# Microporous and Mesoporous Materials 195 (2014) 205-215

Contents lists available at ScienceDirect





journal homepage: www.elsevier.com/locate/micromeso

# Synthesis and characterization of zeolites MTT and MFI, with controlled morphologies using mixed structure directing agents



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## ARTICLE INFO

Article history: Received 29 July 2013 Received in revised form 15 April 2014 Accepted 19 April 2014 Available online 29 April 2014

*Keywords:* MFI MTT Structure directing agent Morphology Carbon dioxide adsorption

# ABSTRACT

Morphologies of zeolites MFI and MTT were controlled using mixed structure directing agents (SDA),  $N^1, N^1, N^3, N^3$ -tetramethylpropane-1,3-diamine (TMPD) and  $N^1, N^1, N^3, N^3, 2, 2$ -hexamethylpropane-1,3-diamine (HMPD) during hydrothermal synthesis. The structure directing agents, TMPD and HMPD, led to the formation of zeolites MTT and MFI, respectively, because of the linear and branched molecular structure of each SDA. The location or the conformation of the SDA in the zeolite pore was investigated by combining the structure determination from synchrotron X-ray powder diffraction with the global optimization method. The presence of mixed SDAs in the hydrothermal synthesis significantly affected the morphologies of the zeolite. The one dimensional zeolite MTT showed the morphology of the three dimensional zeolite, MFI, when the ratio of the mixed SDA was changed.

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# 1. Introduction

The search for zeolites with unique physicochemical properties has been a continuing research subject because of the corresponding practical importance in the field of adsorption and catalysis [1]. For microporous zeolites, diffusion is the major controlling factor for adsorption and catalysis abilities [2]. The diffusion of molecules into the zeolite can be affected by the nature of the pore, and also by the crystalline properties [3]. Recent interest in the preparation of hierarchical zeolitic material reflects the above mentioned facts [4]. Hierarchical zeolitic material can accelerate catalytic reactions without the deterioration of catalytic activity, where both meso and microporous structures were integrated into crystalline particles using novel structure directing agents (SDA) [5,6].

The morphology of the zeolite has also been a very important factor for determination of the corresponding catalytic activity, and also the adsorption properties [2,3,6–8]. Making smaller spherical crystals, rather than layer and needle-shaped crystals, can be advantageous for the corresponding catalysis, because all active sites can be readily exposed to the reactant. Therefore, control of the zeolite morphology is important when the hydrothermal synthetic approach is utilized.

Zeolite MFI, ZSM-5, the most well-known and industrially important polycrystalline aluminosilicates, can be synthesized using various SDAs and tetrapropylammonium hydroxide [1]. Zeolite MTT, ZSM-23, that was synthesized in the presence of pyrrolidine or isopropylamine has similar structural features to that of zeolite MFI, including secondary building units, ring size and framework density (FD) [2,3,9–11]. However, zeolite MFI consists of a three-dimensional structure, while zeolite MTT consists of a one-dimensional, non-circular channel. This MTT zeolite can also be synthesized from the linear diquaternary ammonium compound of  $(CH_3)_3N^+(CH_2)_mN^+(CH_3)_3$  where m value equals 12 [10].

Depending on the m value in the linear diquaternary ammonium compounds, various zeolites can be obtained; however, use of the shorter linear diquaternary ammonium compound of  $(CH_3)_3N^+(CH_2)_3N^+(CH_3)_3$  in hydrothermal synthesis is limited [11]. The *in situ* modification of the SDA in highly basic conditions during hydrothermal synthesis resulted in the formation of Nonasil and ZSM-48.

The tertiary amine, TMPD, (CH<sub>3</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>3</sub>N(CH<sub>3</sub>)<sub>2</sub> was utilized to synthesize zeolite MTT and SSZ-32 [12,13]. Also, various linear amines, which have a branched group separated by 5 Å, was predicted for phase selectivity to MTT framework using a simulation of the optimized van der Waals interactions of the amines in the pore [14]. While, HMPD, (CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub> has similar structural features, it has two methyl groups in the intermediate short alkyl chain, thereby showing the possibility of inducing formation of the three dimensional structure.

In this work, the possibility of controlling morphology under hydrothermal synthesis was explored using a mixture of the SDAs, TMPD and HMPD, which are low cost diamines. Using the well-defined hydrothermal synthesis condition for both SDAs, the

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http://dx.doi.org/10.1016/j.micromeso.2014.04.035 1387-1811/© 2014 Elsevier Inc. All rights reserved.

#### Table 1

Effect of the Si/Al ratio, hydrothermal synthesis temperature and time on the zeolite formation from starting gel compositions of 5 SDA:0.3 Na<sub>2</sub>O:5 SiO<sub>2</sub>:x Al<sub>2</sub>O<sub>3</sub>:156 H<sub>2</sub>O under 40 rpm rotation.

SDA <sup>a</sup>	x	Si/Al	Temp. (K)	Day	Phase
TMPD	1	5	453	2	Am + MOR
TMPD	1	5	453	4	MOR
TMPD	1	5	453	8	MOR
TMPD	0.5	10	433	2	Am
TMPD	0.5	10	433	4	MOR
TMPD	0.5	10	433	8	MOR
TMPD	0.25	20	433	2	Am
TMPD	0.25	20	433	6	MTT
TMPD	0.25	20	433	12	MTT
TMPD	0.125	40	433	6	MTT
TMPD	0.125	40	433	12	MTT
HMPD	1	5	453	2	Am <sup>b</sup> +MOR
HMPD	1	5	453	4	MOR
HMPD	1	5	453	8	MOR
HMPD	0.5	10	433	2	Am
HMPD	0.5	10	433	4	MOR + MFI
HMPD	0.5	10	433	8	MFI + trMOR <sup>c</sup>
HMPD	0.25	20	433	2	Am
HMPD	0.25	20	433	6	MFI
HMPD	0.25	20	433	12	MFI
HMPD	0.125	40	433	6	MFI
HMPD	0.125	40	433	12	MFI

<sup>a</sup> TMPD and HMPD represents  $N^1$ , $N^1$ , $N^3$ , $N^3$ -tetramethylpropane-1,3-diamine and  $N^1$ , $N^1$ , $N^3$ , $N^3$ ,2,2-hexamethylpropane-1,3-diamine, respectively.

<sup>b</sup> Am represented an amorphous phase.

<sup>c</sup> Mostly MFI phase with a trace amount of MOR.

molar ratio of the two SDAs in the synthesis gel mixture was varied, while the other synthetic parameters and conditions were kept constant.

# 2. Experimental

## 2.1. Zeolite synthesis

TMPD (Aldrich) and HMPD (Aldrich) were used as received without further purification. For synthesis, the SDA was first mixed with silica sol (Ludox AS-40) under vigorous stirring. The other solution was prepared by dissolving NaAlO<sub>2</sub> (Alfa) in a solution

containing NaOH (Daejung). The two gel solutions were mixed together, and the resulting mixture was stirred for more than 1 h for complete mixing. The gel composition was 5 SDA:0.3 Na<sub>2</sub>O:5  $SiO_2$ : x Al<sub>2</sub>O<sub>3</sub>:156 H<sub>2</sub>O, where x was controlled to from 0.125 to 1. The hydrothermal synthesis was performed under rotation at 40 rpm, with a temperature ranging from 433 to 453 K. The synthesis time was also varied, from 2 d up to 8 d. After hydrothermal synthesis, the autoclave was quenched with cold water to prevent the formation of impurities. The solid product was recovered by filtration, washed with doubly distilled water, and dried in a vacuum oven for 12 h at 333 K under 1 mm Hg. The obtained zeolites were calcined with under flowing air at 823 K for 6 h, while the temperature was increased to 823 K at the rate of 2 K per min. For hydrothermal synthesis with mixed SDAs, the gel composition was 20 SDA (*x*TMPD + *y*HMPD):1.2 Na<sub>2</sub>O:20 SiO<sub>2</sub>:1.0 Al<sub>2</sub>O<sub>3</sub>:625 H<sub>2</sub>O, where the sum of x and y was fixed to 20. All the hydrothermal synthesis conditions were kept constant for the preparation of all mixed SDA samples.

# 2.2. Characterization

The powder X-ray diffraction spectra were recorded using a D/ MAX Ultima III (Rikagu, Japan) with CuK $\alpha$  radiation for determination of phase purity and the crystallinity of the samples. Data were collected with a fixed divergence slit (0.50°) and Soller slits (incident and diffracted = 0.04 rad). The BET adsorption–desorption isotherms of nitrogen were measured at 77 K with an ASAP2020 (Micromeritics, USA). A carbon dioxide adsorption isotherm was obtained using the same instrumentation at 273 K. Before both nitrogen and carbon dioxide adsorption measurements, the sample was evacuated at 673 K for 2 h in order to remove adsorbed impurities.

Multinuclear MAS NMR measurements were performed mainly on Unity Solid Inova WB 200 MHz and 600 MHz spectrometers (Agilent Technologies, USA) at Korea Basic Science Institute, Daegu Center. The <sup>29</sup>Si MAS NMR spectra were measured at a <sup>29</sup>Si frequency of 119.182 MHz with a  $\pi/2$  rad pulse length of 6.5 µs, a recycle delay of 15 s, and an acquisition of about 1024 pulse transients at a spinning rate of 9.0 kHz. For MAS <sup>27</sup>Al NMR, the sample was spun at a rate of 22 kHz. The <sup>27</sup>Al MAS spectra was taken at



Fig. 1. (Left panel) MTT samples were synthesized with the Si/Al ratio of 20 at 433 K for (a) 2, (b) 6 and (c) 12 days, respectively. Vertical mark is MTT framework. (Right Panel) MFI samples were synthesized with the Si/Al ratio of 20 at 433 K for (a) 2, (b) 6 and (c) 12 days, respectively. Vertical mark is MFI framework.

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