

## 論文の内容の要旨

論文題目 Ultrafast Synthesis of Crystalline Microporous Materials  
(ミクロ多孔質結晶の超高速合成)

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In this thesis, ultrafast synthesis of crystalline microporous materials is described. Crystalline microporous materials such as zeolites and phosphate-based microporous crystals, have long been used as catalysts, adsorbents and ion exchangers, and thus greatly contributed to the chemical and petrochemical industries. However, the synthesis of crystalline microporous materials usually takes a long period ranging from several hours to several days, depending on the targeted framework and chemical composition. The long time hydrothermal synthesis suffers from low efficiency, in terms of time, cost and energy, especially when operations at high temperature and high pressure are considered. Therefore, an ultrafast synthesis of crystalline microporous materials is of high significance. In this thesis, the ultrafast syntheses of a class of industrially important crystalline microporous materials covering aluminosilicate zeolites and (silico)aluminophosphates are described, with general requirements for ultrafast synthesis systematically discussed. Furthermore, the continuous-flow synthesis, a new synthesis process different from the batch process conventionally used, is also presented.

In Chapter 1, the general background and the rationalization of the objective and strategy of this study are described. During the past few decades, considerable efforts have been devoted to shorten the synthesis period of crystalline microporous materials, in particular aluminosilicate zeolites and zeolite analogues like (silico)aluminophosphates. The complexity of zeolite formation, however, hinders a fast synthesis. For one thing, the formation of zeolites is generally viewed as a kinetically controlled process, which determines that a long synthesis period is required to obtain the crystalline product. Furthermore, zeolite is not the thermodynamically most stable phase but only a metastable phase, and different types of zeolites are almost at the same level in view of the free energy. Since any single effort toward accelerating the crystallization rate may only result in the formation of an undesired framework, this thermodynamic aspect further complicates the fast synthesis of zeolites. In the light of this background, the objective of this thesis is to develop an ultrafast synthesis of crystalline microporous materials. To achieve this goal, at first a new type of reactor made of stainless steel

tube with diameters of several millimeters is introduced. Because of its smaller size and higher surface-to-volume ratio, the tubular reactor is able to achieve fast heating and consequently enables the synthesis at minutes level. Fast heating also makes the high temperature synthesis possible, as it helps avoid the decomposition of organic structure-directing agent (OSDA) and the decomposition/dissolution of the seed before the onset of crystal growth. Meanwhile, strategies from the chemistry perspectives, such as the addition of seed, the choice of starting materials and the mechanical treatment of the precursors, are adopted to prompt the crystallization of zeolites. These seemingly normal adjustments, combined with the advantages of the tubular reactor, can generate effects that could not be achieved in the conventional reactors, resulting in the ultrafast synthesis of a class of industrially important crystalline microporous materials.

In Chapter 2, the ultrafast synthesis of aluminosilicate zeolites is described. Aluminosilicate zeolites are the representative members of crystalline microporous materials, because they are the most widely used and intensively studied. In this chapter, SSZ-13 (CHA topology) and ZSM-5 (MFI topology) are presented. To overcome the kinetics barriers, following considerations are made: 1) take advantage of the fast heating in the tubular reactor to avoid the thermal lag and any negative effect thereof; 2) effectively skip the spontaneous nucleation by seeding; 3) enhance the crystal growth rate of the desired phase through optimizing the synthesis conditions (synthesis temperature, raw materials, etc.). With these considerations, ultrafast syntheses of SSZ-13 and ZSM-5, both in 10 min, were achieved in the tubular reactor under a temperature of 210 °C. The synergistic effect of the addition of seed, choice of the proper aluminum source, and the employment of high temperature treatment, is found to be effective in easing the bottlenecks encountered in the overall crystallization process, resulting in a remarkable enhancement on the crystallization. Along with these results, the choice of proper aluminum source deserves special attention because gibbsite  $\text{Al}(\text{OH})_3$  give rise to a higher crystallization rate than did a non-crystalline  $\text{Al}(\text{OH})_3$ . The non-crystalline  $\text{Al}(\text{OH})_3$  tends to easily react with the silicate species derived from colloidal silica to form a hydrogel of primary aluminosilicate, which is an intermediate only able to slowly convert into the crystalline product. On the contrary, with the use of gibbsite  $\text{Al}(\text{OH})_3$ , the reaction is supposed to follow a different pathway as it can avoid the generation of that primary aluminosilicate hydrogel. In this pathway, high availability of soluble silicate enables an easier formation of inorganic-organic composite (as a result of the interaction between soluble silicate and the organic structure-directing agent) that finally gives rise to a faster crystal growth rate.

In Chapter 3, the ultrafast synthesis of aluminophosphate and silicoaluminophosphates are

described. Aluminophosphate is a zeolite analogue composed of tetrahedral  $\text{Al}^{3+}$  and  $\text{P}^{5+}$  arranging in an exactly alternative manner, whereas silicoaluminophosphate is composed of three tetrahedral elements ( $\text{Al}^{3+}$ ,  $\text{P}^{5+}$  and  $\text{Si}^{4+}$ ). In this chapter, an aluminophosphate ( $\text{AlPO}_4\text{-5}$ , with AFI topology) and two silicoaluminophosphates (SAPO-5 and SAPO-34, with AFI topology and CHA topology, respectively) are studied. By combining the fast heating in the tubular reactor with the addition of seed, synthesis of  $\text{AlPO}_4\text{-5}$  could be completed within 1 min. Comparison of the results in the tubular reactor and in the conventional autoclave reveals that fast heating is crucial for the fast synthesis of  $\text{AlPO}_4\text{-5}$ , because VPI-5, a byproduct with VFI topology, could be formed in the conventional autoclave due to the thermal lag therein. Using similar approach, fast syntheses of SAPO-5 (in 5 min) and SAPO-34 (in 20 min) were also achieved. Meanwhile, it was found that SAPO-5 and SAPO-34 are competing phases that may coexist in the hydrothermal synthesis. The synthesis at 190 °C resulted in SAPO-34 as the main product, regardless of whether SAPO-34 seed was used or not; while the synthesis at 210 °C caused the formation of SAPO-5, even that the SAPO-34 seed was added. These results indicate that fast heating is thus crucial to get pure phase of SAPO-5, because slow temperature increase may give rise to a mixed product of both phases. The tubular reactor, heated in an oil bath, offered an opportunity to realize a fast heating and consequently succeeded in the ultrafast synthesis of SAPO-5 at 210 °C. As for SAPO-34, using a milling-treated precursor, the synthesis at 210 °C can avoid the formation of SAPO-5, resulting in the ultrafast synthesis of SAPO-34 in 20 min.

The reasons responsible for the ultrafast synthesis deserve careful review, and therefore, general requirements to the ultrafast synthesis are systematically discussed in Chapter 4. First of all, fast heating (together with fast cooling) is one of the prerequisites. Due to its higher surface-to-volume ratio, the tubular reactor offers the opportunity to achieve fast heating and thus lays a solid foundation to perform ultrafast synthesis. Secondly, the spontaneous nucleation can be effectively avoided by the addition of seed. With this regard, nanosized seed is more useful because it provides higher external surface where secondary crystal growth proceeds. Thirdly, the crystal growth rate should be accelerated based on the understanding of the crystallization of mechanism. Basically, the employment of a high temperature, the proper choice of starting materials and the pretreatment of the starting materials are the methods that can be adopted to enhance the crystal growth rate. Nevertheless, these efforts toward fastening the crystal growth must ensure the purity of the product. On the basis of the analysis into the individual prerequisite, a general scheme was proposed to rationalize the requirements towards the ultrafast synthesis.

In Chapter 5, the continuous-flow synthesis of crystalline microporous materials is presented. Crystalline microporous materials are typically synthesized in the reactors operated in batch, which suffers from drawbacks like frequent start-up and shut-down operations and low energy efficiency. To address this issue, the development of a continuous-flow process is highly desirable. The key to achieve the continuous flow preparation of crystalline microporous materials lies in a condition that can match the kinetics (e.g., crystallization rate), the thermodynamics (e.g., properties of the gel) and the hydrodynamics (e.g., gel fluidity). Therefore, the ultrafast synthesis offers an opportunity to make the continuous-flow synthesis easily achievable. Based on the ultrafast synthesis of  $\text{AlPO}_4\text{-5}$ , the continuous-flow synthesis of  $\text{AlPO}_4\text{-5}$  was achieved by combining the seed-assisted method with a continuous flow reactor that could achieve fast heating. As for SSZ-13, however, this straightforward one-stage continuous-flow process did not work due to that the gel viscosity drastically increased after being heated. To address the hydrodynamic problem, a two-stage continuous-flow synthesis was designed, where the gel was firstly heated for 3 min and then diluted with a mother liquid before being synthesized for another 10 min. This two-stage synthesis can overcome the problem of viscosity increase, leading to a successful continuous-flow synthesis of SSZ-13.

Finally, the general conclusions and a future perspective are given in Chapter 6. Overall, this thesis presented an entirely novel methodology aiming at efficiently and economically synthesizing crystalline microporous materials. Along with the ultrafast synthesis of a class of industrially important materials, the findings in this thesis undoubtedly provided a deeper insight into the understanding of the crystallization mechanism, which would be helpful in directing the synthesis of other types of microporous materials. Representing one of the most promising synthesis routes, the continuous-flow synthesis of crystalline microporous materials was also demonstrated, which would stimulate the industrial scale production of crystalline microporous materials using continuous-flow systems. As demonstrated in this thesis, the tubular reactor has opened a window for developing new synthesis routes as well as for performing mechanistic study of crystallization. Since the crystallization mechanism of zeolites is far from fully understood, the tubular reactor is expected to be able to offer a different perspective in the following studies: 1) precise control over the properties, for example, morphology and the distribution of T-atoms; 2) preparation of zeolites for which competing phases often coexist, and 3) fast incorporation of heteroatoms into zeolite framework. From a chemistry point of view, the insights obtained from this study, for example, the influence of aluminium sources on the ultrafast synthesis, are helpful to direct the synthesis and property control of other types of microporous materials.