Progress in seed-assisted synthesis of zeolites without using organic structure-directing agents

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ABSTRACT

Recent progress in the development of methods that do not require the use of organic structure-directing agents (OSDAs) has enabled the synthesis of useful zeolites under the use of zeolite seed crystals. This novel approach has attracted considerable attention as a low-cost, environmentally friendly technique for the production of zeolites. In this review, the conventional seed-assisted synthesis of zeolites in addition to the seed-assisted preparation of zeolite membranes are introduced, and an overview of recent developments in the seed-assisted, OSDA-free synthesis of various zeolites, such as beta, ZSM-12, TTZ-1, levyne, and so on, is presented. Although some mechanistic studies have been reported, the details of seed-assisted synthesis remain under investigation; recent OSDA-free syntheses have been estimated to be kinetically controlled systems. A new working hypothesis, designated as the "composite building unit (CBU) hypothesis" was proposed by us in order to broaden the range of zeolite types that can be prepared via seed-assisted synthesis. This hypothesis focuses on the structural relationship between the seed (target) zeolite and the zeolite obtained from a reactant gel without seeds. It was confirmed that several zeolites, such as ZSM-11, ECR-18, and so on, can be synthesized without OSDAs for the first time, by applying this hypothesis. The requirements for the successful synthesis of zeolites are introduced in addition to the unique features of the zeolites that are obtained by the seed-assisted synthesis method.

1. Introduction

To date, 206 types of zeolites and related structures have been recognized [1], and the number of structures is still increasing. The synthesis of novel zeolite structures largely relies on the use of various organic structure-directing agents (OSDAs), fluoride ions, and the introduction of metal atoms other than aluminum to the framework [2–9]. From a historical perspective, zeolites such as A (LTA), X, Y (FAU), L (LTL), and mordenite (MOR) have been synthesized without the use of OSDAs and have played important roles in industrial processes [10–12]. On the other hand, most zeolites have been synthesized in recent years using bulky OSDAs, such as tetraalkylammonium cations [2,3]. These new zeolites have unique features, such as a high silica content [8,9] and extra-large (greater than 12-membered ring (MR)) pore channels [13,14], and are expected to be used for new applications [15]. However, the cost of OSDAs accounts for a larger part of the total cost of the starting materials. In addition, for zeolites synthesized with OSDAs, calcination (or an alternative process [16]) is indispensable, and thus, processing/treatment of the waste gas and water produced by these processes is also necessary, which further increases the production costs. Moreover, using fluoride ion or metals other than aluminum is also unfavorable for indus-

trial production. Therefore, the synthesis of aluminosilicate zeolites without using OSDAs has been one of the most important topics for the commercialization of zeolites [17–19].

Recently, interesting results have been reported; several zeolites that were believed to require the use of OSDAs were synthesized without the addition of organic matter but with seed crystals (Fig. 1). This new seed-assisted approach is expected to reduce the cost and enable the development of environmentally friendly production processes of useful zeolites. Historically, seed crystals have been used mainly for the reduction of the synthesis time, elimination of impurities, controlling the particle size, and for the preparation of membranes [20]. Thus, while seed-assisted synthesis of zeolites has been well-known as a production technique, recent progress in the seed-assisted approach has opened the door to OSDA-free synthesis of zeolites.

2. Conventional seed-assisted synthesis of zeolites

Herein, we briefly review the conventional seed-assisted synthesis of zeolites, which has been mainly used to increase the crystallization rate or control the purity and properties (e.g., the crystal size) of the products. In the 1960s, Kerr investigated the factors affecting the formation of zeolites (A, B, and X) and showed that the presence of zeolite seed crystals eliminated the induction period [21,22]. A mechanism involving liquid-mediated supply of the

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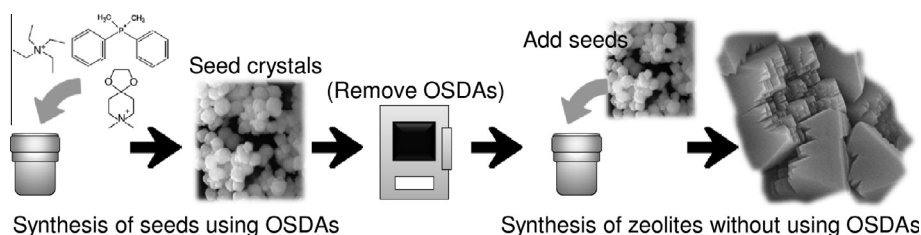E-mail address: okubo@chemsys.t.u-tokyo.ac.jp (T. Okubo).

Fig. 1. Schematic illustration of the seed-assisted, OSDA-free synthesis of zeolties.

Table 1
Maximum yield for zeolite Y crystallization using seed crystals. Data are from Ref. [28].

	Crystal sizes of seeds	SiO$_2$/Al$_2$O$_3$ ratios of seeds	Maximum yield of zeolite Y (%)
Without seeds	–	–	20
Zeolite X seeds	2–3 μm	2.5	25
Zeolite Y seeds	0.4 μm	5.5	30
Zeoltie X seeds	0.05 μm	2	50

dissolved silicate species to the surface of the seed crystals was also claimed in these and following papers [23,24]. Ueda et al., subsequently reported that the crystallization of zeolites from clear, homogenous, aqueous solutions, and seed crystals was also effective in these crystallizations, which supported the concept of a liquid-mediated crystallization formation mechanism [25–27]. In addition to increasing the crystallization rate, the presence of seed crystals also prevents the formation of other byproducts. Kasahara et al., investigated a synthesis system for the preparation of zeolite Y, in which impurities such as chabazite and philipsite were readily formed, and found that the size of the seed crystals affected the maximum yield of Y (see Table 1) [28]. Secondary nucleation via the initial breeding mechanism caused by microcrystalline dust washed out from seed surfaces has been investigated [29–37]. It was claimed that the size of the seeds significantly influenced the formation of secondary nuclei; that is, large zeolite A crystals (40 μm) promoted nucleation of a new population of zeolite crystals, while small seed crystals (approximately 1–3 μm) did not promote such a population [35]. Small seed crystals will provide large surfaces for the newly growing crystals, and they effectively act in many cases; however, not always small crystals are effective. On the other hand, polycrystalline breeding formed over seed crystals has been reported in a hydroxysodalite seed system [30]. In addition, Valtchev et al., reported the effect of tribochemical pretreatment of seeds for rapid crystallization of zeolite Y [38], and very recently, seed-assisted methods were applied for fluoride media to synthesize nanosized zeolite beta [39]. Analytical and theoretical investigations have also been reported on the synthesis of MFI-type zeolites (silicalite-1 or ZSM-5) [40–42]. Although these mechanisms have not been fully understood and some conflicting results have been obtained, this study has been summarized in reviews [43,44]. It should be noted that in these conventional methods, the addition of zeolite seeds to the reactant mixture yields the same zeolites that are obtained even when no seed crystals are used. In most cases, the presence of seeds with different crystal structures does not promote the crystallization of the target phases [45,46].

3. Seed crystals for the fabrication of zeolite membranes, films, and other macrostructures

The secondary growth of zeolites from seed crystals has also been used for other applications, such as the preparation of

zeolite membranes. In addition to an increase in the crystallization rate and improvement in the purity level, the seeding approach is advantageous for the highly reproducible preparation of dense and stable membranes with oriented crystal growth of the zeolite layer [47–57]. Lovallo et al., first demonstrated the preparation of zeolite L membrane by the secondary growth of zeolite L seeds on the porous substrate [49]. Matsukata and co-workers reported that ZSM-5 and mordenite membranes prepared via in situ hydrothermal synthesis using seed crystals in OSDA-free media (shown in Fig. 2) showed a very high separation factor for a water–isopropyl alcohol mixture compared to membranes prepared without seeding [58–60]. The synthesis conditions were optimized for controllable growth of the seed crystals by adjusting the water content in the reaction mixture [59,60]. Notably, both mordenite and ZSM-5 seed crystals grow in the same synthesis mixture under the same hydrothermal conditions [59], as do zeolites A and Y [61]. Lai et al., reported that controlled secondary crystal growth of silicalite-1 using OSDAs also results in improved membranes with high permeance and selectivity in xylene isomer separation [62].

Moreover, secondary growth of nano-seed crystals are also used for the preparation of macrostructured zeolite materials. Zeolite seeds can be deposited on various supports such as polystyrene beads, carbon fibers, and biological templates. The successive hydrothermal treatment and template removal by calcination result zeolite replicas of these templates. This topic has been reviewed by Tosheva and Valtchev [63,64].
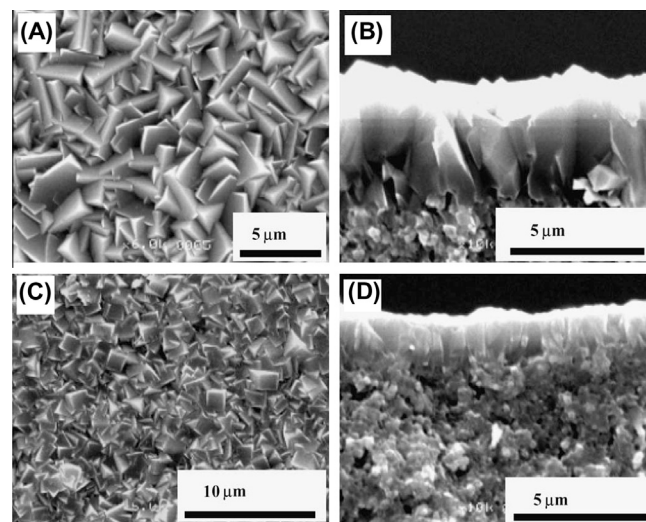

Fig. 2. Typical SEM images: (A) top surface and (B) cross section of a mordenite membrane, (C) top surface, and (D) cross section of a ZSM-5 membrane. The membranes were prepared on a porous α-Al$_2$O$_3$ plate at 180 °C for 12 h using a synthesis mixture with the molar composition Na$_2$O:Al$_2$O$_3$:SiO$_2$:H$_2$O = 10:0.15:36:960. Reprinted with permission from Ref. [57]. Copyright (2003) Elsevier.