

Preparation and Application Advances of MFI-Type Zeolite

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Abstract. MFI-type zeolites are crystalline aluminosilicate materials with the typical ten-membered-ring channel system formed by straight and sinusoidal pores. Their stable framework, tunable acidity and molecular-size channels make them useful in adsorption, separation and catalysis, especially when reaction selectivity depends on diffusion and pore confinement. This review summarizes recent progress in the preparation of MFI-type zeolites, including conventional hydrothermal routes, morphology regulation, solvent-free crystallization and rapid low-energy synthesis. The discussion also compares the advantages and remaining restrictions of these methods, such as template consumption, heat transfer during scale-up and control of acid sites. On this basis, representative catalytic applications in isomerization, alkylation, aromatization and biomass conversion are reviewed. By connecting synthesis conditions with pore structure and catalytic behavior, this paper provides a practical reference for the greener preparation and more targeted use of MFI zeolites.

Keywords: zeolite, MFI, synthesis, catalysis

1. Introduction

Zeolites are formed by $\text{SiO}_4/\text{AlO}_4$ tetrahedra connected through shared oxygen atoms. Their regular pore channels, high thermal stability and tunable acid sites are key features that set them apart from ordinary porous materials. After decades of research, over 250 types of zeolite framework structures have been reported. ZSM-5 and silicalite-1 with MFI topology are particularly representative. Their dual ten-membered ring channels combine size sieving and acid catalysis functions, so they hold high application value in petrochemical production, pharmaceutical intermediate preparation and fine chemical processes. As industrial processes raise higher requirements for energy consumption, selectivity and catalyst service life, how to prepare MFI-type zeolites in a more controllable way, and understand the roles of their channels and active sites in reactions, remains a topic worthy of further discussion.

From the preparation perspective, the conventional hydrothermal method is still the most widely used route in MFI-type zeolite research, but it is not without flaws. This method usually relies on organic silicon sources, organic ammonium structure-directing agents and long crystallization time, bringing prominent pressure from raw material cost, waste liquid treatment and template calcination. To solve these problems, recent studies have shifted to approaches like dry gel conversion, seed-

induced crystallization, mother liquor recycling and low-solvent systems. Meanwhile, structural regulation has moved beyond "achieving successful synthesis" toward "design for specific applications". For example, ultrathin MFI nanosheets help shorten diffusion paths, and hierarchical pore structures can ease mass transfer limitations in macromolecular reactions. These strategies all show that the relationship between synthesis methods and final performance is not a simple linear one.

Overall, MFI-type zeolites have developed from conventional hydrothermal synthesis to a stage where green synthesis, rapid crystallization and fine structural regulation advance side by side, showing steady advantages in catalysis and separation. Still, issues such as template dosage, crystal defects, large-scale production and post-modification stability restrict their further application. On this basis, this paper sorts out the main preparation routes and application progress of MFI-type zeolites in recent years, compares the characteristics and applicable scope of different methods, and discusses key directions for follow-up research with catalytic examples.

2. Synthesis methods of MFI-type zeolites

2.1. Hydrothermal synthesis

The hydrothermal method is the most classic route for zeolite synthesis, with a history of more than 80 years. A typical synthesis system for MFI-type zeolites generally includes a silicon source (such as silica sol, tetraethyl orthosilicate or sodium silicate), an aluminum source (such as aluminum sulfate, aluminum nitrate or aluminum isopropoxide), a template, a mineralizer (sodium hydroxide or potassium hydroxide) and water. Different raw material combinations affect gel polymerization, nucleation rate and crystal growth, thus changing the crystallinity and morphology of the product [1]. Even in the same system, tiny changes in component ratios may lead to differences in grain size, defect quantity and acid site distribution.

Among all influencing factors, the template often determines whether the MFI framework can form properly. Tetrapropylammonium hydroxide (TPAOH) is widely used to guide framework construction, as its cation size matches the MFI pore channels. Existing studies show [2] that when the TPAOH/SiO₂ molar ratio rises from 0.05 to 0.15, the zeolite crystal size decreases from 1.2–2.0 μm to 200–500 nm, while maintaining good crystallinity in this range. In recent years, organic-inorganic mixed alkali systems have also been applied to adjust the structure of ZSM-5. For instance, the TPAOH/NaOH system can alter the ratio of micropores to mesopores, reducing micropore quantity and increasing mesoporous structure [3]. Such regulation does not simply pursue smaller crystals, but serves to optimize subsequent diffusion and catalytic performance.

Besides templates, surfactants and external field conditions are often used to modify MFI crystal morphology. Additives like polyethylene glycol and cetyltrimethylammonium bromide can change the relative growth rate of different crystal faces, producing special morphologies such as sheet-like and fibrous shapes. These products usually have larger external surface area and shorter diffusion distance, performing better in reactions involving macromolecules or prone to carbon deposition. Microwave-assisted synthesis improves the crystallization process through uniform and fast heating, which shortens reaction time and improves product uniformity, offering another approach for controllable preparation of MFI zeolites.

2.2. Green synthesis routes

2.2.1. Solvent-free synthesis

Solvent-free synthesis is a widely noticed route for green preparation of MFI-type zeolites [4]. Compared with the conventional hydrothermal method, it removes a large amount of aqueous medium from the system and lets solid reactants take part in crystallization directly, so it has advantages in atom utilization, waste discharge and equipment footprint. Reports show that the solid-phase density of such systems can reach 80–95%, the crystallization temperature can drop to 120–150°C, and the reaction time is usually shortened to 12–24 hours, with efficiency about 2–3 times that of the conventional route.

The key of this method is not just "using less solvent", but the changed contact pattern between the template and silicon-aluminum species. Under low-water or anhydrous conditions, TPAOH forms local enrichment zones mainly through solid-phase diffusion, which promotes the directed assembly of the MFI framework. At present, the solvent-free route has been applied to prepare ZSM-5 and silicalite-1. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio can be adjusted by the dosage of aluminum source, obtaining a series of samples with the ratio ranging from 30 to infinity. In propane aromatization [5], the ZSM-5 catalyst prepared by the solvent-free method shows 15% higher initial activity and 30% longer service life than conventional samples, which is usually related to more reasonable acid distribution and lower defect density. It should be noted that this route has high requirements for the purity of raw materials such as SiO_2 (SiO_2 purity $\geq 99.9\%$), and solid-phase mixing and heat release control are more technically demanding. If local hot spots cannot be removed effectively, industrial scale-up will still face great difficulties.

2.2.2. Energy-efficient rapid crystallization

The energy-efficient rapid crystallization method focuses on shortening the time required for nucleation and crystal growth, rather than simply lowering the reaction temperature [6]. Microwave-assisted heating is a common measure. Compared with conventional hydrothermal synthesis, it can shorten crystallization time by 60–80% and reduce reaction temperature by 30–50°C [7]. Studies show that under 2.45 GHz microwave radiation, an initial gel system with TPAOH as template and a silicon-aluminum ratio of 50 can form the MFI crystal phase in about 30 minutes, and crystallization energy consumption drops to 40% of the conventional method [8]. This effect is associated with the dielectric heating of polar components such as H_2O and TPAOH by the microwave field, which makes silicon-aluminum species reach a state suitable for rearrangement and assembly faster [9].

Seed-induced crystallization further enhances the advantage of rapid crystallization. When pre-synthesized MFI nanoseeds (20–50 nm in size) are added to the system, the nucleation energy barrier can be reduced from 120 kJ/mol (conventional method) to 80 kJ/mol. Research indicates [10] that 5 wt% seeds can further cut crystallization time to 15 minutes and raise product crystallinity to over 95%. The mechanism can be explained as providing epitaxial growth interfaces and reducing crystal size dispersion caused by random nucleation. However, the source, dispersion state and batch consistency of seeds will directly affect the final product, which is a key point to control when applying this method to continuous production.

3. Catalytic applications of MFI-type zeolites

3.1. Shape-selective catalysis and isomerization

The catalytic selectivity of MFI-type zeolites first comes from their three-dimensional intersecting channels. The straight channel along the [010] direction is about 0.51×0.55 nm, and the sinusoidal channel along the [100] direction is about 0.53×0.56 nm. This pore size range is close to that of many small-molecule hydrocarbons, so it presents obvious shape-selective effects at the 0.5–0.6 nm scale [11]. In the petrochemical industry, isomerization of C4–C8 straight-chain alkanes is a typical application of MFI zeolites. Pore confinement and acid sites jointly determine reaction activity and product distribution.

In isomerization reactions, the strength, density and spatial position of acid sites all influence catalytic results. It is generally accepted that when the silicon-aluminum ratio is 30–50, MFI zeolites can provide necessary acid amount while reducing excessive cracking and carbon deposition to some extent. Steam treatment or chemical dealumination can further adjust acid site distribution. Norfleet et al. [12] used structure-directing agents to control the position of trivalent heteroatoms in the MFI framework, improving the catalyst's selectivity for 2-methylpentane. Crystal size also matters: 50–100 nm MFI crystals have higher apparent activity due to shorter diffusion paths. Yi et al. [13] modified MFI zeolite membranes via ozone activation, and found that the degree of surface hydroxylation affects proton migration efficiency, thus changing the distribution of isomerization products. Density functional theory calculations show [13] that when the distance between specific aluminum atoms in MFI channels is about 0.8–1.0 nm, it is more favorable for stabilizing the carbocation transition state.

In practical use, deactivation by carbon deposition is still an unavoidable problem for MFI isomerization catalysts. Fan Xiao et al. [14] optimized the pore orientation of MFI zeolite membranes to accelerate the diffusion and desorption of carbon deposition precursors, extending catalyst service life by 3–5 times. Another approach is to compound MFI with mesoporous materials to build a hierarchical pore structure for better macromolecular diffusion [15]. Zhu Shaolin et al. [15] synthesized microporous-macroporous MFI zeolites by an in-situ template method, and observed good performance in long-chain alkane isomerization. It can be seen that simply increasing acid sites cannot solve all problems; mass transfer paths and pore connectivity also determine whether the catalyst can run stably for a long time.

3.2. Alkylation and aromatization

MFI-type zeolites are also widely used in alkylation and aromatization reactions [16]. The former increases the value of target products by introducing alkyl groups into organic molecular skeletons, while the latter converts non-aromatic hydrocarbons into aromatic hydrocarbons, serving as an important way to upgrade light hydrocarbons [17]. The ten-membered ring intersecting channels (0.51–0.56 nm) of MFI can both restrict the configuration of reaction intermediates and inhibit the formation of some bulky by-products, providing a suitable shape-selective catalytic environment for these two types of reactions.

Experimental data show [18] that at 250°C and 3 MPa, ZSM-5 zeolite catalyzes phenylethylation with a conversion rate of 85% and ethylbenzene selectivity over 95%. The high selectivity mainly comes from the restriction of pore channels on transition states and diffusion paths, which reduces by-products such as polyethylbenzene [19]. With the addition of 0.5–1.0 wt% La or P, catalyst service life can be extended to 3–5 times that of conventional catalysts [19]. At 500°C, Ga/ZSM-5

catalyzes n-hexane aromatization with a conversion rate of 72% and aromatic selectivity above 65% [19]. Characterization results show that Ga species may exist in the form of $[\text{GaO}]^+$ inside the channels, and form synergistic centers with protonic acid sites. Alkanes are first dehydrogenated to form olefin intermediates, which then go through cyclization and further dehydrogenation to produce aromatics. The silicon-aluminum ratio has a remarkable impact on product distribution: a higher ratio usually favors the formation of target aromatics such as benzene, toluene and xylene, but too low acid amount may limit conversion rate, so a balance between activity and selectivity is needed.

3.3. Catalytic biomass conversion

In environmental catalysis and energy conversion research, catalytic biomass conversion opens up new application scenarios for MFI-type zeolites. Studies show [20] that the three-dimensional intersecting channels of ZSM-5 facilitate the diffusion and secondary conversion of some macromolecular intermediates, giving it good deoxygenation performance in biomass pyrolysis oil upgrading. By adjusting the silicon-aluminum ratio, the number and strength of acid sites can be changed, achieving a deoxygenation efficiency of up to 85% at 350–450°C.

Metal modification is a common method to improve the biomass conversion performance of MFI zeolites. Introducing metals such as Ga and Zn (loading 1–5 wt%) via ion exchange can enhance the catalyst's hydrodeoxygenation activity for furan compounds. Experimental data show [21] that when Ga/ZSM-5 is used for furfural hydrogenation, the conversion rate reaches 92% and 2-methylfuran selectivity is 78%. The confinement effect of MFI channels can also stabilize metal particles to some extent and reduce sintering risk, so that the catalyst retains over 80% of its initial activity after 100 hours of continuous reaction. Theoretical calculations further indicate that the synergy between metal sites and acid sites can lower the reaction energy barrier, allowing hydrodeoxygenation to proceed under relatively mild conditions.

For carbohydrate conversion, the pore confinement of MFI zeolites also affects product trends. When glucose reacts on H-ZSM-5, the 0.51–0.56 nm microporous structure favors the formation of C2–C4 olefins. If hierarchical pores are introduced, the residence time of intermediates in micropores can be reduced and target product selectivity improved. Studies show [22] that composite zeolites with lower acid content can inhibit the further degradation of glucose, thus improving glucose selectivity and yield. This result suggests that in biomass conversion, stronger acidity is not always better; properly reducing acid amount and improving the diffusion environment are usually more helpful for controlling side reactions.

4. Conclusion

This paper summarizes the research progress of MFI-type zeolites in preparation methods and catalytic applications. Conventional hydrothermal synthesis still has the advantages of mature system and wide applicability; solvent-free synthesis and low-energy rapid crystallization stand out in reducing solvent consumption, shortening crystallization time and improving raw material utilization. Meanwhile, morphology regulation, seed-induced crystallization and hierarchical pore construction have gradually become important bridges between synthesis conditions and practical performance. In terms of application, the pore structure and acid sites of MFI zeolites enable them to serve reactions including shape-selective catalysis, isomerization, alkylation, aromatization and biomass conversion.

However, the further application of MFI-type zeolites is still limited by several factors. The problems of template cost and waste discharge in conventional routes have not been fully solved, and green synthesis still needs more verification in raw material compatibility, heat transfer control and industrial scale-up. In catalytic processes, carbon deposition deactivation, limited macromolecular mass transfer and uneven active site distribution will also weaken long-term stability. Future research can advance in three directions: first, develop low-consumption synthesis routes such as template-free or bio-based template systems to reduce environmental burden in scale-up; second, combine hierarchical pore structure and precise metal heteroatom modification to improve diffusion performance, acid distribution and carbon deposition resistance; third, use in-situ characterization and multi-scale simulation to reveal the actual interaction between framework sites, guest molecules and reaction intermediates. Only by combining synthesis sustainability, structural controllability and reaction mechanism research can MFI-type zeolites better move toward functional integration and green processing.

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