



MFI-type zeolite with a core–shell structure with minimal defects synthesized by crystal overgrowth of aluminum-free MFI-type zeolite on aluminum-containing zeolite and its catalytic performance

Masaki Okamoto*, Yukio Osafune

Department of Applied Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552, Japan

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ABSTRACT

MFI-type zeolite with a core–shell structure and minimal defects was synthesized by crystal overgrowth of aluminum-free MFI-type zeolite on aluminum-containing MFI-type zeolite crystals. The purpose of the zeolite shell is to passivate acid sites on the external surface of the zeolite core. When both the shell and the core are synthesized in the presence of fluoride ion, defects are minimal. In the case of synthesizing the shell in the absence of fluoride ion, core growth does not occur. When the core is synthesized in the absence of fluoride ion, significant defects develop and cause mesopores to form in the core–shell zeolite. As catalysts for methylation of toluene with methanol, only the core–shell zeolite with minimal defects shows high selectivity for *p*-xylene (96%).

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1. Introduction

Zeolites are attractive for their high thermal stability, high surface area, cation-exchange capacity, uniform micropores, and other qualities, and have proven useful as cation exchangers, adsorbents and catalysts. When they are used as heterogeneous catalysts, shape selectivity can be achieved when reaction proceeds in the restricted space of their micropores, but not when reaction proceeds on their external surface. Therefore, for consistent shape selectivity, it is necessary to passivate the active sites on the external surface.

Many efforts to passivate the external surface of MFI-type zeolites have been reported. Niwa et al. passivated the external surface of MFI-type zeolite with amorphous silica formed by chemical vapor deposition of silicon alkoxides [1,2], and thereafter other groups also reported the passivation by chemical vapor deposition [3–7]. Various researchers have covered the external surface with silicalite-1 (aluminum-free MFI-type zeolite) shell to form so-called core–shell zeolite [8–14]. Among them, Lee et al. [9] and Weber et al. [10] obtained core–shell zeolite (ZSM-5 core with silicalite-1 shell) by hydrothermal crystallization of silicalite-1 gel in the presence of ZSM-5 crystals. Bouizi et al. reported the existence of pinholes in the silicalite-1 shell [11]. Li et al. reported that acid treatment of core zeolite (ZSM-5) is suitable for growth of the core

[12]. Nishiyama et al. [13–15] coated core zeolite with small crystallites of MFI-type zeolite by adding the core to a synthesis gel of aluminum-free zeolite, and demonstrated both successful epitaxial overgrowth of small crystallites on the parent zeolite and high catalytic performance with the obtained core–shell zeolite for methylation of toluene with methanol to give highly selective formation of *p*-xylene [14,15]. Furthermore, they also reported a single-crystalline silicalite/ZSM-5 core–shell composite and its high selectivity for *p*-xylene [16].

The ideal method of passivating the external surface is crystal overgrowth of aluminum-free zeolite (the shell zeolite) on single crystals of zeolite (the core zeolite) with no defects. In the preparation of zeolites, however, defects usually develop and cause mesopores to form. When zeolites with defects are used as core zeolites, defects then presumably grow in the shell zeolites and act there as pinholes, hindering perfect passivation of the external surface. It is thus important to be able to synthesize perfect core–shell zeolite.

In the conventional synthesis of MFI-type zeolite, tetrapropylammonium cation and hydroxyl anion are used as structure-directing and mineralizing agents, respectively. When the mineralizing agent is changed from hydroxyl anion to fluoride ion, reaction gives large particles of MFI-type zeolite with a coffin shape that is characteristic of MFI-type zeolite [17]. Axon et al. reported that the presence of fluoride ion in the synthesis gel leads to large zeolite crystals with no defects [18]. Large crystals are thought to form when nucleation and crystal growth occur at

* Corresponding author. Tel./fax: +81 3 5734 2625.

E-mail address: mokamoto@apc.titech.ac.jp (M. Okamoto).

slower rates over longer times [18], and occlusion of fluoride ion affords charge balance of the structure-directing agent without resource to Si–O[−] defects [19]. The use of fluoride ion is thus simple and suitable for obtaining core zeolite with minimal defects. Recently, Lombard et al. reported that under proper synthesis conditions using fluoride ion, core-shell zeolite (ZSM-5 core with silicalite-1 shell) was formed, however distribution of aluminum is on a gradient [20].

In this study, we examined synthesis conditions for crystal overgrowth without defects, and overgrew core zeolite prepared in the presence of fluoride ion to form core-shell zeolite with minimal defects. The studies using zeolites with no acidic sites on the external surface and no defects are important to obtain the information about catalytic properties of the inside of zeolites. We also tested the catalytic activity of the core-shell zeolite.

2. Experimental

2.1. Preparation of core zeolite

Core zeolite was prepared with fluoride ion as a mineralizing agent according to the method of Aiello [21,22]. Tetrapropylammonium bromide (TPABr) and ammonium fluoride (NH₄F) were dissolved in water, after which aluminum hydroxide and fumed silica were added. The mixture was stirred for 2 h, then heated in an autoclave at 180 °C for 90 h with stirring. The formed particles were filtered, washed, and calcined at 550 °C for 7 h under a dry air stream. The gel composition ratio was Si:TPABr:NH₄F:Al:H₂O = 1:0.125:0.9:0.05:33.

Core zeolite was also prepared by the conventional method. Aluminum nitrate, sodium hydroxide, and TPABr were dissolved in water, and tetraethyl orthosilicate was added dropwise. The mixture was stirred for 2 h, and then heated in an autoclave at 180 °C for 24 h. The formed particles were washed thoroughly, and then dried. The gel composition ratio was Si:TPABr:NaOH:Al:H₂O = 1.5:0.5:0.5:0.05:120.

2.2. Crystal overgrowth to synthesize the core-shell zeolite

Crystal overgrowth was achieved as follows. Fumed silica was added to an aqueous solution of TPABr and NH₄F. The mixture was stirred for 2 h, following which the core zeolite was added. The mixture was stirred for 80 min, then heated in an autoclave at 180 °C for 90 h without stirring. The formed particles were filtered, washed, and calcined at 550 °C for 7 h under a dry air stream. The gel composition ratio was Si (fumed silica):TPABr:NH₄F:H₂O:Si (core zeolite) = 1:0.125:0.9:33:1. Three types of zeolite were used as the core zeolite; zeolite prepared in the presence of fluoride ion before and after calcination and zeolite prepared by the conventional method in the absence of fluoride ion and without calcination.

Crystal overgrowth was also attempted under the same synthesis conditions used to prepare conventional zeolite. The gel composition ratio was Si:TPAOH:ethanol:H₂O:Si (core zeolite) = 2:0.5:8:120:2 [14].

2.3. Characterization of the zeolites

Scanning electron microscopy (SEM) images were taken using a VE-8800 (Keyence) operated at an accelerating voltage of 12 kV; samples were prepared by coating with thin layers of gold (20 nm). X-ray diffraction (XRD) patterns were obtained using CuK α with a MiniFlex diffractometer (Rigaku). Nitrogen adsorption-desorption was measured using a Belsorp 28 adsorption apparatus (Bel Japan); samples were prepared by drying at

200 °C for 3 h under vacuum. Pore-size distributions was calculated using desorption isotherms. Aluminum distribution across the particle cross-section was measured by field emission-scanning electron microscopy (FE-SEM) using an FE-SEM S4700 (Hitachi) equipped with an energy-dispersive X-ray (EDX) Genesis microanalyzer (EDAX); samples were prepared by embedding in epoxy resin, then cut using a diamond cutter.

Elemental analyses were performed using an inductively coupled plasma (ICP) JY38 analyzer (Rigaku). Temperature-programmed desorption (TPD) of ammonia was performed using a multitask TPD (Bel Japan); samples were prepared by heating at 500 °C for 1 h, exposure to ammonia at 100 °C for 1 h, and treatment under a helium stream at 100 °C for 12 min. When the Si:Al ratio was calculated from the TPD results, the amount of ammonia desorbed around 200 °C was excluded from the number of acid sites because of desorption of physically adsorbed ammonia [23].

2.4. Methylation of toluene with methanol

Methylation reaction was carried out in an atmospheric fixed-bed continuous-flow reactor. Catalyst (0.2 g) was placed in the reactor tube and heated at 550 °C for 2 h under a dry air stream. Reaction was performed at 400 °C at 42 kPa (1.43 mmol h^{−1}) of toluene and 42 kPa (1.43 mmol h^{−1}) of methanol. Trapped products were analyzed by gas chromatography every 1 h.

3. Results and discussion

3.1. Synthesis of the core-shell zeolite

As mentioned previously, three types of zeolite were used for the core zeolite. We adopt the following terminology: CF(NC) = core prepared in the presence of fluoride ion but not calcined; CF(C) = core prepared in the presence of fluoride ion and calcined; and CA(NC) = core prepared in the absence of fluoride ion but not calcined. Each was added to aluminum-free synthesis gel in the presence of fluoride ion, and the mixtures were heated under hydrothermal conditions at 180 °C for 90 h to produce the following zeolites (the suffix SF denotes shell synthesis in the presence of fluoride ion): CF(NC)SF, CF(C)SF, and CA(NC)SF. For CF(NC), a second hydrothermal synthesis in the absence of fluoride ion was also performed to produce CF(NC)SA.

To determine particle size, we examined the morphology of the core and core-shell zeolites by SEM. Fig. 1 shows images of the zeolites; Table 1 summarizes the lengths of the major axes. In agreement with published reports [17,18], the crystals prepared in the presence of fluoride ion, CF(C), were coffin-shaped and large (15 μ m), see Fig. 1a and Table 1. On the other hand, zeolite particles prepared by the conventional method, CA(C), were rounded and small (Fig. 1e).

During second hydrothermal synthesis on CF(C) and CF(NC) core in the presence of fluoride ion, the core crystals with coffin shape grow and small particles form around the large zeolites by new nucleation of aluminum-free zeolite [Supplementary material, Fig. S-1a, b]. To measure the size of the large zeolites, we removed the small particles by sonication and decantation. The amount of small particles removed is equal to about 20% of silicon charged as tetraethyl orthosilicate in the synthesis gel used for the second hydrothermal synthesis. Images of CF(C)SF and CF(NC)SF after sonication and decantation (Fig. 1b and c) show that the small particles is removed completely. The main particles grow from 15 to 18 μ m of major axis (Table 1) and maintain their shape through the second hydrothermal synthesis. These strongly suggest that crystal overgrowth on the main particles occurs during the second synthesis. When overgrowth is attempted in the absence of fluoride ion

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