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The effects of seeding in the synthesis of zeolite ZSM-48 in the presence of tetramethylammonium ion

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Abstract

The hydrothermal synthesis of ZSM-48 has been investigated using tetramethylammonium (TMA) ion with and without addition of ZSM-48 seeds. Without addition of seed crystals, main product was ZSM-39. Only cristobalite was formed without addition of TMA in the seeded system. Hence, addition of both seeds and TMA ions is essential to obtain the well-crystallized ZSM-48 samples. The morphology of resultant ZSM-48 crystals in the seeded system was hexagonal rod. It was suggested that the ZSM-48 seeds would accelerate the crystallization of ZSM-48 zeolite and avoid the formation of ZSM-39. TMA might assist the growing process of ZSM-48 over seed crystals and stabilize the ZSM-48 structure.

Keywords: ZSM-48; Seed; Synthesis; Tetramethylammonium; ZSM-39

1. Introduction

A lot of work has been carried out on the synthesis of high-silica zeolites as they are supposed to have a high thermal and catalytic stability. ZSM-48 is a high silica zeolite with one-dimensional medium channels. It was first found as an impurity phase in ZSM-39 synthesis and grew epitaxially from the octahedral faces of the ZSM-39 structure [1]. ZSM-48 in pure phase was later synthesized hydrothermally from a synthesis mixture of silica, alumina, TMA ion and *n*-propylamine [2]. It was also prepared with 1,8-octanediamine as SDA (Structure Directing Agent) by Rollmann et al. [3] and with various polyamines by Gunawardane et al. [4].

The structure of this zeolite is complicated because its framework is highly disordered. However, it was proposed by Schlenker et al. that ZSM-48 has a framework structure that is based on the ferrierite sheets linked via bridging oxygen located on mirror planes [1]. It has linear non-interconnecting 10 member-ring channels whose dimension is 0.53 × 0.56 nm running perpendicular to the sheet. Lobo et al. re-examined the structure of this zeolite and described the disorder in ZSM-48 based on an array of tubular pores [5]. They concluded that ZSM-48 is not a code for one material but for a family of materials consisting of tubular pores.

ZSM-48 has been used as a useful catalyst for many reactions due to its unique pore structure and acid property [6–10]. Disorder of the zeolite might become a disadvantage as they block the pore system and lead one-dimensional channels inaccessible. Hence, it is desired to control disorder of ZSM-48 structure in the synthesis process.

Addition of seed crystals was demonstrated to be one of the efficient methods to accelerate the zeolite formation in the hydrothermal systems in which the nucleation

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process is the rate-determining step [11]. Crystallization processes during zeolite synthesis with seeding have been studied and addition of small amounts of zeolite crystals into the synthesis gel has been applied to various zeolite syntheses [12].

In this work, we attempted to synthesize ZSM-48 type zeolite with high crystallinity via seeding. Thus, the crystallization field of ZSM-48 has been identified as a function of key parameters such as reagent concentrations and synthesis time.

2. Experimental

The hydrothermal synthesis experiments were carried out in Teflon-lined Parr autoclaves with a capacity of 25 ml. For the synthesis, tetramethylammonium chloride (TMACl from Wako Ltd.), Cataloid SI30 colloidal silica (30 wt.% from Catalysis and Chemicals Co.), aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$ from Wako Ltd.) and sodium hydroxide from Wako Ltd. were used as source materials. Synthesis conditions are summarized in Table 1. In a typical synthesis of zeolites, NaOH dissolved in deionized water and TMACl were mixed and stirred till the solid dissolved. Then, the colloidal silica was added to the above solution and stirred till the gel became homogeneous. Aluminum nitrate was then added in some cases. The resulting composition of the gel was $0–0.16Na_2O:SiO_2:0–0.5TMACl:40H_2O:0–0.01Al_2O_3$. Basic composition was $0.08Na_2O:SiO_2:0.1TMACl:40H_2O$. To this gel, 0–5% of seeds was added. The amount of seed added was calculated on basis of the amounts of SiO_2 in the synthesis mixture (Si atomic base). The suspension was then transferred to a Parr autoclave and crystallization was carried out at 170 °C under autogenous pressure in static conditions for appropriate time. Upon completion of the synthesis, the autoclave was quenched to room temperature by cold water. The products thus obtained were separated by centrifuging from the remaining liquid phase and washed with distilled water several times. The solid materials were dried at 120 °C overnight. The organic material was removed by calcination in air at 550 °C for 6 h.

Seed crystals were synthesized by using decyl-*N*,*N*,*N*-trimethylammonium bromide ($C_{10}H_{21}(CH_3)_3NBr$ from Tokyo Kasei Co. Ltd.) as SDA (sample D1). The synthesis gel of the composition $0.08Na_2O:SiO_2:0.1C_{10}H_{21}(CH_3)_3NBr:40H_2O$ was prepared. The gel was then transferred to a Teflon-lined autoclave and crystallization was carried out at 170 °C for 40 h under the autogenous pressure with stirring. ZSM-48 zeolites synthesized with $C_{10}H_{21}(CH_3)_3N^+$ are called as ZSM-48 (C_{10}) hereinafter.

The X-ray powder diffraction patterns were obtained with CuKα radiation on a MAC Science MXP18 diffractometer with a graphite monochrometer. The peak area of the solid product for ZSM-48 was calculated by com-

Table 1
Synthesis conditions and representative zeolite phases obtained

Sample	Synthesis gel (molar ratio)							Time (h)	Product (Listed in order of decreasing quantity)	Peak area (a.u.)[a]
	SiO_2	H_2O	NaOH	TMACl[b]	C_{10}[c]	Seed[d]	Al			
D1[e]	1	40	0.16	–	0.1	–	–	40	ZSM-48	92
S01	1	40	0.16	0.1	–	–	–	40	ZSM-39 + ZSM-48	9
S02	1	40	0.16	–	–	–	–	40	PhaseX2	–
S03	1	40	0.16	0.1	–	0.01(D1)	–	40	ZSM-48	92
S04	1	40	0.16	0.1	0.0015	–	–	40	ZSM-39	–
S05	1	40	0.16	0.1	–	0.01(D1[f])	–	40	ZSM-48	92
S06	1	40	0.16	0.1	–	0.05(S03)	–	40	ZSM-39	–
S07	1	40	0.16	0.1	–	0.01(S03[g])	–	40	ZSM-48 + A[h]	57
S08	1	40	0.16	–	–	0.01(D1)	–	40	Cristobalite	–
S09	1	40	0.16	0.05	–	0.01(D1)	–	40	ZSM-48 + Cristobalite	60
S10	1	40	0.16	0.1	–	0.01(D1)	–	185	Cristobalite	–
S11	1	40	0.16	0.5	–	0.01(D1)	–	192	ZSM-48	92
S12	1	40	0.16	0.1	–	0.01(D1)	0.0025	40	ZSM-48	95
S13	1	40	0.16	0.1	–	0.01(D1)	0.005	40	ZSM-48 + A	62
S14	1	40	0.16	0.1	–	0.01(D1)	0.01	40	ZSM-48 + A	14
S15	1	40	0.16	0.1	–	0.01(D1)	0.02	40	A	–

All syntheses except D1 were carried out at 170 °C in static conditions.

[a] XRD peak area of ZSM-48 phase.

[b] Tetramethylammonium chloride.

[c] $C_{10}H_{21}(CH_3)_3NBr$.

[d] Calculated on silicone atom base.

[e] Synthesis was carried out with stirring.

[f] Calcined sample.

[g] Crushed sample.

[h] Amorphous phase.