A New Synthesis Route for MWW Analogues Using Octyltrimethylammonium Cations as Structure-directing Agents under Alkali-free Conditions

Na Liu, Yueming Liu, Chaochao Yue, Li Chen, Haihong Wu, Xiaohong Li, Mingyuan He, and Peng Wu*
Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry,
East China Normal University, North Zhongshan Rd. 3663, Shanghai 200062, P. R. China

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Crystalline zeolites with the MWW topology are readily synthesized under hydrothermal conditions using long-chain quaternary ammonium cation like octyltrimethylammonium from high silica gels free of alkali metal ions, which implies a new route for preparing MWW-type metallosilicates.

MWW-type zeolite, aluminosilicate well known as MCM-22, is one of the most important and fascinating zeolites from the viewpoint of basic researches and industrial applications. Originated from a lamellar precursor, the MWW structure consists of intralayer 10-membered ring (MR) channels, independent interlayer 10-MR channels containing 12-MR supercages of 0.71 × 1.82-nm dimension and exterior 12-MR side cups.[1] This unique pore structure has allowed MCM-22 to find industrial application to the liquid-phase processes of selective benzene alkylation to produce ethylbenzene and cumene. On the other hand, MWW-type titanosilicate, Ti-MWW, is also shown to be a promising catalyst in the selective oxidation of a variety of organic chemicals with H_2O_2 as an oxidant.[2] Thus, to develop new synthesis methods for MWW zeolites has been of great interests last decades.

In addition to MCM-22,[1] manly MWW analogues such as PSH-3,[3] SSZ-25,[4] ERB-1,[5] ITQ-1,[6] and ITQ-30[7] have been reported so far in the forms of aluminosilicate, borosilicate as well as pure silica. All these materials are commonly synthesized using cyclic or polycyclic structure-directing agents (SDA) such as hexamethyleneimine (HMI), piperidine (PI), 1-trimethylammonioadamantane and *N*(16)-methylsparteinium. The organic additives with relatively bulky molecular size seemly favor to occupy the interlayer space of MWW sheets, which is presumably advantageous to stabilize the structure in the process of crystallization. Nevertheless, to our knowledge, the only exception using linear-type diquaternary ammonium cations is reported recently.[8] Deliberately designed *N*,*N*,*N*,*N*′,*N*′,*N*′-hexamethyl-1,5-pentanediammonium ion serves as a useful SDA in the synthesis of MWW aluminosilicate with the cooperative effect of alkali cataions.

With respect to the selective redox catalysts of metallosilicates containing highly dispersed tetrahedral transition-metal ions, their hydrothermal synthesis prefers a preparation system without alkali ions in order to avoid condensation of metal ions into oxides. However, the crystallization of most MWW analogues shown above requires the use of alkali ions as mineralizing agents. Although siliceous ITQ-1 and ERB-1 borosilicates are readily synthesized without using Na^+ or K^+ sources,[5,6] the incorporation of transition-metal ions into the former is still impossible whereas the incorporation of Ti into the latter is achieved only in the presence of an excess of crystallization-supporting agent like boric acid at a Si/B ratio of 0.75.[2] It is still challenging to develop new alternative routes to synthesize MWW metallosilicates more economically and effectively.

We have found that a commercially available linear quaternary ammonium, octyltrimethylammonium (OCTMA), was capable of directing the formation of MWW borosilicate in the absence of alkali cations. Furthermore, Ti-MWW was synthesized successfully using this SDA from the gel containing greatly reduced boric acid in comparison to the synthesis with PI or HMI.

A typical synthesis of MWW borosilicate was carried out by dissolving boric acid into an aqueous solution of OCTMA hydroxide which was prepared through reacting OCTMA bromide (TCI) with Ag_2O instead of anion exchange in order to avoid contamination by alkali ions like Na^+ in anion-exchange resin. Fumed silica (Cab-o-sil M5) was added into above clear solution to obtain a homogeneous gel with a molar composition of $1.0SiO_2:xB_2O_3:0.3OCTMA:15H_2O$, where x was varied in the range of 0.01–0.25. The gel was then transferred into Teflon-lined autoclaves and heated at 423 K under rotation (100 rpm) for 10 days. The product was collected by filtration, washed with deionized water and further calcined in air at 823 K for 6 h to remove organic species occluded.

The as-synthesized borosilicates showed XRD patterns in agreement with that of the lamellar precursor of MWW topology, which featured the 001 and 002 diffractions due to layered structure as well as broad peaks in high angle region (Figures 1a–1c). The *d* spacing of 001 plane was ca. 2.7 nm, which is very similar to the MWW zeolites synthesized by conventional mehods. A direct calcination caused interlayer dehydroxylation, which made the 001 and 002 diffractions almost disappear (Figure 1d). This phenomenon was consistent with that reported on various MWW analogues. The products with comparable crystallinity were prepared at Si/B ratios of

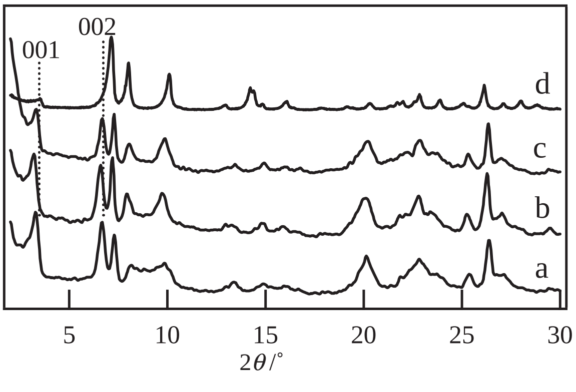

Figure 1. XRD patterns of MWW borosilicate as-synthesized using OCTMA from the gel at Si/B of 5 (a), 10 (b), 20 (c), and calcined sample of Si/B = 10 (d).

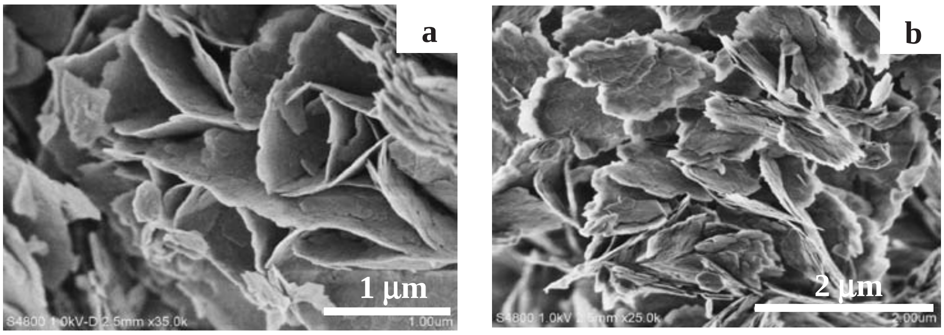

Figure 2. SEM images of as-synthesized MWW borosilicate (a) and Ti-MWW (b) synthesized using OCTMA.

Table 1. The catalytic properties of Ti-MWW synthesized with OCTMA[a]

No.	SDA	Si/Ti	1-Hexene		H_2O_2/%	
			Conv./%	TON[b]	Conv.	Eff.
1	OCTMA	95	16.5	176	19.2	86
2	OCTMA	132	14.6	215	17.5	84
3[c]	PI	72	22.4	198	25.6	88

[a] Reaction condition: cat., 0.05 g; 1-hexene and H_2O_2 (30 wt %), 10 mmol; MeCN solvent, 10 mL; temp., 333 K; time 2 h. [b] Turnover number in mol (mol-Ti)$^{-1}$. [c] Synthesized according to ref 2.

2–20. The crystallinity turned to be lower at Si/B of 30, while only amorphous phase was obtained at Si/B > 40 (not shown). With PI or HMI as a SDA, the MWW borosilicate can be synthesized only in the presence of an excess of boric acid over silica when Na^+ or K^+ is absent,[2] and at least at Si/B < 6 even with the cooperation of alkali ions.[9] The present synthesitic system using OCTMA is obviously a great advantage to produce MWW borosilicates of higher silica.

N_2 adsorption measurement showed that the specific surface areas of borosilicates synthesized with OCTMA at Si/B ratios of 2–20 were in the range of 430–475 m^2 g^{-1}, which is of the same order of conventional MWW analogues. SEM micrographs of the present samples showed that all crystals are agglomerates consisting of thin hexagonal plates of approximately 0.3 µm in length and 0.05 µm in thickness. This was extremely similar to the materials synthesized with PI.[2]

ICP analyses revealed that the Si/B ratio was around 11–13 for the products synthesized at Si/B of 2–10, while it was almost the same as the Si/B ratio of gel in the range of 15–20, indicating an effective boron incorporation. Both TG and CHN elemental analyses indicated that the samples synthesized at Si/B of 10 contained ca. 18 wt % of organic species with a C/N ratio of 11.3 that was close to the value of OCTMA (11). When the as-synthesized sample was refluxed in 2 M HNO_3 for 20 h, the 001 and 002 diffractions in XRD pattern disappeared almost to form a 3D MWW structure as a result of preferential removal of organics occluded between the layers. The acid-treated but uncalcined sample had a surface area of 350 m^2 g^{-1} but still contained about 8 wt % of SDA probably located in intralayer 10-MR channels. These results suggest that linear and flexible OCTMA with a relatively mall girth is not only capable of occupying the intralayer sinusoidal 10-MR channels (0.41×0.51 nm^2) but also serves as an intercalating agent or spacer to construct the interlayer structure. This kind of cooperative structure-directing effect would make OCTMA, the shape and size of which are distinctly different from those of cyclic amines adopted in conventional synthesis, possibly initiate a phase-selective nucleation and subsequently direct the crystal growth to MWW structure in crystallization process.

The system using OCTMA allowed the hydrothermal synthesis of Ti-MWW at Si/B of 10 while the Si/Ti ratio of the gel was varied in the range of 50–100. Higher Ti contents corresponding to Si/Ti of 20–30, however, led to amorphous or even mesophase owing to surfactant effect of OCTMA. Notice the fact that the crystallization of Ti-MWW requires an excess of boron over silicon and is totally impossible at such a less boron content like Si/B = 10 when using PI or HMI as SDA,[2] the present method opens a more efficient synthesis way for Ti-MWW. OCTMA-directed Ti-MWW had very similar SEM images almost free of amorphous phase (Figure 2b). After selective removal of extraframework Ti species located on exterior surface of the layers together with a partial of boron by the acid treatment on as-synthesized samples, Ti-MWW catalyst containing essentially tetrahedral Ti species was obtained. As for TON and H_2O_2 utilization efficiency in the epoxidation of 1-hexene (Table 1), they were comparably active and efficient to the Ti-MWW catalyst prepared previously using PI.

As a conclusion, a new synthesis route for MWW metallosilicates has been developed by using linear and flexible OCTMA as a SDA. This method allows the synthesis to proceed under alkali-free conditions and with greatly reduced crystallization-supporting agent like boric acid.

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10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

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