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Microwave-assisted hydrothermal synthesis of mordenite zeolite: Optimization of synthesis parameters

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ABSTRACT

Sustainable industrial processes demand rapid and cost-effective synthesis procedures of zeolites. Herein, we report the synthesis zone of pure mordenite (MOR) zeolite under microwave irradiations. Phase purity, crystallinity, and morphology were carefully studied through optimization of synthesis parameters such as crystallization time, aging time and Si/Al ratio. Without the seeds, the organic-structure directing agent (OSDA)-free synthesis of pure MOR crystals was achieved in the shortest time of 12 h. Moreover, the addition of two different OSDAs, namely o-phenylenediamine (OPDA) and tetramethylammonium hydroxide (TEAOH), decreases the crystallization time up to 6 h with the same gel composition. Whereas, minimum crystallization time through conventional heating was 24 h with an OSDA and 48 h without the template. Rectangular and spherical shaped crystals with low aspect ratio were formed under this condition. The same optimized condition was used with different gel compositions (i.e. Si/Al of 15, 25, 50) to crystallize pure MOR. Also, effect of alkalinity was investigated at different Si/Al ratios.

1. Introduction

The demand of zeolite as a crystalline aluminosilicate material has exponentially increased for last few years. Industrial applications of zeolites such as petroleum refining, petrochemicals, and water treatment, stimulate the scientific research for the cost-effective production of zeolites [1,2]. Although many zeolite frameworks such as MFI, MTW, MTT, TON, and MOR have been synthesized successfully at laboratory scale with different morphologies and properties [3–6]. Sustainable production at an industrial level always remains a problem because of complex and energy consuming synthesis methods of zeolites. Complexity and cost of synthesis processes increase with the addition of organic structure directing agent (OSDA) and mode of heating respectively. Herein, we report the optimization of synthesis parameters of mordenite (MOR) under microwave irradiation without seeds, templates, and organic solvents. Seeds and the OSDA were used for better crystallization and control morphology [7]. However, careful preparation of gel mixture and adjusting parameters with controlled heating technique can achieve same required results, without OSDA. Energy consumption can also be reduced remarkably as microwave irradiation decreases the synthesis time to less than a quarter of the time required in conventional synthesis with the classical heating method.

Mordenite zeolite has unique significance over other 12-membered ring zeolites i.e. FAU and Beta because of its one-dimensional pore structure and high activity. These properties make MOR important in many industrial applications such as hydroisomerization, alkylation, dewaxing, reforming and cracking reactions [8–10]. Mordenite has chemical formula $Na_8(H_2O)_{24}[Si_{40}Al_8O_{96}]$ with parallel 12-membered ring (MR) channels (0.67 × 0.70 nm) along the c-axis direction and these channels are interconnected by 8-MR (0.34 × 0.48 nm) channels along b-axis [11].

Previously, many researchers synthesized MOR with different morphologies using OSDAs/templates, seeds or organic solvents. Conventional heating time of micro-sized MOR was reported minimum for 48 h while nano-zeolite was crystallized above 72 h using OSDA [12,13]. Microwave-assisted hydrothermal synthesis (MAHyS) of ZSM-23 (MTT), ZSM-12 (MTW), ZSM-22 (TON), and EU-1 (EUO) was reported previously by our group and it was confirmed that crystallization time under microwave irradiation decreases

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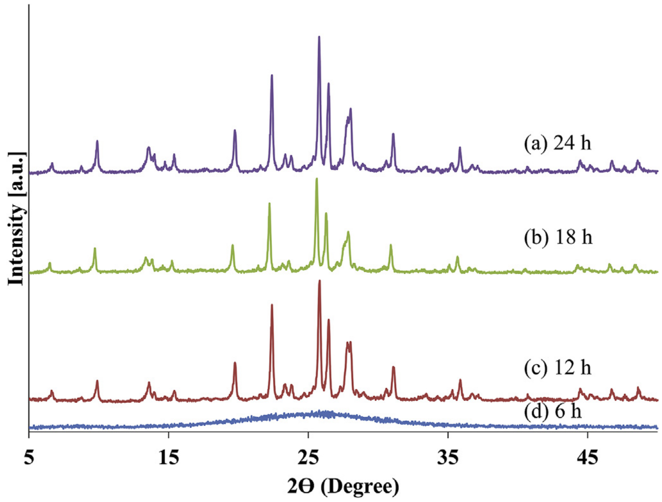

Fig. 1. XRD patterns of MOR samples at fixed Si/Al ratio of 15 at 180 °C synthesized with microwave-assisted hydrothermal synthesis (MAHyS) with different crystallization times of (a) 24 h, (b) 18 h, (c) 12 h, (d) 6 h.

significantly [6,14,15]. Controlled size distribution, less synthesis time and shorter crystal size can easily be achieved through MAHyS [15]. MAHyS of extra large MOR crystals was previously reported by Gang et al. in crystallization time of 6 h with 20 μm crystal size [16].

In this study, synthesis zone of MOR is studied by optimizing different parameters such as crystallization time, aging time, Si/Al ratio. Moreover, MAHyS is compared with conventional heating synthesis. It was observed that templates further reduced the crystallization time in both heating modes and the presence of OSDA also increases the crystallization rate and reduces crystal growth. Hence, two different templates namely o-phenylenediamine (OPDA) and tetramethylammonium hydroxide (TEAOH) were introduced in gel mixture. Morphology, crystallinity and phase purity of MOR was studied in detail and it was observed that rectangular-shaped and spherical sub-micron crystals were obtained after optimizing above mentioned parameters.

2. Experimental

Conventional and microwave hydrothermal heating techniques were used to synthesize MOR of different Si/Al ratios. PTFE-lined stainless steel autoclaves were used for conventional hydrothermal synthesis while for MAHyS, microwave reactor (MycroSYNTH, Microwave Lab Station, MILESTONE, 800 W) was used. Silica gel (Sigma-Aldrich grade 7734 pore size 60 Å, 70–230 mesh) and sodium aluminate (13,404, Sigma-Aldrich) were used as silica and aluminum source respectively. Alkalinity was controlled using sodium hydroxide (NaOH) pellets.

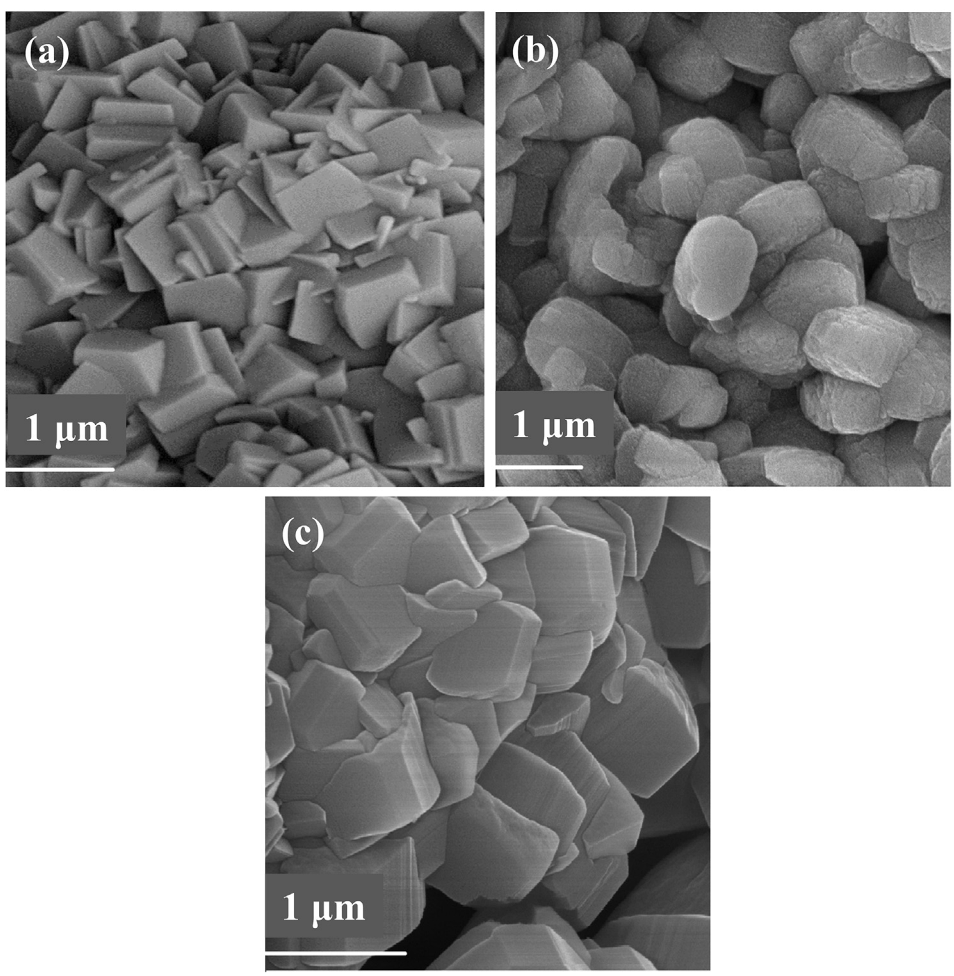

Fig. 2. SEM micrographs of MOR samples synthesized with MAHyS at fixed Si/Al ratio of 15 at 180 °C with different crystallization times of (a) 12 h (b) 18 h (c) 24 h.