論 文 の 内 容 の 要 旨

論文題目　A Study on Crystallization Mechanism of Nanosized Aluminosilicate Zeolites
(アルミノケイ酸塩ゼオライトナノ結晶の結晶化メカニズムに関する研究)

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Zeolites are a family of microporous materials whose intricate pores and channels are in the size range of 0.3 nm to 1 nm, and have been widely used as catalysts, adsorbents and ion-exchangers. Generally, zeolites are synthesized from basic aluminosilicate hydrogel under hydrothermal conditions by using inorganic cations and/or organic compounds as structure-directing agents (SDAs). Although the synthesis of novel zeolitic solids continues to dominate the field, elucidation of the complex mechanism involved in the formation of zeolites under hydrothermal conditions remains as one of the most difficult challenges. Considerable efforts (employing both in situ and ex situ techniques as well as the latest, computational methods) have been performed on the topic, however, due to its complexity, the crystallization mechanism of zeolite has not been completely understood.

The aim of this thesis is to elucidate the crystallization mechanism of aluminosilicate zeolites from an atomic level to nanosized particle level. Nanosized aluminosilicate zeolites are selected as model systems in the thesis. Study on the nanosized aluminosilicate zeolites facilitates the interpretation of the results, and enable to avoid ambiguous conclusions. To probe these large structures (precursor particles and crystals) formed during the crystallization process, in situ small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) are used. By combining SAXS/WAXS and several ex situ characterization techniques including high energy X-ray diffraction (HEXRD), the crystallization mechanisms of nanosized aluminosilicate zeolites with and without using organic SDAs are studied.

The phase selection of FAU and LTA in the presence of TMA^+ and Na^+ is studied by controlling the synthesis parameters in chapter 2, which indicates that the aging time and the concentration of Na^+ influence on the structure of the precursor particles formed before the formation of crystals. In order to elucidate the crystallization process of the aluminosilicate zeolites, the crystallization process of nanosized LTA is studied in detail. The primary units, the precursor particles and crystals, existing during the whole course of the crystallization process of nanosized aluminosilicate LTA on a continuous range from ca. 0.5 nm to 200 nm, are investigated by employing in situ SAXS/WAXS. During the crystallization process, the primary units in size of ca. 0.5 nm and the precursor particles in size of ca. 4.5 nm are formed. Both the primary units and the precursor particles are consumed during the formation of LTA crystals. By investigating the influences of the synthesis conditions on the formation and consumption of these particles, their roles in the crystallization process are clarified (chapters 3 and 4). Most of nanosized zeolites are synthesized from homogeneous clear solutions using

However, some nanosized zeolites have been synthesized without using any organic SDAs. In order to study the difference between the crystallization mechanisms of nanosized aluminosilicate zeolites with and without using organic SDAs, the crystallization process of nanosized LTL without using any organic SDAs is studied in chapter 5. It is found that the preparation of homogeneous aluminosilicate solution followed by the formation of hard gel composed of nanosized precursor particles with a hierarchical network structure is a critical point for the formation of nanosized LTL. Based on the crystallization mechanism of nanosized LTL, nanosized SOD is synthesized without using any organic SDAs (chapter 6).

In this doctoral thesis, the crystallization processes of the nanosized aluminosilicate zeolites with and without using organic SDAs have been systemically studied from an atomic level to nanosized particle level. The crystallization mechanism of nanosized aluminosilicate zeolites has been comprehensively discussed. I belive that the present thesis contributes to the synthesis of zeolite by approaching from both fundamental and applicational aspects.