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Controlled and rapid growth of MTT zeolite crystals with low-aspect-ratio in a microwave reactor

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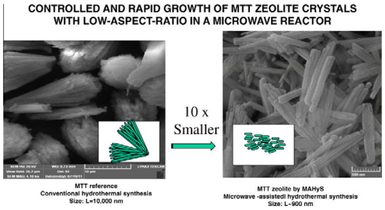
HIGHLIGHTS

- Microwave-assisted synthesis rapidly produced MTT zeolites.
- Secondary growth of MTT crystals further reduced synthesis time to 6 h.
- Desilication improved pore volume of calcined MTT.
- MTT zeolites were applied in *n*-hexane cracking and demonstrated better selectivity to propylene.

GRAPHICAL ABSTRACT



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ABSTRACT

The nucleation and growth of MTT zeolite, an important 10-membered ring (10 MR) zeolite, was controlled by a microwave-assisted hydrothermal synthesis. The effect of irradiation time (12,18, and 24 h), seed-assisted synthesis with 1 wt.% seeds for 6 h and desilication under microwave irradiation on crystallinity and porosity were investigated. Under microwave-assisted synthesis, uniform crystal size, with lower crystal aspect-ratio and suppressed phase-impurity has been obtained. The tendency of column-like crystal to form bundle of columns was reduced significantly. Seeded growth further reduced synthesis time to 6 h. Post-synthetic treatment was used to obtain larger pore volume of MTT zeolites. Some of the protonated MTT samples were tested in *n*-hexane cracking as model reaction. Characterization techniques such as XRD, FE-SEM, N_2 adsorption–desorption, ^{27}Al MAS NMR and NH_3-TPD have been carried out to obtain insight in the physico-chemical properties of zeolite catalysts.

1. Introduction

Zeolites as the most widely used catalytic materials in oil refining and petrochemicals typically have micropores less than 1 nm which cause mass-transfer limitation [1]. Apart from the mass-transfer limitation, some zeolites with one-dimensional (1D) pore system have rod-like morphology where the pore-mouth can be blocked by coke deposition quickly [2]. Efficient mass-transfer properties of zeolite catalysts can be obtained by reducing the crystals size of zeolites to sub-micrometer and even to nanometer range. This mechanism of size reduction is aimed at reducing the diffusion path length of reactant molecules into the active sites in zeolite crystals. The small dimensions of zeolite crystals were expected to be more robust to prevent deactivation as longer contact time in micron-size zeolites may lead to production of unwanted products (cokes) [1,3–9]. The nanosized zeolites also provided abundantly available active sites as they have larger external surface area compared with the conventional ones.

Zeolites with the MTT topology such as ZSM-23 have medium pore silica which composed of non-intersecting 5-, 6-, and 10-membered-rings (MR) channels [10–18]. ZSM-23 was reported to be potential catalyst for skeletal isomerization of paraffin, selective catalytic cracking and related shape-selectivity reactions [19–21]. The typical synthesis time in hydrothermal synthesis is between

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66 and 72 h with small synthesis window [10]. Window of acidity (Si/Al ratio) range of MTT zeolite is believed to be small. However, the higher Si/Al value will be targeted in this work. The unique properties of H-ZSM-23 zeolite correspond with its one-dimensional non-interacting 10 member-ring (10-MR) structures with pore channels of 0.46 × 0.57 nm [14]. The blockage of the zeolite pore mouth by the coke species might be the reason of the relatively rapid deactivation of H-ZSM-23 [2]. One common method to improve porosity such as desilication provided detrimental effects to zeolite morphology, blockage of microporosity, and uncontrolled Al removal [22]. Therefore, before desilication, the rapid synthesis by using microwave was optimized to obtain better crystallinity, reduced the crystal size as well as the crystal aspect-ratio (length per width of crystal).

ZSM-23 can be synthesized by using different organic structure directing agents (OSDA) such as pyrolidine [10,13], isopropyl amine (IPA) [10,11] and a range of organic amines and quaternary ammonium templates [12]. Rollmann and co-workers extended the OSDAs which can be applied in MTT synthesis [12]. By considering simple preparation method and cheaper OSDA, which are crucial for industrial scale, in this work, MTT zeolite were synthesized merely using IPA as OSDA. As the scope of this study is limited to one simple and cheap template (IPA), other more complex and expensive quaternary ammonium templates were not covered.

The objective of this study was to control the nucleation and growth of MTT zeolites by using microwave-assisted hydrothermal synthesis. Rapid fabrication, smaller crystal size and narrow crystal size distribution were targeted by optimizing the synthesis parameter, microwave reactor parameter and secondary growth by using seeds. The high crystal-aspect-ratio (length/width) of ZSM-23, above 400 was reported by Möller and Bein [10]. This high aspect-ratio induces fast deactivation and this rod-like morphology can be easily poisoned by cokes at the pore-mouth. Therefore, development of MTT crystals with shorter crystal with low aspect-ratio to reduce diffusion constraint is aimed. The other challenge in the ZSM-23 zeolite is the small synthesis window and the presence of impurity phases such as cristobalite and dodecasil [10,13]. We optimized the synthesis protocols of sub-micrometer of MTT zeolite under microwave-assisted hydrothermal synthesis (MAHyS) using isopropyl amine as OSDA.

Microwave-assisted synthesis has found many applications in synthetic chemistry to shorten synthesis time, to produce narrow size distribution and to obtain different morphologies [23–33]. Synthesis of a range of nanozeolites by using microwave-assisted hydrothermal synthesis (MAHyS) was also reported (e.g., MFI, BEA, LTL, and LTA) with controlled crystal size and shape.

In a microwave reactor, the temperature can be raised quickly compared with conventional heating. The heat can be transferred to the aqueous species rapidly and efficiently [32]. With this high heating rate, the tendency to produce by-product can be suppressed. Meanwhile in conventional autoclave reactor, the heat is transferred consecutively from heating source (oven) to the PTFE-lined autoclave then finally to the water medium. In this study, the rapid heating is expected to accelerate nucleation and to reduce impurity phases.

2. Experimental

Rapid synthesis of MTT zeolites has been carried out by using microwave reactor. Modification of the crystal aspect ratio was initiated by optimization of synthesis parameters (viz. synthesis time). The applicability of seed-assisted synthesis and post-treatment were also investigated. Zeolites were synthesized in static mode (without stirring) and dynamic mode (with stirring or rotation).

2.1. Microwave-assisted hydrothermal synthesis (MAHyS) of ZSM-23 (MTT)

2.1.1. Synthesis of MTT zeolites under microwave irradiation

Controlled nucleation and crystallization of zeolites were optimized in microwave reactor. The synthesis was performed with colloidal silica (40 wt.%), aluminum sulfate ($Al_2(SO_4)_3$. 18 H_2O), isopropyl amine (IPA), Sodium hydroxide (NaOH) and de-ionized water (H_2O). The molar ratio of the synthesis solution was: 1 SiO_2:0.006 Al_2O_3:0.125 NaOH:1.68 isopropyl amine: 45 H_2O. A typical solution gel was prepared by dissolving 0.31 g of NaOH in 43.96 g of de-ionized water, then adding 0.25 g of $Al_2(SO_4)_3$.18 H_2O to form an aluminate solution. After vigorous stirring for 5 min, 6.17 g IPA was added with a drop-wise manner to form a clear solution. Finally, 9.31 g colloidal silica (40 wt.%) was added and the mixture was stirred vigorously before being transferred to a PTFE vessel. For each synthesis attempts, one reaction vessel was heated. The volume of the gel in the PTFE vessel was 60 g. The colloidal silica (Snowtex-40, ST-40, 40 wt.% of SiO_2 and 0.5 wt.% Na_2O) was kindly provided by Nissan Chemicals. SiO_2 particle size is in the range of 10–20 nm.

Solution gel prepared was heated at 453 K (180 °C) in a microwave reactor (MicroSYNTH, Milestone, 800 W) with different synthesis time from 12 to 24 h under constant stirring speed of 300 rpm. The as-synthesized zeolites were centrifuged and washed then dried at 393 K (120 °C) for 12 h. The OSDA was removed by calcination at 823 K (550 °C) for 12 h under a flow of air with the heating rate of 1 K/min. The calcined zeolites (Na-ZSM-23) were ion-exchanged and calcined again to obtain H-ZSM-23. All ZSM-23 (MTT) samples are referred according to the synthesis time, seeding growth and desilication. For examples, sample obtained by microwave-assisted synthesis (M) at 180 °C for 18 h irradiation time is referred as MTT-M-180-18 h. The sample with prolonged 72 h aging time is designated with A72 h.

2.1.2. MTT seeds

The zeolite seeds were prepared from calcined MTT-M-180-18 h. The weight percentage of the seeds was 1 wt.% (of the total synthesis mixture) or 16 wt.% relative to the content of silica source.

2.1.3. Ion Exchange under microwave irradiation

The protonated ZSM-23 (H-ZSM-23) samples were obtained by ion-exchange under microwave irradiation (250 W). Each 1 g of calcined Na-ZSM-23 was treated with 20 ml of 2 M NH_4NO_3 according to the two steps:

(i) Sample was heated from room temperature to 85 °C with ramping rate of 30 °C/min, and then dwelled at 85 °C for 10 min followed by cooling step, then catalyst was separated from main solution by centrifugation at 4000 rpm.
(ii) Replacing fresh NH_4NO_3 solution, then ramping in 10 min from room temperature to reach 150 °C and sample was cooled down to 20 °C. Then, the NH_4-ZSM-23 zeolites were washed several times with 2 propanol. Similar method in ion-exchange under microwave irradiation was reported elsewhere [34]. The NH_4-ZSM-23 was calcined at 550 °C for 12 h.

2.1.4. Desilication to obtain protonated H-ZSM-23 samples

The H-ZSM-23 (3330 mg) was treated in 10 ml of 0.2 M of NaOH [22,35] under microwave irradiation. Temperature was increased from room temperature, ramped in 2 min to reach 85 °C, then dwelled at 85 °C for 10 min. Afterwards, sample was cooled down to room temperature by natural convection and washed to bring