Abstract

Zeolites are crystalline microporous materials with three-dimensional frameworks built from corner-sharing TO_4 tetrahedra. Traditionally, zeolites are defined as aluminosilicates (T = Si and Al). Nowadays, the skeleton atoms have been expanded to other tri-/tetra-valent elements, including B, Ga, Ge, Ti, etc., due to the chemical flexibility of zeolites. Resulting materials are termed as elementosilicates for respective element-containing zeolites. Such materials exhibit fascinating properties due to the different nature of elements in the framework, *e.g.* structural flexibility and tunable acidity. Taking advantage of the unique properties of elementosilicate zeolites, their applications as the starting solids for the synthesis of new materials and as adsorbents for gas separation have made great progress. However, the complexity of the factors affecting the zeolite synthesis limits the possibility to control the key parameters of zeolites formation, *e.g.* crystallization mechanism, crystal growth rate, and phase selectivity. From the another side, for particular zeolite systems being perspective for gas separation, correlation between the chemical composition of designed structures and their adsorption performance is elusive.

Considering the above statements, this thesis was focused on the design of a series of elementosilicate zeolites with tunable properties (in particular, morphology, porosity, or acidity) either through controlling the crystallization mechanism or by manipulation with the zeolite structure and chemical composition.

The main achievements of this thesis are as follows:

A truly reversed crystal growth mechanism, in which crystallization starts at the surface of amorphous aggregates and then proceeds towards their centers, is demonstrated in zeolite synthesis systems for the first time. Using the zeolite **AST** as a representative structure, it was established that the concentration of structure-directing agent (SDA) in reaction mixture determines the facilitation of particular crystallization mechanism as it is responsible for driving the agglomeration of small particles into large amorphous aggregates at very early stages of the synthesis before crystallization starts. At low x = SDA/SiO_2 ratio ($0.3 \leq x \leq 0.4$) the crystal growth follows the classical route, while at high values ($0.5 \leq x \leq 0.7$) it switches to the reversed crystal growth mechanism. Besides, the F ions were revealed to govern the rate of crystal growth: a higher concentration of F^- results in a greater growth rate.

Two new zeolites (IPC-17 and IPC-18) were prepared using the ADOR (*assembly-disassembly-organization-reassembly*) approach by taking advantage of the structural lability of particular building units in the germanosilicate zeolites. For the realization of successful structural transformation, different strategies were applied for respective germanosilicates possessing unique chemical/structural properties. For the preparation of IPC-17, optimization of ADOR synthetic strategy was carried out through the control of the chemical composition of starting germanosilicate **IWR**. For the synthesis of IPC-18, the suppression of mass transport in the interlayer space of the products of germanosilicate **IWW** zeolite transformation was the core idea of the newly developed vapor-phase-transport rearrangement technique.

Direct synthesis of isomorphously substituted M-CHA (M = B, Al, Ga, and Ti) zeolites free of metal cations at ion-exchange positions was developed utilizing the assistance of pure siliceous Si-CHA as the crystal growth seeds. The synthesis time for respective M-CHA zeolites was significantly reduced compared with the previously known protocols. The introduction of heteroatoms to the framework of **CHA** zeolite was confirmed by the solid-state MAS NMR, UV-vis, and FTIR spectroscopies. It was established that the change in heteroatoms' nature alters the geometry of 8-ring in **CHA** structures and also influences the zeolite-CO_2 host-guest interaction and thus the zeolite performance in CO_2/CH_4 separation. The overall separation ability of M-CHA zeolites was found to follow the order Ti-CHA < Si-CHA ≈ B-CHA < Ga-CHA < Al-CHA.