involves the replacements of the primary SDAs

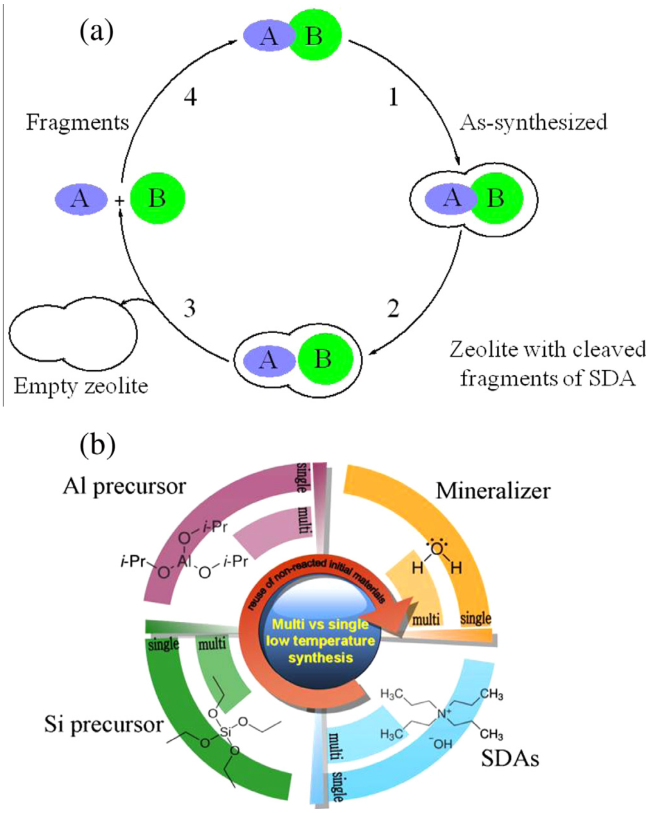

Fig. 3. Development of recyclable SDAs: (a) possibility of fragmentation and recovery, and (b) reuse of non reacted SDAs after low temperature synthesis.

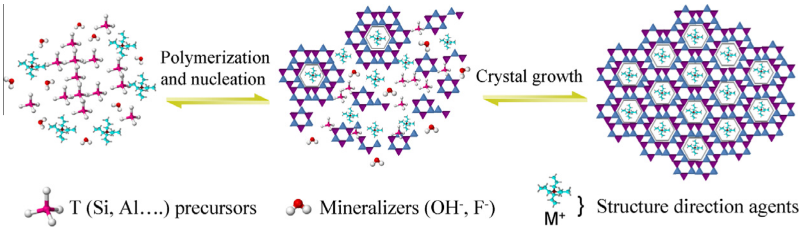

Fig. 2. General scheme of zeolites synthesis.

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