

long-term treatments and/or less-controlled production. To address these disadvantages, the objective of this doctoral thesis is to achieve ultrafast and controllable preparation functional zeolite materials with desired properties in extremely short periods, which could further allow the establishment of continuous flow chemistry for industrial production.

There have been some case studies for synthesizing zeolites in just several minutes (*e.g.* CHA, MFI, and AFI), in which the favorable influences of seeding effect, aging effect, employment of high temperatures, and fast heating have been proved in accelerating the hydrothermal synthesis. However, the investigation on accelerating post-synthesis modifications is very rare despite conditions similar to zeolite synthesis are often involved. The interaction between treating conditions and the parent materials has not been fully characterized, especially when the processes can possibly be finished in several minutes. By considering the beneficial effects of distinguished high temperatures and ultrashort periods involved, the possibility of introducing desired properties are studied carefully.

The SSZ-13 zeolite with CHA topology has gained significant attention in recent years because of its excellent catalytic performance in the ammonia selectively catalytic reduction (NH_3 -SCR) reaction. In particular, considering the highly humid atmosphere and high temperature at automobile engine where the catalysts work, preparing nanosized CHA zeolite with sufficient hydrothermal stability will be quite profitable. In Chapter 2, direct-synthesis of nanosized SSZ-13 zeolite with enhanced hydrothermal stability was investigated through a two-stage synthetic way under different temperature programs. The first low-temperature stage (95 °C, 0–24 h) showed substantial effects determine the amounts of the nuclei formed before crystal growth; the high-temperature stage (210 °C, 5–60 min) allowed the crystal growth finished in several minutes. Resultantly, nanosized SSZ-13 zeolite was obtained with facilely controllable ranges of 50–300 nm. Moreover, the high-temperature stage not only accelerated the crystal growth, but also helped heal the intrinsic defects formed in the previous low-temperature stage. Compared with the micronsized SSZ-13 zeolite obtained through a conventional way (150 °C, 48 h) or nanosized counterpart obtained after saturated synthesis under low-temperature (95 °C, 72 h), the nanosized SSZ-13 prepared by the fast way showed remarkably enhanced hydrothermal stability.

The acidity of zeolites is attributed to the Brønsted acid sites, which is located on the oxygen atoms bridging Si and Al atoms. In practical reactions, the acid sites located in confined micropores impose shape selectivity for both reactants and products. However, the external surface acidity is often undesirable because of possible side reactions. Surface passivation technology has been proposed to be an effective way to remove the external surface acidity of zeolite catalysts. In chapter 3, an ultrafast post-synthesis modification for preparing core-shell structured zeolite catalyst was achieved in 5 minutes under high temperature of 190 °C. The

surface acidity of zeolite catalysts is often undesired for possible non-selective side reactions. Growing an inert shell (Silicalite-1) on the active surface of zeolite core (ZSM-5) was proved to be effective to reduce the surface active sites, as confirmed by catalyzing the cracking of large molecules (TIPB). The thickness of the shell part being important to adjust the surface acidity was facilely controllable by changing the treating periods, reaction compositions and temperatures. Compared with traditionally method for preparing core-shell structured zeolites in under low temperatures for long periods (150 °C, 14 h), the ultrafast method not only provide an efficient way for tailoring the active sites but also showed superior selection on avoiding the formation of isolated shell zeolite other than core-shell structure.

Despite of the unique shape-selectivity of zeolite catalysts, restricted utilization of the intracrystalline pores often occurs due to the slow mass-transfer to and from the active sites located in the micropores. Zeolites with hierarchical pore systems, *i.e.*, zeolites containing inter-connected micro- and mesopores, are highly desirable to overcome those diffusion limitations. In chapter 4, an ultrafast surfactant-templating treatment was described to efficiently introducing uniform mesopores in USY zeolite in just 2 minutes. The treatment was conducted under high temperatures in an alkaline solution containing the surfactant molecules. The process was proved to have followed two steps in such a short periods: 1) opening of the Si-O-Si bonds with the consumption of OH⁻; 2) re-arrangement of the isolated species in local areas with the assistance of surfactant micelle. The amounts and/or sizes of the mesopores created through this ultrafast method can be easily controlled by changing the initial alkaline concentration and/or the micelle size of surfactants. The precisely controllable formation of mesopores in such a short periods further allowed a kinetic study on the ultrafast surfactant-templating treatment (150 – 220 °C, 0–5 min). The calculated apparent activation energy, 29 kJ·mol⁻¹, is comparable to the crystallization of zeolite structures, which indicate the feasibility of the ultrafast formation of the mesoporous zeolite. This method further showed potential in introducing large amounts of uniform mesopores in other kind of zeolites such as ZSM-5, although careful modifications are still needed.

Ultrafast syntheses have been reported to be reproducible in continuous flow reaction systems. Considering the difference between the direct-synthesis and post-synthesis, improvements on the continuous flow reactor were made to accommodate an appropriate condition for corresponding post-synthesis modification. Consequently, the preparation of core-shell structured zeolite through ultrafast secondary growth, as well as the introduction of mesoporosity in zeolites through alkaline treatments are also achieved in continuous flow reactors.

In conclusion, this thesis demonstrates the successful developments of ultrafast strategy in introducing desired properties in zeolite products through either direct-synthesis or

post-synthesis modification. Realizing such kinds of ultrafast preparation of functional zeolite materials is of highly valuable from both of i) fundamental aspect that how fast the creation or re-arrangement of zeolite structures under hydrothermal conditions could be achieved and ii) practical aspect that a more efficient and economical way for functional zeolite materials could be expected. Consequently, the main contributions of this thesis are as follows: first of all, the ultrafast post-syntheses of tailoring the zeolite structures for desired acidity distribution and pore system were achieved in several minutes, indicating a surprisingly structural flexibility of existed zeolites to accommodate the improved properties. The kinetic study had proved the feasibility of the ultrafast post-synthesis modifications as the traditionally hydrothermal synthesis of zeolites. More importantly, continuous flow reaction systems were established to reproduce the ultrafast tailoring of the zeolite properties, which can be a great progress to prompt the industrial production of functional zeolite materials.