Effect of Heating Sources and Template-Free Secondary Growth Synthesis on MFI-type Zeolite Microstructure

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ABSTRACT

MFI-type zeolite membranes have great potential application in the separation of gas and liquids, which are difficult to achieve by traditional techniques [1]. Thus, research on high-quality MFI zeolite membrane and zeolite microstructure is increasing rapidly. In general, MFI-type zeolite membranes are synthesized by conventional heating (CH), which needs a long crystallization time ranging from several hours to a few days and usually results in the formation of impure materials because of the low heating rate and the inhomogeneous heating [2]. Additionally, MFI-type zeolite membranes are usually synthesized in the presence of organic templates. The organic agent, however, needs to be removed by calcination in order to open up the zeolite channels; then intercrystalline gaps tend to enlarge in the membranes, which affect the separation performance of the membranes [3]. It was found that in order to obtain a high quality MFI-type zeolite membrane, a homogeneous heating source and template removal are important factors. Therefore, it is very important to examine the influence of heating sources and template-free synthesis on zeolite microstructure.

This paper reports synthesis of MFI-type zeolite powders by a template-free method using microwave heating (MH). The influence of heat sources, the amount of silicalite nanoparticle seeds, treatment with an NaOH solution, etc., on the formation of MFI zeolite microstructure were studied. In the present work, MFI zeolite powder was prepared according to both heating sources (CH or MH) and the methods (with template or without template). In case of using template, MFI zeolite powders were synthesized by in situ crystallization with a composition of 18.7g TEOS/20ml TPAOH/0.27g NaOH/75g H_2O/Xg Al2(SO4)318 H_2O. The X values varied were 0 and 0.25 for silicalite-1 (Al-free) and ZSM-5 (with Al), respectively. In preparing template-free samples, silicalite nanoparticle seeds were prepared by hydrothermal treatment (at 80□×84h) from a molar ratio of 0.33 SiO_2/0.1 TPAPH/0.035 NaOH/5.56 H_2O. After hydrothermal synthesis, the resultant silicalite nanoparticle slurry was washed in DI water with the assistance of centrifuge. MFI zeolite powders were synthesized by in situ crystallization with a composition of 2.0g silicalite nanoparticle seed/5.0g SiO_2/1.9g NaOH/100g H_2O/Xg $Al_2(SO_4)_3 18H_2O$. The X values varied were 0 and 0.25 for silicalite-1 and ZSM-5, respectively. After the hydrothermal synthesis, the zeolite powder was washed and dried overnight. The powder was then fired at 450□ for 8h with a heating and cooling rate of 1.0□/min. The names and synthesis conditions for all samples are presented in Table 1.

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Table 1. Preparation conditions for MFI zeolite powder samples

Sample	Type	Template	Heating source	Si/Al	Synthesis temperature	Silicalite seed (g)	Alikali-treatment (mol l^{-1})
1	ZSM-5	TPAOH	CH	111	180℃×10h	-	-
2	ZSM-5	TPAOH	MH	111	180℃×4h	-	-
3	Silicalite-1	TPAOH	CH	∞	180℃×10h	-	-
4	Silicalite-1	TPAOH	MH	∞	180℃×4h	-	-
5	ZSM-5	-	CH	111	180℃×10h	0.5	-
6	ZSM-5	-	MH	111	180℃×4h	0.5	-
7	Silicalite-1	-	CH	∞	180℃×10h	0.5	-
8	Silicalite-1	-	MH	∞	180℃×4h	0.5	-
9	Silicalite-1	-	CH	∞	180℃×10h	1.0	-
10	Silicalite-1	-	CH	∞	180℃×10h	1.5	-
11	Silicalite-1	-	CH	∞	180℃×10h	2.0	-
12	ZSM-5	-	MH	111	180℃×4h	0.5	0.025

The results of pore-structural parameters derived from the nitrogen adsorption data are shown in Table 2. The pore structures of the samples were investigated by physical adsorption of nitrogen at 77K on an automatic volumetric analyzer (Micromeritics ASAP 2020). Prior to measurements, the samples were degassed at 350℃ for 10h under vacuum. The specific surface areas (S_{BET}) were determined according to BET method. The total volumes (V_t), the micropore volumes (V_{mi}), the mesopore volumes (V_{me}) and the median pore width were also obtained. Samples between 1 and 4 possess similar BET surface areas and pore volumes. MH synthesis drastically reduced the crystallization time of zeolites, which resulted from the simultaneous nucleation and homogeneous heating by microwave. Samples between 5 and 8 display lower pore volumes and smaller BET surface areas than the former samples. Since there is no template in the synthesis solution, zeolite growth is limited to silicalite seed crystals [4] and the amorphous materials can be made. BET surface areas of silicalite-1 are lower than that of ZSM-5, which means that the particle obtained from the aluminum free precursor did not have enough intergrown polycrystalline structures.

Table 2. Characterizations of MFI zeolite powder samples

Sample	S_{BET} (m^2/g)	V_t (cm^3/g)	V_{mi} (cm^3/g)	V_{me} (cm^3/g)	Median pore width (Å)
1	421	0.18	0.13	0.05	5.51
2	410	0.18	0.13	0.05	5.47
3	430	0.16	0.14	0.03	5.53
4	427	0.18	0.13	0.05	5.58
5	354	0.15	0.12	0.04	5.35
6	371	0.15	0.11	0.04	5.35
7	106	0.05	0.03	0.02	5.21
8	56	0.03	0.01	0.02	-

To further investigate the template-free zeolite microstructure, the amount of silicalite nanoparticle seeds was increased. Table 3 also shows that the amount of silicalite nanoparticle seeds has obvious influence on both BET surface areas and pore volumes of template-free silicalite-1 powders. After 1.5g or more of seeds is added, BET surface areas were found to be slightly larger than those of powders with template. These observations are in accordance with the XRD characterization. It means that the amount of crystals increases with the amount of silicalite nanoparticle seeds, on which zeolite can grow.

Table 3. Characterizations of MFI zeolite powder samples

Sample	S_{BET} (m^2/g)	V_t (cm^3/g)	V_{mi} (cm^3/g)	V_{me} (cm^3/g)	Median pore width (Å)
7	106	0.05	0.03	0.02	5.21
9	140	0.06	0.04	0.02	5.21
10	435	0.17	0.14	0.03	5.51
11	465	0.19	0.15	0.04	5.50

Alkali-treatment is another way of modifying zeolite. The results of porous structural parameters of alkali-treated zeolite samples and the morphology of them are shown in Table 4. When MFI type zeolite powder is treated with NaOH aqueous (0.025mol l^{-1}) solution, the surface area increased slightly in the micorpore region, and pore volume also increased in the mesopore region. It means that the large pores were newly generated at the boundary of the microcrystallites by alkaline dissolution of Si and Al. SEM and XRD measurements revealed that amorphous phases present at the boundary of the crystallities were dissolved. By NaOH treatment, the aggregates containing of the primary microcrystallines and the amorphous SiO_2 as cement changed to those of the primary microcrystallines through the removal of the amorphous phase [5].

Table 4. Characterizations of MFI zeolite powder samples after alkali-treatment

Sample	S_{BET} (m^2/g)	V_t (cm^3/g)	V_{mi} (cm^3/g)	V_{me} (cm^3/g)	Median pore width (Å)
6	371	0.15	0.11	0.04	5.35
12	399	0.18	0.12	0.06	5.81

MFI zeolite powders synthesized by a template-free secondary growth method display lower pore volumes and smaller BET surface areas than MFI zeolite powders synthesized with template. However, both the amount of silicalite nanoparticle seeds and the alkali-treatment have obvious influence on both BET surface areas and pore volumes of template-free MFI zeolite powders, which were found to be similar to those of powders with template.

Reference

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