

Green Chemistry and Sustainable Technology

Feng-Shou Xiao
Xiangju Meng *Editors*

Zeolites in Sustainable Chemistry

Synthesis, Characterization and Catalytic
Applications

 Springer

Green Chemistry and Sustainable Technology

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The series *Green Chemistry and Sustainable Technology* is intended to provide an accessible reference resource for postgraduate students, academic researchers and industrial professionals who are interested in green chemistry and technologies for sustainable development.

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Editors

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Preface

Crystalline microporous zeolites have been considered as mineral curiosities for a long time since their discovery in 1756. Currently, there are myriads of applications of zeolites and related porous crystals in the fields of industrial, environmental, and social relevance. Particularly, after revolutionizing the refinement of crude oil and the petrochemical industry as a whole by vastly enhancing the efficiencies of the existing process, great efforts have been devoted to the hydrothermal synthesis of zeolites and their properties, giving many breakthrough achievements. Summaries of these exciting results have already led to the publication of some great and successful books.

In recent years, with the development of green chemistry and shortage of energy around the world, there has been a major leap for the synthesis, characterization, and practical applications of zeolite, in terms of both its fundamental and industrial aspects. For instance, hierarchically porous zeolites with excellent mass transfer have been templated; solvent-free route for synthesis of zeolites has been achieved; interlayer expansion methodology has been established and created many new zeolite structures; the great strides made in modern techniques such as electron microscopy, solid NMR spectroscopy, and X-ray diffraction have significantly advanced our understanding of the syntheses and structures of zeolites; sustainable and important processes such as methanol to light olefins (MTO) and selective catalytic reduction of NO_x with ammonia (NH₃-SCR) catalyzed by zeolite catalysts have been commercialized already. Therefore, it is time to collect the works recently done by the outstanding scientists active in this field to establish an essential handbook.

This book mainly contains three parts, devoting to novel strategies for synthesizing zeolites, new developments in characterizations of zeolites, and emerging applications of zeolites for sustainable chemistry, respectively. In the first part, my colleague Dr. Xiangju Meng and I briefly summarize the synthesis of zeolites via sustainable routes (Chap. 1). Prof. Zhijian Tian from the Dalian Institute of Chemical Physics introduces in detail the ionothermal synthesis of zeolites (Chap. 2). Prof. Toshiyuki Yokoi and Prof. Takashi Tatsumi from the Tokyo Institute of Technology

provide a detailed review of the interlayer expansion of the layered zeolites (Chap. 3). Prof. Ryong Ryoo and his colleagues describe the synthesis of meso-structured zeolites (Chap. 4). In the second part, Prof. Xiaodong Zou and her colleague from Stockholm University present the different electron crystallographic techniques and their applications on structure determination of zeolites (Chap. 5). Prof. Hermann Gies and his colleague from Ruhr University Bochum elucidate the solution and refinement of zeolite structures (Chap. 6). Prof. Feng Deng and his colleague from the Wuhan Institute of Physics and Mathematics introduce the solid state NMR method for structural characterization of zeolites (Chap. 7). In the third part, Dr. Bilge Yilmaz and Dr. Ulrich Muller and their colleagues from BASF review the refinery applications (Chap. 8) and catalytic reactions (Chap. 14) of zeolites in industry. Prof. Weiguo Song from the Institute of Chemistry and Prof. Zhongmin Liu and Prof. Yingxu Wei from the Dalian Institute of Chemical Physics demonstrate the conversion process of methanol to light olefins over zeolites (Chap. 9). Prof. Emiel Hensen from TU/e discusses the application of zeolites as catalysts in the conversion of biomass into fuels and chemicals (Chap. 10). My colleague Dr. Liang Wang and I provide a concise review of the new developments of titanosilicate zeolites and their applications in various oxidations (Chap. 11). Prof. Hong He and his colleague from the Research Centre for Eco-Environmental Science explore the emerging applications of zeolites in environmental catalysis (Chap. 12). Prof. Zhengbo Wang from Zhejiang University and Prof. Yushan Yan from the University of Delaware summarize the recent progress in preparation and applications of zeolite thin films and membranes (Chap. 13). In the last Chapter (Chap. 15), Dr. Xiangju Meng and I also give a brief summary of the opportunities and challenges in the research and development of zeolites.

This book provides a comprehensive and an in-depth coverage of this rapidly evolving field from both academic and industrial points of view. We believe it can be used as an essential reference for the researchers who are working in the field of zeolites and related areas. It can also be used as a textbook as well as one of the key references for graduate and undergraduate students in chemistry, chemical engineering, and materials science.

Finally, we, the editors, would like to express our heartfelt gratitude to the authors for their contributions to this book.

Hangzhou, China

Feng-Shou Xiao

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Part I
Novel Strategies for Synthesizing Zeolites

Chapter 1

Sustainable Routes for Zeolite Synthesis

Xiangju Meng, Liang Wang, and Feng-Shou Xiao

Abstract The modern synthesis of zeolites mainly involves the use of organic templates, the addition of solvent, the preparation of starting gels, and the heating of the gels. Each step could be made greener in the future. This chapter presents a brief overview on the recently reported green routes for synthesizing zeolites, mainly focusing on the reduction or elimination of organic templates as well as the complete elimination of solvent. To overcome the disadvantages of using organic templates, nontoxic templates and template recycling steps have been employed in the zeolite syntheses. In addition, organotemplate-free synthesis has become a popular and universal methodology for synthesizing zeolites. Particularly, seed-directed synthesis in the absence of organic templates is a general route for synthesizing a series of zeolites. From an economic and environmental standpoint, solvent-free synthesis is a great move toward “green” synthesis of zeolite due to the following: high yields, high efficiency, low waste, low pollution, low pressure, hierarchical porosity, and simple and convenient procedure. Combining the advantages of solvent-free and organotemplate-free synthesis would particularly open the pathway to a highly sustainable zeolite synthesis protocol in industry.

Keywords Zeolites • Sustainable template • Template recycling • Organotemplate-free synthesis • Solvent-free synthesis

1.1 Introduction

Hydrothermal synthesis of zeolites from silicate or aluminosilicate gels in alkaline media has occupied an important position in zeolite synthesis science, where the temperature is ranged from 60 to 240 °C and the pressure is about 0.1–2 MPa [1, 2]. R. M. Barrer and R. M. Milton, the founders of zeolite synthesis science, started their studies in zeolite synthesis in the 1940s, successfully synthesizing a series of

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artificial zeolites such as P, Q, A, and X [1, 3–6]. Later, a milestone for zeolite synthesis is the introduction of organic quaternary ammonium cations in the hydrothermal synthesis, which opens a door to synthesize novel zeolites [1, 7, 8]. Up to now, more than 200 types of zeolites have been hydrothermally synthesized in the presence of organic templates.

Although hydrothermal synthesis of zeolites has been widely used for decades, it does not meet the critical terms of sustainable chemistry that refers to reduce or eliminate negative environmental impacts, involving the reduction of wastes and improvement of efficiency, due to the use of organic templates and a large amount of water [9].

Currently, organic templates play very important roles in the zeolite synthesis due to the templating of the assembly pathway, filling the pore space, and balancing the charges [1, 9]. However, most organic templates are toxic, which potentially threaten human health. In addition, removal of these templates normally requires high-temperature combustion that produces hazardous greenhouse gases such as NO_x and CO₂. On the other hand, water is always regarded as the “greenest” solvent, but a large amount of the water used in industries still results in a series of shortcoming such as waste of polluted water, high autogenous pressure, and consequently safe issues [9].

To solve these problems caused by conventional hydrothermal synthesis, sustainable routes for zeolite synthesis have been developed recently. In this chapter, several novel sustainable routes will be systemically illustrated.

1.2 Synthesis of Zeolites Using Sustainable Templates

Organic quaternary ammonium cations were first introduced into the zeolite synthesis by Barrer and Denny in 1961, and they have successfully synthesized several pure siliceous and high-silica zeolites [1, 7–9]. Different from the inorganic cations, organics play an additional role for templating or structure directing in the zeolite synthesis. Thus, these organics are called templates or structure-directing agents (SDAs). Conventional organic templates mainly include amines, amides, pyrrolidines, quaternary ammonium cations, and metal chelate complex [1, 2, 9].

1.2.1 Synthesis of Zeolites Using Low-Toxicity Templates

EMT zeolite is of great importance in fluid catalytic cracking (FCC) industry, due to its excellent catalytic performance compared with commercial catalyst Y zeolite [10, 11]. However, EMT zeolite is normally prepared in the presence of costly and toxic template of 18-crown-6, which greatly limited its wide applications in industry [12, 13]. Recently, Liu et al. reported successful synthesis of EMT-rich faujasites using polyquaternium-6 as a template, a component of shampoo, which is nontoxic and inexpensive since its extensive use in daily human life [14].

Wang et al. reported another successful example for the preparation of zeolite using nontoxic template [15]. They prepared a family of microporous aluminophosphate zeolite with AFI structure (AIPO-5) using tetramethylguanidine (TMG) as template. Guanidine and its derivatives with relatively low toxicity and low cost are biologically and industrially important chemicals, which could be found in the products of animal metabolism and classified as sustainable templates [16]. Notably, guanidines, containing three nitrogen atoms, might offer stronger coordination ability to aluminum species than conventional amines (e.g. triethylamine) with only one nitrogen atom [16]. As a consequence, the crystallization rate of AIPO-5 in the presence of TMG is much higher than that using triethylamine as templates, and the crystallinity reaches nearly 100 % only after 5 h. Moreover, this kind of sustainable template is not limited to prepare AIPO-5; heteroatom-substituted AIPO-5 crystals such as SAPO-5, MnAPO-5, together with CoAPO-5, and other microporous aluminophosphate (e.g. AIPO-21 with AWO structure) can also be synthesized using TMG as a template [15].

1.2.2 Synthesis of Zeolites Using Low-Cost Templates

Zones et al. have developed a new approach for the synthesis of zeolites, in which a minor amount of SDA is used to specify the nucleation product, and then a larger amount of a nonspecific amine is used to provide both pore-filling and basicity capacities in the synthesis [17]. The concept used in this method was to have the SDA provide the initial nucleation selectivity and then hope that a cheaper, less selective molecule could provide the pore-filling aspect as the crystal continuously grows. For example, various small amines including even ammonia and methylamine were shown to function in conjunction with the imidazole SDA to produce SSZ-32. A number of zeolites including SSZ-13 (CHA), SSZ-33 (CON), SSZ-35 (STF), SSZ-42 (IFR), and SSZ-47 can be prepared in the same manner [18]. There are a number of cost-saving benefits described for this synthesis route including reduced structure-directing agent cost, waste stream cleanup costs, and time in reactor and reagent flexibility.

Similar to this concept, UOP scientists have developed the charge density mismatch (CDM) approach to prepare zeolites via addition of alkali and alkaline Earth cations at low levels, which cooperate with organic templates [19–21]. Such cooperation allows the use of commercial available organic templates for a new material discovery. For example, they prepared hexagonal 12-ring zeolites UZM-4 (BPH) and UZM-22 (MEI) using choline-Li-Sr template system based on the charge density mismatch approach. Notably, the CDM approach to zeolite synthesis was initially proposed as a cheaper alternative to the trend of using ever more complicated quaternary ammonium species.

Ren et al. have designed a copper complex of Cu–tetraethylenepentamine (Cu–TEPA) as candidate for synthesizing CHA-type aluminosilicate zeolite (SSZ-13) [22, 23], which is generally directed by the expensive template of *N,N,N*-trimethyl-1-1-adamantammonium hydroxide, due to (1) good match between the stable

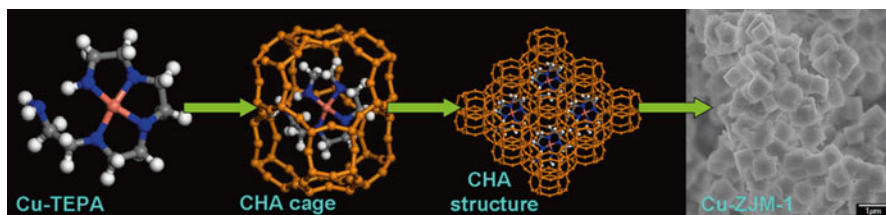


Fig. 1.1 Mechanism on Cu-TEPA-templated Cu-SSZ-13 zeolites (Reprinted with permission from Ref. [22]. Copyright 2011 Royal Society of Chemistry)

molecular configuration of Cu-TEPA with CHA cages, (2) strong interaction between the template molecule and negatively charged silica species, and (3) high stability in strongly alkaline media. They reported rational one-pot synthesis of Cu-SSZ-13 zeolites with molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ at 8–15, designated as Cu-ZJM-1, from using Cu-TEPA as template (Fig. 1.1). Compared with the traditional Cu^{2+} ion-exchange method, Cu-ZJM-1 shows much higher copper content and better dispersion of copper cations. More importantly, Cu-ZJM-1 exhibits excellent catalytic properties in SCR of NO_x by NH_3 [22].

1.2.3 Synthesis of Zeolites Using Recyclable Templates

Davis et al. have performed pioneer works in the field of extracting organic templates from micropores of zeolites [24–29]. Firstly, they reported that TEA^+ cations could be easily extracted from CIT-6 zeolite (BEA-type structure) with acetic acid-containing solution [24], because of the weak interaction between the TEA^+ cations and CIT-6 framework. The ease of liberation of charge-balancing tetraethylammonium (TEA) cations from the various metallosilicates was shown to be $\text{Zn} > \text{B} > \text{Al}$ [28]. This method can also be utilized in pure-silica MFI zeolite. They also pointed out that the amount of organic templates removed by extraction was strongly dependent on the size of the organic templates and the strength of interaction between the templates and the zeolites [28].

Later, they reported a complete recycle of an organic template in the synthesis of ZSM-5 [29]. They chose a cyclic ketal as organic template that would remain intact at zeolite synthesis conditions (high pH) and be cleavable at conditions that would not destroy the assembled zeolite (Fig. 1.2). The ^{13}C CP/MAS NMR spectrum showed that the as-synthesized zeolite material contains intact 8,8-dimethyl-1,4-dioxo-8-azaspiro [4, 5] decane (**1**). When the ZSM-5 was treated with 1 M HCl solution at 80 °C for 20 h, the ^{13}C CP/MAS NMR spectrum obtained was consistent with the presence of the ketone fragment, suggested that **1** could be cleaved into the desired pieces inside the zeolite pore space. After ion-exchange treatment by a mixture of 0.01 M NaOH and 1 M NaCl at 100 °C for 72 h, 1,1-dimethyl-4-oxo-

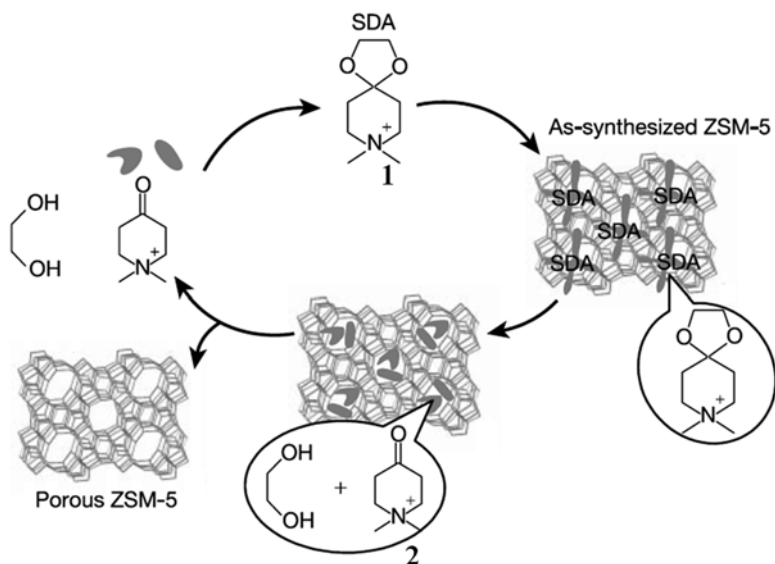


Fig. 1.2 Schematic representations of synthetic methodology for ZSM-5 using **1** as template. Step 1: assemble the SDA with silica precursor, H₂O, alkali metal ions, and so on, for zeolite synthesis. Step 2: cleave the organic molecules inside the zeolite pores. Step 3: remove the fragments. Step 4: recombine the fragments into the original SDA molecule (Reprinted with permission from Ref. [29]. Copyright 2003 Nature Publishing Group)

piperidinium (**2**) could be completely removed as shown in ¹³C CP/MAS NMR spectrum. Conceptually, this strategy is to assemble an organic template from at least two components using covalent bonds and/or non-covalent interactions that are able to survive the conditions for assembly of the zeolite and yet be reversed inside the microporous void space. The fragments formed from the organic template in the zeolite can then be removed from the inorganic framework and be recombined for use again. Other zeolites such as ZSM-11 and ZSM-12 can also be synthesized using the same manner, suggesting that it can be used as a generalized methodology in the field of zeolite preparation [29].

1.3 Synthesis of Zeolites Without Using Organic Templates

Recently, organotemplate-free synthesis of zeolites has been the hot topic in zeolite area, since it completely avoids the use of organic templates and consequently disadvantages [9, 30]. Several groups have devoted to synthesize a series of zeolites in the absence of organic templates by adjusting molar ratios of the starting gels, addition of zeolite seed solution, and addition of zeolite crystal seeds.

1.3.1 MFI Zeolite

The discovery of ZSM-5 was regarded as a milestone in the history of hydrothermal synthesis of zeolites [1, 2, 31]. The ZSM-5 is the most widely studied zeolite due to its special features (e.g., morphology, zigzag channels, Si/Al ratio) and its importance in petrochemical and fine chemical industry [1, 2]. Notably, ZSM-5 is the first example for organotemplate-free synthesis of high-silica zeolites. In the initial stage of synthesis of ZSM-5, it was widely accepted that ZSM-5 could only be made using a suitable organic template (usually TPA⁺) [1, 9, 31]. Grose and Flanigen prepared well-crystallized ZSM-5 zeolite from the Na₂O–SiO₂–Al₂O₃–H₂O in the absence of organics and seeds for the first time [32–34]. Later, Shiralkar and Clearfield reported that the factors of adjusted Si/Al and Na/Al ratios are keys for the organotemplate-free synthesis of ZSM-5 zeolite [35].

1.3.2 BEA Zeolite

Beta zeolite was successfully synthesized using tetraethylammonium cation as the templates in 1967 [36]. In the past 40 years, there is a belief that beta zeolite can only be synthesized in the presence of suitable organic templates [9, 35, 37]. However, in 2008, Xie et al. reported an organotemplate-free and fast route for synthesizing beta zeolite by the addition of calcined beta crystals as seeds in the starting aluminosilicate gel in the absence of any organic templates for the first time [37]. Nitrogen sorption isotherms of as-synthesized sample exhibited a steep increase in the curve at a relative pressure $10^{-6} < P/P_0 < 0.01$, characteristic of Langmuir adsorption due to the filling of micropores, which confirmed that as-synthesized sample had opened micropores already, and therefore the combustion of the sample could be avoided. Later, Kamimura et al. systemically studied various parameters on the seed-directed synthesis of beta zeolite in the absence of organic templates, such as the molar ratios of SiO₂/Al₂O₃, H₂O/SiO₂, and Na₂O/SiO₂ in the starting gels, amount and Si/Al ratios of seeds, and crystallization time [38]. They found that beta zeolite can be successfully synthesized with a wide range of chemical compositions of the initial Na⁺–aluminosilicate gel (SiO₂/Al₂O₃=40–100, Na₂O/SiO₂=0.24–0.325, and H₂O/SiO₂=20–25) by adding calcined beta seeds with the Si/Al ratios in the range of 7.0–12.0. Very importantly, such seed-directed beta seed crystals can be used as renewable seed crystals to establish a completely organotemplate-free process for the production of beta zeolite, which is a vital development from the viewpoint of green chemistry. Thus, this kind of seed-directed beta was termed as “green beta zeolite” by the authors.

In a recent report, Zhang et al. reported a rational synthesis of beta-SDS at 120 °C (beta-SDS₁₂₀) with good crystallinity and improved zeolite quality in the presence of a very small amount of beta seeds (as low as 1.4 %) by decreasing zeolite crystallization rate [39]. X-ray diffraction patterns show that calcination at 550 °C for 4 h

Table 1.1 Textural parameters of as-synthesized beta-SDS and calcined beta-TEA zeolites

Sample	BET surface area (m ² /g)	Micropore area (m ² /g)	Micropore volume (cm ³ /g)	HK pore size (nm)
Beta-SDS ₁₄₀	450	386	0.18	0.70
Beta-SDS ₁₂₀₋₁	655	545	0.25	0.70
Cal-beta-TEA	577	447	0.21	0.66

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results in the loss of crystallinity at 8.0 and 15.8 for beta-SDS₁₂₀ and beta-SDS₁₄₀, respectively, suggesting that beta-SDS₁₂₀ has higher thermal stability than beta-SDS₁₄₀. N₂ sorption isotherms show that beta-SDS₁₂₀ has much higher surface area (655 m²/g) and micropore volume (0.25 cm³/g) than beta-SDS₁₄₀ (450 m²/g, 0.18 cm³/g) (Table 1.1). These phenomena are reasonably assigned to that beta-SDS₁₂₀ samples have much less framework defects such as terminal Si–OH groups than beta-SDS₁₄₀. The beta-SDS₁₂₀ samples with good crystallinity, high thermal stability, and large surface area and pore volume offer a good opportunity for their industrial applications as efficient and low-cost catalytic and adsorptive materials.

The mechanism on seed-directed synthesis of beta zeolite has been independently discussed by Xiao and Okubo's groups at nearly the same time [40, 41]. By using a series of modern techniques (XRD, TEM, SEM, XPS, Raman, MAS NMR), Xie et al. have extensively investigated seed-directed synthesis of beta-SDS under various conditions, suggesting that seed-directed beta zeolites are grown from solid beta seeds, and final beta-SDS crystals are mainly alike core–shell structure [40]. The core part of beta seeds has relatively high Si/Al ratios, and the shell part grew from aluminosilicate gels has relatively low Si/Al ratios (Fig. 1.3).

De Baerdemaeker et al. have systemically investigated the catalytic performance of beta-SDS in various reactions, and they found that beta-SDS has different properties than the usual commercial beta zeolites [42]. Part of the differences can be explained by the higher aluminum content and different crystal size. The high aluminum content leads to a large number of acid sites of considerable strength resulting in an active ethylation catalyst even at 150 °C. The large crystal size of beta-SDS makes them sensitive to deactivation through pore blocking. In alkylation reactions with propene and 1-dodecene, this resulted in low activities. An appropriate dealumination treatment can improve the accessibility and delay the deactivation. The high aluminum content also leads to a high framework polarity which is a cause for fast deactivation in acylation reactions. This can be prevented by dealumination where an activity optimum is obtained between framework polarity and acid site concentration. The high amount of strong acid sites also leads to a high yield of cracked products in the *n*-decane hydroconversion at very low temperatures (Fig. 1.4). Clearly, more Pt should be added to improve the balance between the acid sites and the (de)hydrogenation sites. A reduction in the amount of acid sites by dealumination at constant Pt loadings resulted in higher isomerization yields. Yilmaz et al. also pointed out that beta-SDS possesses a high density of active sites with exceptional stability and distinctively ordered nature, useful in, e.g., ethylation

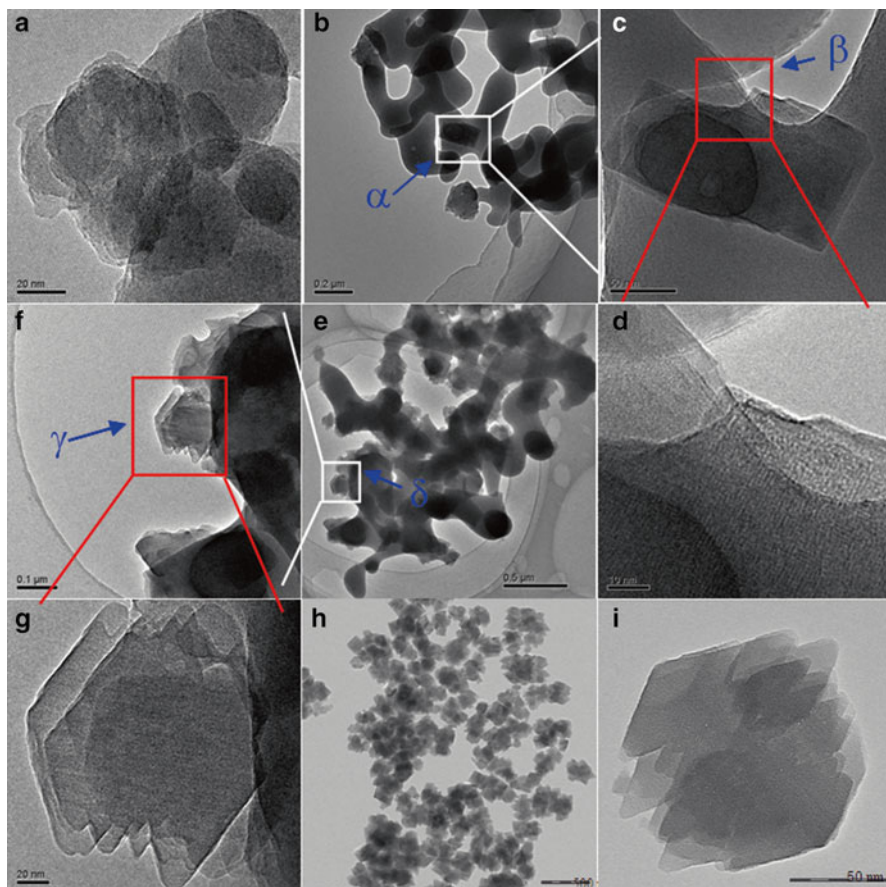


Fig. 1.3 TEM images of beta-SDS samples crystallized for (a) 1, (b–d) 4, (e–g) 8, and (h and i) 18.5 h at a temperature of 140 °C by addition of 10.3 % beta seeds (Si/Al=10.2) in the starting aluminosilicate gels. Areas of a, b, d, and g in (b), (c), (e), and (f) are enlarged as (c), (d), (f), and (g), respectively (Reprinted with permission from Ref. [40], Copyright 2011 Royal Society of Chemistry)

of benzene; after dealumination and/or other post-synthesis treatments, catalysts with varying Si/Al ratios, suitable, e.g., for acylation of anisole, are obtained [43]. The ability to manipulate the framework aluminum content in a very broad range, while maintaining structural integrity, proves that beta-SDS zeolites constitute a powerful toolbox for designing new acid catalysts.

Notably, heterogeneous atoms can also be incorporated into the framework of BEA via SDS route [44]. Zhang et al. have demonstrated that an organotemplate-free and seed-directed route has been successfully applied for synthesizing Fe-beta zeolite with good crystallinity, high surface area, uniform crystals, and tetrahedral Al^{3+} and Fe^{3+} species. Catalytic tests for the direct decomposition of nitrous oxide indicate that the Fe-beta exhibits excellent catalytic performance.

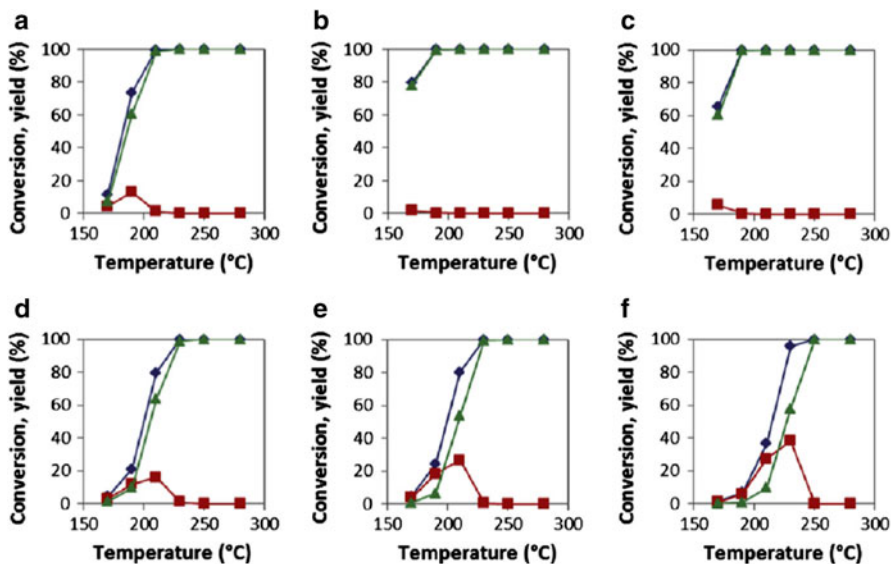


Fig. 1.4 Catalytic results from the n-decane hydroconversion: n-decane conversion (◆), yield of isomerization products (■) and yield of cracking products (▲) for Beta-1 (a), OF-Beta (b), OF-Beta-ST (c), OF-Beta-ST-0.1 (d), and OF-Beta-ST-0.5 (e) and OF-Beta-ST-6.0 (f) (Reprinted with permission from ref 42. Copyright 2013 Elsevier)

1.3.3 EMT Zeolite

Zeolite EMT is a hexagonal polymorph of faujasite-type zeolites, with one of the lowest framework densities for microporous zeolites. Similar to the FAU zeolite, the EMT framework topology has a three-dimensional large (12-membered ring) pore system. The cubic FAU polymorph features only one type of supercage (with a volume of 1.15 nm³), but a different stacking of faujasite sheets creates two cages in the EMT zeolite: a hypocage (0.61 nm³) and a hypercage (1.24 nm³) [45]. EMT zeolite showed excellent catalytic performance as FCC catalyst, but its high cost precludes its practical applications, compared with Y zeolite [10, 11]. An expensive and toxic template of 18-crown-6 is the most used template for EMT zeolite. Recently, Ng et al. reported organotemplate-free synthesis of ultrasmall hexagonal EMT zeolite nanocrystals (6–15 nm in the sizes) at very low temperature from Na-rich precursor suspensions [46]. Notably, the ratios between different compounds, nucleation temperature and times, and type of heating should be carefully controlled to avoid phase transformations (e.g., to FAU and SOD) and to stabilize the EMT zeolite crystals at a small particle size. The author proposed that under appropriate conditions the EMT was the first kinetic, metastable product in this synthesis field, followed by conversion into the more stable cubic FAU and more dense SOD structures [46].

1.3.4 MTW Zeolite

ZSM-12 is the type zeolite with the framework of MTW with one-dimensional, non-interpenetrating 12-ring pores (with the size of 5.6×6.0 Å along b-axis), which was first reported by Rosinski and Rubin in 1974 [47]. Since then, ZSM-12 has attracted much attention because of its excellent catalytic properties in the cracking of hydrocarbons or in other petroleum refining processes. The conventional synthesis of ZSM-12 has been achieved by using tetraalkylammonium cations such as methyltriethylammonium (MTEA^+), tetraethylammonium hydroxide (TEA^+) as organic SDAs [47–51]. Kamimura et al. have reported the synthesis of highly crystalline, pure MTW-type zeolite which has been studied by the addition of calcined ZSM-12 seeds [52, 53]. They have systemically investigated the various parameters on the seed-directed synthesis of MTW zeolite in the absence of organic templates, such as the molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{H}_2\text{O}/\text{SiO}_2$, and $\text{Na}_2\text{O}/\text{SiO}_2$ in the starting gels, amount of seeds, and crystallization time. They found that MTW zeolite can be successfully synthesized in a wide range of the initial OSDA-free sodium aluminosilicate gel compositions: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 60\text{--}120$, $\text{Na}_2\text{O}/\text{SiO}_2 = 0.1\text{--}0.2$, and $\text{H}_2\text{O}/\text{SiO}_2 = 8.25\text{--}13.3$ (Table 1.2). Notably, SDS-MTW samples are rodlike crystals with well-defined morphology, which is quite different from the round-shaped, irregularly aggregated morphology of the seeds. Additionally, the crystal size of SDS-MTW is in the range of $0.2\text{--}1.5$ µm in length and $50\text{--}200$ nm in diameter, which is larger than the size of the seeds. The solid yield of SDS-MTW was ca. 47 %, which is obviously higher than that in the case of the organotemplate-free synthesis of beta. More importantly, the green production of MTW-type zeolite referred as “Green MTW” is achieved for the first time, by using the product of OSDA-free synthesis as seeds [53].

Interestingly, Kamimura et al. found that pure MTW-type zeolites can also be prepared in the presence of beta zeolite seeds instead of ZSM-12 seeds [54]. To understand the crystallization behavior and the role of beta seeds in the present organotemplate-free Na-aluminosilicate gel systems, the crystallization processes were carefully studied by XRD. Before 55 h, small diffraction peaks of beta seeds were clearly observed and then became smaller possibly because of the partial dissolution of beta seeds, and the diffraction peaks corresponding to the MTW phase simultaneously appeared, suggesting the formation of MTW zeolite. The intensity of the MTW phase gradually increased, indicating the growth of MTW zeolite crystals. Finally, complete crystallization of MTW-type zeolite was obtained after 96 h of heating. Such phenomenon can be explained by that ZSM-12 and beta zeolites possess very similar topology in which their a–c projection viewed along and perpendicular to the 12R straight channels. This fact indicates that beta seeds would possibly provide a specific growth surface for the crystallization of the MTW phase through their structural similarity. Also, as evidenced by the crystallization behavior of MTW, beta seeds were partially dissolved in the course of the hydrothermal treatment. Hence, the fragments from partially dissolved seeds with BEA structure might have a role to induce the crystal growth of MTW phase, although it is still difficult to evaluate and observe the amount of dissolved seeds and fragments under highly alkaline condition. Moreover, the crystallization of MTW is induced by not only the structural similarity between seeds and target zeolite but also the chemical composition of the non-seeded, organotemplate-free gel.

Table 1.2 Chemical compositions of the initial sodium aluminosilicate gel, synthesis conditions, and characteristic properties of the products in the seed-assisted, OSDA-free synthesis of MTW-type zeolite

Sample	SiO ₂ /Al ₂ O ₃ ^a	Na ₂ O/SiO ₂ ^a	H ₂ O/SiO ₂ ^a	Amount of seeds (wt.%) ^b	Time (h) ^c	Phase ^d	Crystallinity (%) ^e	Si/Al ratio ^f
MTW-No. 1	20	0.100	10	10	72	MTW + Arm	10	–
MTW-No. 2	40	0.150	10	10	72	MTW + Arm	30	–
MTW-No. 3	60	0.100	10	10	72	MTW	100	–
MTW-No. 4	60	0.150	10	10	55	MTW	100	14.5
MTW-No. 5	60	0.200	13.3	10	36	MTW	100	11.7
MTW-No. 6	80	0.125	8.25	10	72	MTW + Cri	100	–
MTW-No. 7	80	0.175	11.5	10	36	MTW	100	16.2
MTW-No. 8	80	0.175	11.5	1	70	MTW	100	–
MTW-No. 9	100	0.100	10	10	72	MTW + Cri	100	23.4
MTW-No. 10	100	0.150	10	10	65	MTW + Cri	100	25.7
MTW-No. 11	100	0.200	13.2	10	65	MTW	100	14.5
MTW-No. 12	120	0.125	8.3	10	96	MTW + Cri	100	33.0
MTW-No. 13	120	0.175	11.7	10	96	MTW + Cri	100	26.7

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^aChemical composition of the initial reactant gel

^bWeight ratios of the seeds relative to the silica source

^cTime for the hydrothermal treatment at 165 °C

^dPhase of the solid product. The phase shown in the parenthesis indicates the relatively small amount of impurity. *Arm* amorphous, *Cri* cristobalite

^eCrystallinity of the MTW phase

^fSi/Al ratio of the product determined by ICP-AES

1.3.5 TON Zeolite

TON-type zeolites including ZSM-22, Theta-1, Nu-10, KZ-2, and ISI-1 have a one-dimensional 10-membered ring pore system with medium-sized pores of ca. 0.47×0.55 nm [55, 56]. The channels run along the longest dimension of the crystals (crystallographic *c* direction). The unique structure of TON zeolites offers

superior catalytic performance in petrochemical processes such as isomerization, hydroisomerization dewaxing, and propylene oligomerization. Generally, TON zeolite can be hydrothermally synthesized from aluminosilicate gels using a series of oxygen- or nitrogen-containing linear organics as SDAs such as amines, long-chain polyamines, and quaternary ammonium compounds [55–60]. Recently, Wang et al. have reported a successful seed-directed and organotemplate-free synthesis of TON zeolites (denoted as ZJM-4) [61]. XRD pattern of ZJM-4 sample synthesized in the presence of ZSM-22 seeds without using organic templates under rotation conditions showed a series of characteristic peaks associated with TON structure. Furthermore, SEM image shows that ZJM-4 has uniform rodlike crystals with length at 2–4 μm and width at 100–200 nm, in good agreement with the typical morphology of TON-type zeolites reported previously. Ar sorption isotherms of as-synthesized ZJM-4 exhibited a steep increasing in the curve at a relative pressure $10^{-6} < P/P_0 < 0.01$, which is characteristic of Langmuir adsorption due to the filling of micropores, confirming that as-synthesized sample had opened micropores (Fig. 1.5).

It is worth mentioning that the seed-directed synthesis of ZJM-4 has very high silica utilization, compared with the seed-directed synthesis of beta zeolite. For example, the silica utilization for seed-directed synthesis of ZJM-4 is 88 %, much

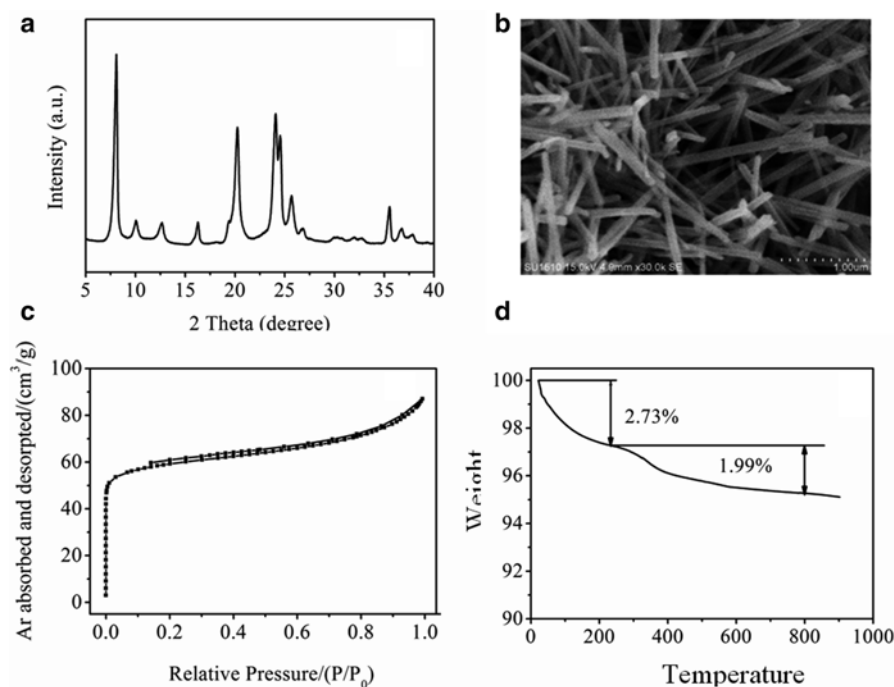


Fig. 1.5 (a) XRD and (b) SEM image of the as-synthesized ZJM-4 sample, (c) Ar sorption isotherms of the H-form of the ZJM-4 sample, and (d) TG curve of the as-synthesized ZJM-4 sample (Reprinted with permission from Ref. [61], Copyright 2014 Elsevier)

higher than that of beta-SDS (ca 30 %). The high silica utilization in the synthesis of ZJM-4 might be resulted from similar Si/Al ratios of the product with the starting gels.

1.3.6 MTT Zeolite

MTT zeolite family including ZSM-23, KZ-1, EU-13, ISI-6, and SSZ-32 possess a teardrop-shaped channel system with dimensions 0.52×0.45 nm [62–67]. The organic templates for MTT zeolites mainly includes pyrrolidine, diquaternary ammonium cations, isopropylamine, dimethylamine, and N,N-dimethylformamide (DMF) [62–69]. Recently, Wu et al. reported an organotemplate-free, seed-directed, and rapid synthesis of Al-rich MTT zeolite (Si/Al ratio at 20, denoted as ZJM-6) in the presence of ZSM-23 seeds [70]. Similar to ZJM-4 (TON-SDS), ZJM-6 exhibits a series of characteristic XRD peaks associated with MTT structure and rodlike crystal morphology (length at 1–2 μm and diameter at about 100 nm), in good agreement with those of ZSM-23 zeolites reported previously.

It is worth mentioning that the crystallization time of ZJM-6 is very short (5 h at 170 °C), compared with conventional ZSM-23 zeolite synthesized in the presence of organic templates. Generally, conventional hydrothermal synthesis of ZSM-23 zeolite in the presence of pyrrolidine template under rotation still takes 43 h at 180 °C (82 h at 160 °C) in the presence of 10 % seeds to achieve full crystallization [71]. Thus, it is believable that the rapid crystallization of ZJM-6 with MTT structure is reasonably attributed to the unique crystallization process. Generally, hydrothermal synthesis of zeolites includes induction and crystallization periods. However, there is nearly no inductive period in the crystallization of ZJM-6 (Fig. 1.6). In contrast, the inductive period for synthesizing ZSM-23 zeolite in the presence of DMF template is quite long, requiring at least 12–34 h. The addition of ZSM-23 seeds in the synthesis system containing DMF template significantly shortens the induction period, but it still takes 6–15 h. The presence of DMF template in the synthesis system induces the interaction with silica species, forming the zeolite nuclei. The formation of zeolite nuclei in the synthesis will delay the crystallization because the formation of zeolite nuclei takes some time (induction period). Very interestingly, it is observed that, under the same temperature, various samples (ZJM-6, ZSM-23, ZSM-23-S) have very similar crystallization time, but their inductive periods are quite different. These results suggest that rate-determined step for crystallization process of MTT zeolite is the induction period, which significantly reduces the crystallization time in the organotemplate-free and seed-directed synthesis, compared with conventional ZSM-23 synthesis.

ICP analysis shows that Si/Al ratio of ZJM-6 is about 20, which is much lower than conventional ZSM-23 zeolite (ca. 32–62), indicating that ZJM-6 is more Al sites than conventional ZSM-23. This feature would benefit the catalytic performance in acid-catalyzed reactions. The catalytic performance of MTT zeolites has been investigated in isomerization of *m*-xylene. ZJM-6 and ZSM-23 samples show

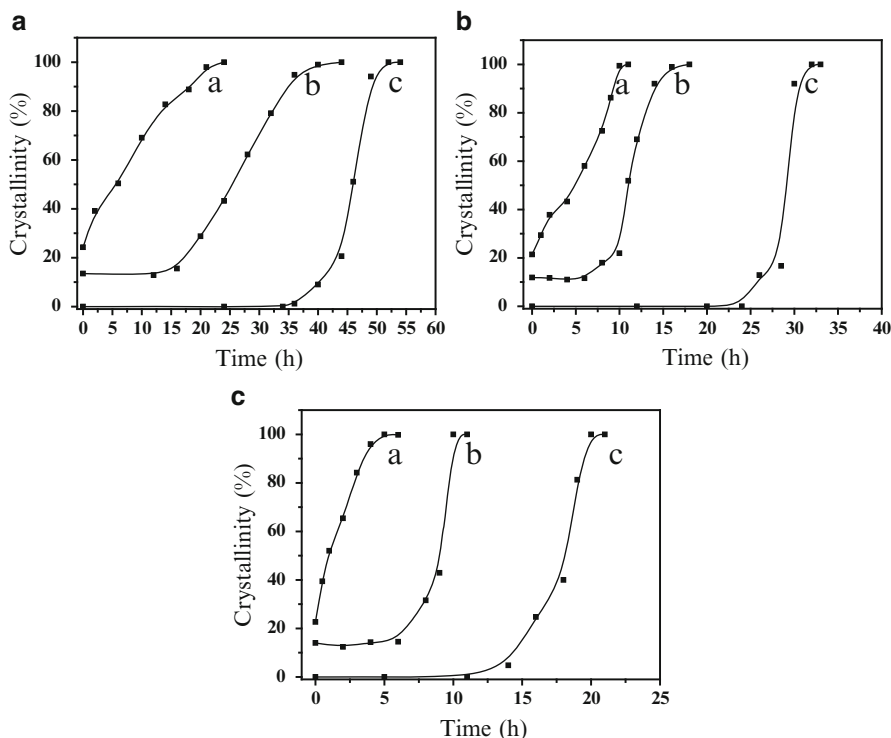


Fig. 1.6 The dependences of crystallinity on the crystallization time of (a) ZJM-6, (b) ZSM-23 synthesized in the presence of both DMF template and ZSM-23 seeds (ZSM-23-S), and (c) ZSM-23 synthesized in the presence of DMF template at (A) 150 °C, (B) 160 °C, and (C) 170 °C, respectively (Reprinted with permission from Ref. [70], Copyright 2014 Elsevier)

very high selectivity for *p*-xylene (ca. 86 %), but ZJM-6 exhibits higher conversions (10.4 %) than those (4.1–9.4 %) of ZSM-23 zeolites, which should be assigned to the contribution of more Al species in the framework of ZJM-6 (Fig. 1.7).

1.3.7 RTH Zeolite

RTH-type zeolite (e.g., borosilicate RUB-13, aluminosilicate SSZ-50) consisted of RTH cages with 8MR openings and two-dimensional channels with aperture size of 0.41×0.38 and 0.56×0.25 nm, parallel to the *a* and *c* axis, respectively [72, 73]. RTH-type zeolites have shown excellent catalytic properties in methanol-to-olefins (MTO) reaction. However, the synthesis of RUB-13 and SSZ-50 always requires using organic templates such as 1,2,2,6,6-pentamethylpiperidine (PMP), ethylenediamine (EDA), or N-ethyl-N-methyl-5,7,7-trimethylazoniumbicyclo[4.1.1]octane cation [72, 73]. Yokoi et al. have reported a successful synthesis of RTH-type zeolites (denoted as TTZ-1) without using organic templates by addition of calcined

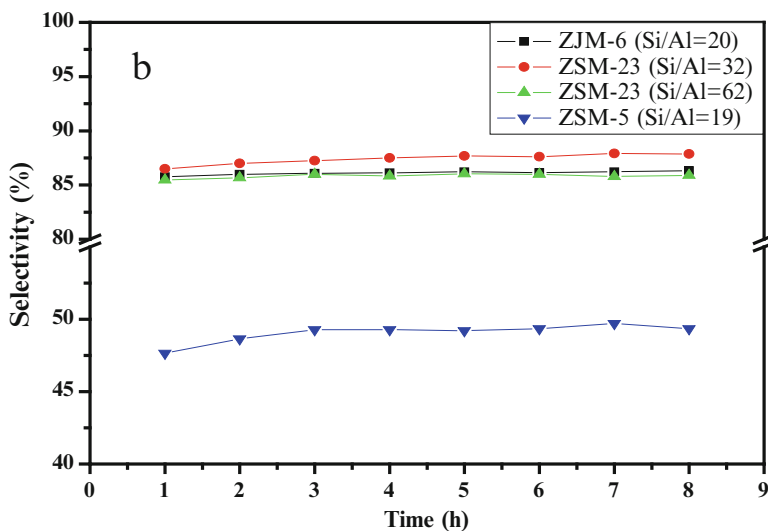


Fig. 1.7 Catalytic performance in isomerization of *m*-xylene to *p*-xylene over ZSM-5 (Si/Al=19), ZJM-6 (Si/Al=20), and ZSM-23 (Si/Al=62 and 32) catalysts as a function of time (Reprinted with permission from Ref. [70], Copyright 2014 Elsevier)

B-RUB-13 as seeds shortly after the discovery of SDS-beta [74]. Direct introduction of Al and Ga heteroatoms into the RTH framework during crystallization of B-TTZ-1 in the absence of organic templates had also been successfully performed. NMR spectra confirmed the tetrahedrally coordinated heteroatoms in the framework. The catalytic properties in MTO over these SDS-RTH zeolites have also been tested. The selectivity for propene was obviously higher than that of SAPO-34 and ZSM-5 zeolites, and the catalytic life of RTH-type zeolites was much longer, which should be assigned to their unique structure.

1.3.8 FER Zeolite

Ferrierite (FER) zeolite, with an anisotropic framework composed of two-dimensional straight channels including a 10MR channel (0.42×0.54 nm) along [001] direction and a 8MR channel (0.35×0.48 nm) along [010] direction, has been carefully studied, due to its excellent catalytic performance [75–78]. Notably, FER zeolite with low ratios of Si/Al could be synthesized in the absence of organic templates [79], but high-silica FER zeolite (ZSM-35) is always prepared in the presence of organic templates. Zhang et al. have demonstrated successful synthesis of high-silica FER zeolite (Si/Al at 14.5) from the introduction of RUB-37 zeolite (CDO structure) in the absence of organic templates (designated as ZJM-2) [80]. To understand the crystallization behavior and the role of RUB-37 zeolite seeds, the crystallization processes were carefully studied by XRD patterns. Before 12 h, small diffraction peaks of RUB-37 zeolite seeds were clearly observed at 9.6° and then

became smaller until they disappear after 24 h possibly because of the dissolution of RUB-37 seeds. At the same time, the diffraction peaks corresponding to the FER phase simultaneously appeared at 9.4° , suggesting the formation of FER zeolite. The intensity of the FER phase gradually increased, indicating the growth of FER zeolite crystal. Finally, highly crystallized FER-type zeolite was obtained after 72 h of heating. It is well known that the building units of FER and CDO are the same, and their difference is only a shift of layers in the horizontal direction. Therefore, it is reasonable to use the building units of RUB-37 zeolite to induce the crystallization of FER-type zeolite, which has been confirmed by UV-Raman spectroscopy of the samples.

1.3.9 LEV Zeolite

Levyne (LEV) zeolite is a typical small-pore zeolite, with relative smaller pore size ($3.6 \times 4.8 \text{ \AA}$) and low framework density ($15.2 \text{ T/1000 \AA}^3$), characterized by $4^6 6^5 8^3$ heptadecahedral cavity [81]. The natural levyne zeolite with typical composition at $\text{Ca}_9(\text{Al}_{18}\text{Si}_{36}\text{O}_{108}) \cdot 50\text{H}_2\text{O}$ was first discovered in 1825 [82]. Synthetic LEV zeolite named ZK-20 was synthesized from an aluminosilicate gel using 1-methyl-1-azonia-4-azabicyclo[2.2.2]octane cation as SDA [83]. Subsequently, other aluminosilicate LEV zeolites were successfully prepared by using a series of organic compounds as SDAs, including N-methylquinuclidinium cation, diethyldimethylammonium, N,N'-bis-dimethylpentanediyldiammonium, N,N-dimethylpiperidine chloride, and choline hydroxide [84–88]. Additionally, phosphate-based LEV-type zeolites were also obtained in the presence of tropone hydroxide, quinuclidine, and 2-methyl-cyclohexylamine; boron-containing LEV-type zeolites were reported by using organic compounds of 3-azabicyclo[3.2.2]nonane and quinuclidine as templates [89–92]. Recently, Zhang et al. reported organotemplate-free and seed-directed synthesis of LEV zeolite (SDS-LEV) in the presence of RUB-50 seeds with the aid of a small amount of alcohol [93]. In this synthesis, the alcohol plays an important role in the synthesis of highly pure SDS-LEV zeolite.

To understand the role of alcohol in the synthesis, various alcohols (e.g., methanol, ethanol, *n*-propanol, and *n*-butanol) were added into the starting aluminosilicate gels. Notably, without using any alcohol in the starting aluminosilicate gel, the product contained impurity phase of MOR zeolite in addition to the LEV product. In contrast, after addition of a small amount of alcohol in the synthesis, the samples showed pure phase of Na-LEV-SDS zeolite (Fig. 1.8). These results indicate that the alcohols strongly prevent the formation of MOR zeolite in this seed-directed synthesis. FTIR spectra and C/N/H elemental analysis confirmed that alcohol molecules did not exist in the micropores of SDS-LEV zeolites. The addition of alcohols could delay the nucleation of MOR zeolite, reducing crystallization rate of MOR zeolite. As a consequence, highly pure SDS-LEV zeolite could be obtained.

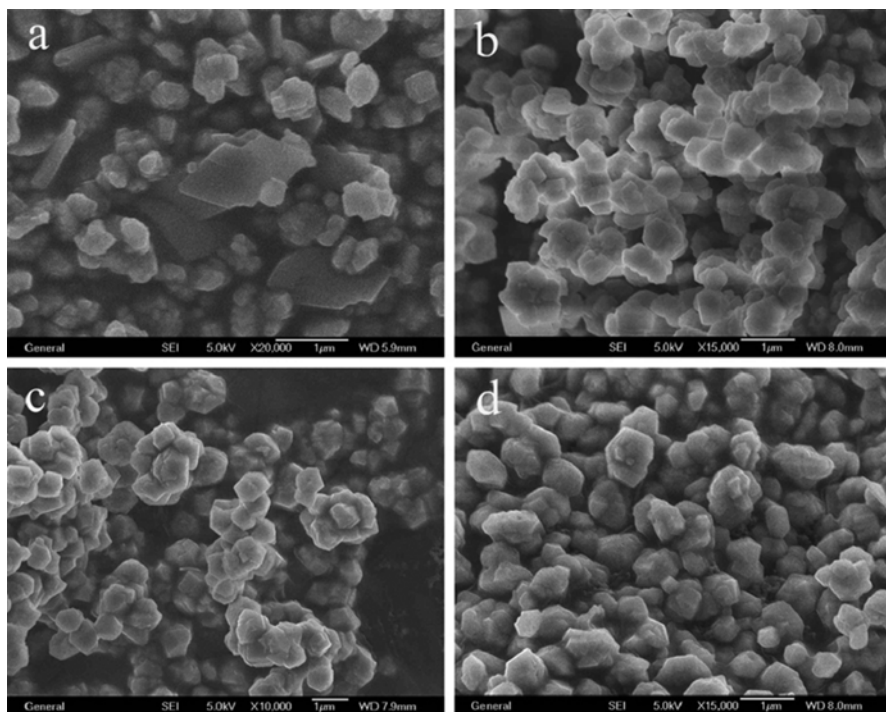


Fig. 1.8 SEM images of Na-LEV-SDS zeolites synthesized (a) in the absence of alcohol and in the presence of (b) methanol, (c) *n*-propanol, and (d) *n*-butanol, respectively (Reprinted with permission from Ref. [93], Copyright 2012 Elsevier)

1.3.10 SZR Zeolite

SUZ-4 zeolite (SZR) is an aluminosilicate zeolite with the three-dimensional topology consisting of 5-, 6-, 8-, and 10MRs, which was first reported using TEOH and quinuclidine as SDAs under rotation conditions [94]. Later, it was successfully synthesized in the presence of N,N,N,N,N-hexaethylpentanediammonium bromide ($\text{Et}_6\text{-diquat-5}$) [95]. Zhang et al. reported an organotemplate-free route for hydrothermally synthesizing zeolite SUZ-4 under static conditions by adding the calcined SUZ-4 seeds in the starting aluminosilicate gels [96]. To further understand the crystallization of SUZ-4 in the absence of organic templates, different crystallization stages of the crystallization process have been carefully studied by SEM and TEM techniques. The observations suggest that the addition of the seed crystals into the organotemplate-free crystallization mixture causes the deposition of amorphous particles formed by depletion of the heterogeneous hydrogels, and