

Hydrothermal synthesis of ZSM-5 zeolite using siliceous mudstone

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ZSM-5 zeolite was successfully synthesized by a hydrothermal reaction method using siliceous mudstone. The major chemical composition of siliceous mudstone is 85.85 wt.% of SiO₂ and 6.99 wt.% of Al₂O₃, and the crystalline phases are opal-CT, quartz, smectite and muscovite. The experimental conditions were varied with the weight ratio between sodium silicate solution (SS) and siliceous mudstone (SM) from 0.8 to 1.6, the reaction temperature from 130 to 200 °C and reaction time from 12 to 30 hours. Within these experimental conditions, the most suitable combination to synthesize ZSM-5 zeolite was SS/SM = 1.2, reaction temperature = 170 °C and reaction time = 24 hours. The particle shape was a faceted-sphere and the median particle size was 5.2 μm. The BET surface area was 324 m²·g⁻¹ after calcination at 500 °C and this value was sustained up to 700 °C.

Key words: hydrothermal reaction, siliceous mudstone, sodium silicate, ZSM-5 zeolite, BET surface area, thermal stability.

Introduction

ZSM-5 zeolite, a type of microporous crystalline aluminosilicate material, is an important catalyst from the industrial and academic points of view due to its unique microstructure and thermal stability. It has been widely used for separation, adsorption and catalytic processes mostly in the petrochemical industry. Therefore, much attention has been paid reducing the manufacturing cost and improving the reactivity [1-6]. Recently, many studies have been made of the synthesis of ZSM-5 zeolite using natural materials such as perlite [6], serpentine [7] and fly ash [8].

Siliceous mudstone is abundantly distributed all over the world [9-12] and also in Korea (Pohang area) [13]. It is composed with opal-CT (SiO₂·nH₂O) as the major mineral and small amounts of quartz, smectite and muscovite [13]. Siliceous mudstone can be considered as an applicable material for the synthesis of zeolites because it contains a high content of silica and is a chemically reactive material [14, 15]. However, a study of the synthesis ZSM-5 zeolite using siliceous mudstone is hard to find.

In this study, a sodium silicate solution was added to siliceous mudstone because it acts as a solvent for silica, supplies additional silica and sodium, and increases the pH. The effects of experimental parameters such as, the amount of sodium silicate solution to the amount of siliceous mudstone, the reaction temperature and reaction time on the formation of ZSM-5 zeolite were investigated and its thermal stability was examined.

Experimental Procedure

Siliceous mudstone (SM) was used as the starting material and its chemical composition is shown in Table 1. Its main constituents are SiO₂ (85.85 wt.%) and Al₂O₃ (6.99 wt.%). As shown in Fig. 1, opal-CT is the major mineral and quartz is the secondary mineral. Also small amounts of smectite and muscovite are present.

The siliceous mudstone was pulverized using a jaw crusher, after drying at 100 °C for 12 hours, followed by ball milling for 3 hours in the dry condition. The median particle size after ball milling was 42 μm (d_{0.5}) and the BET surface area was 62 m²·g⁻¹.

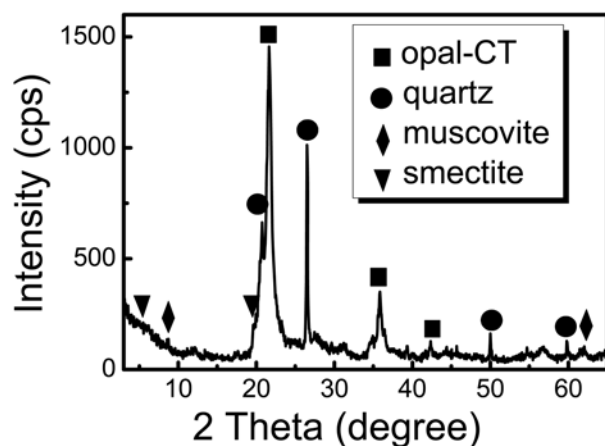
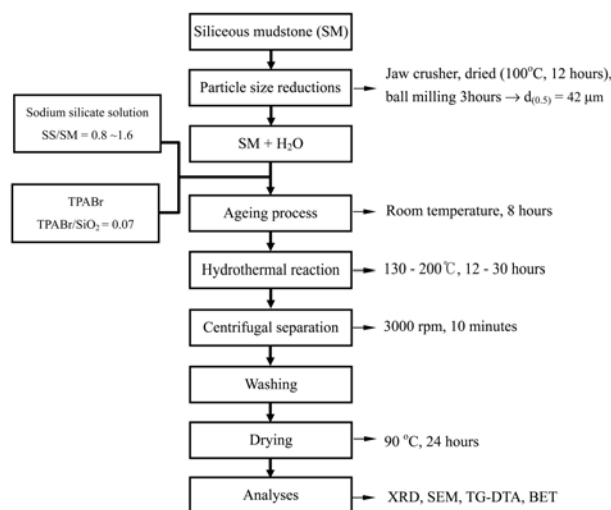
Some previous studies have reported that the molar ratio of Na₂O : SiO₂ : H₂O must be about 0.05 : 1 : 50 and the pH must be around 12 in order to synthesize ZSM-5 zeolite [16]. However, the Na₂O : SiO₂ molar ratio of the siliceous mudstone is only 0.0025 : 1. Therefore, sodium silicate solution (Na₂O·3SiO₂·nH₂O) was added in order to supply sodium and silicon in an ionic state and also to increase the pH. The composition of the sodium silicate solution (DC Chemical Company Ltd, Korea) was SiO₂ 29 wt.%; Na₂O 10 wt.%; and H₂O 61 wt.%. Tetrapropyl ammonium bromide (TPABr C₁₂H₂₈NBr, 98%, Aldrich) was used as a template and the molar ratio of TPABr : SiO₂ was fixed at 0.07 : 1 by referring to Fegan and Lowe [17].

A schematic experimental procedure is given in Fig. 2. The siliceous mudstone powder, sodium silicate solution and TPABr were mixed with de-ionized water and aged for 8 hours at room temperature. A hydrothermal reaction was carried out at various temperatures (130, 150, 160, 170, 180 and 200 °C) and reaction times (12, 16, 20, 24, and 30 hours). The heating rate to the reaction temperature was 2.8 Kminute⁻¹. After the hydrothermal reaction, the

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Table 1. Chemical composition of natural siliceous mudstone.

Elements:	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	MnO	P ₂ O ₅	Ig. loss	Sum
(wt. %):	85.85	6.99	1.27	0.22	0.29	0.73	0.22	0.31	0.01	0.03	3.97	99.89

**Fig. 1.** XRD pattern of siliceous mudstone.**Fig. 2.** Synthesis processes for the preparation of ZSM-5 zeolite using siliceous mudstone.

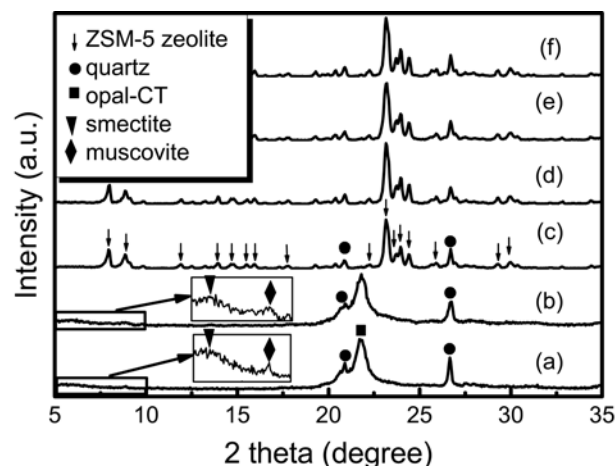
precipitates were separated by a centrifugal method (3000 rpm, 10 minutes) and then dried (90 °C, 24 hours).

Results and Discussion

Effect of reaction temperature

The reaction temperature is one of the most important parameters to synthesize zeolite because the reactivity and solubility of the material are greatly influenced by temperature [16]. Fig. 3 shows XRD patterns of precipitates which were synthesized at various reaction temperatures. The other parameters were fixed as the weight ratio of SS/SM = 1.4, and reaction time = 24 hours.

Opal-CT, smectite and muscovite, which are present in siliceous mudstone, remained up to 150 °C (Fig. 3(a), (b)). However, they were completely dissolved above 160 °C

**Fig. 3.** XRD patterns of precipitates, which were synthesized at various reaction temperatures. Others reaction conditions: reaction time = 24 hours and SS/SM = 1.4.

(a) 130 °C, (b) 150 °C, (c) 160 °C, (d) 170 °C, (e) 180 °C, (f) 200 °C.

(Fig. 3(c)–(f)). By contrast, quartz remained even after reacting at 200 °C. This means that Opal-CT, smectite and muscovite were dissolved more easily than quartz.

ZSM-5 zeolite did not form at a low reaction temperature (130 and 150 °C), however, it was formed above 160 °C (Fig. 3(e)–(f)). As described earlier, opal-CT, smectite and muscovite dissolved completely at 160 °C, and then the supersaturation of silica for the nucleation and crystal growth of the ZSM-5 zeolite was fulfilled.

The diffracted intensity at 160 °C (Fig. 3(c)) was lower than that of 170, 180 and 200 °C, which is due to the incomplete crystallization at 160 °C. However, the diffracted intensities at 170, 180 and 200 °C were similar (Fig. 3(d)–(f)). Hence, a reaction temperature of 170 °C was fixed to conduct the further experiments.

The morphologies of the particles with different reaction temperatures are shown in Fig. 4. The particle shape was changed from an irregular shape to a rounded shape and the particle size was reduced due to dissolution of siliceous mudstone with an increase in the reaction temperature from 130 to 150 °C (Fig. 4(a), (b)). However, the morphology of the precipitates was a faceted-spherical shape at a higher reaction temperature above 160 °C (Fig. 4(c)–(f)). This is the typical shape of a well-developed ZSM-5 zeolite.

The median particle size became larger and was measured as 3.9, 5.2, 7.6 and 9.7 μm with respect to reaction temperatures of 160, 170, 180 and 200 °C (Fig. 4(c)–(f)). This indicates that the dissolution of siliceous mudstone was accelerated with an increase in the reaction temperature, thus the degree of supersaturation became higher, resulting in an increase of the crystal growth rate [16].

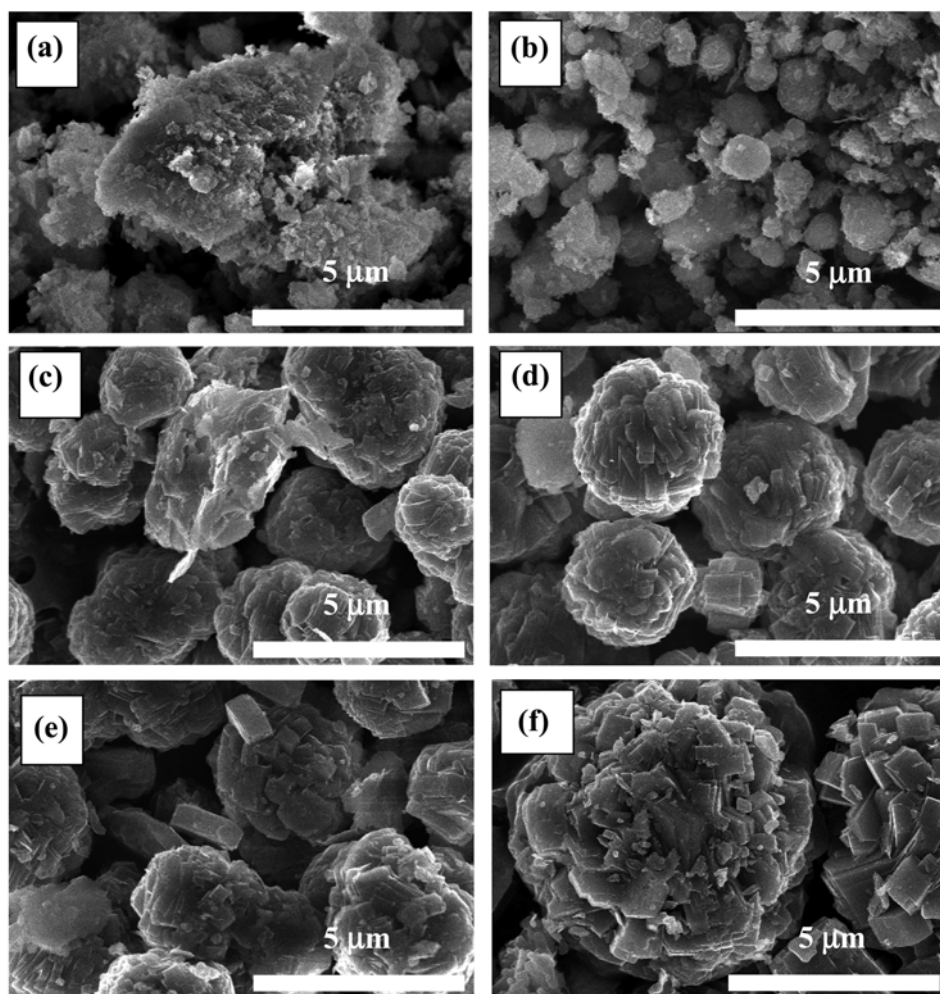


Fig. 4. SEM micrographs of precipitates, which were synthesized at various reaction temperatures. Others reaction conditions: reaction time = 24 hours and SS/SM = 1.4.

(a) 130 °C, (b) 150 °C, (c) 160 °C, (d) 170 °C, (e) 180 °C, (f) 200 °C.

Effect of reaction time

To find out the effective reaction time for the formation of ZSM-5 zeolite, the reaction time was varied from 12 to 30 hours. The others parameters were fixed as the weight ratio of SS/SM = 1.4 and reaction temperature = 170 °C.

The XRD patterns at various reaction times are shown in Fig. 5. Opal-CT, smectite and muscovite remained until 16 hours reaction time. The concentration of silica was not high enough for ZSM-5 zeolite formation with a reaction time of less than 16 hours (Fig. 5(a), (b)). After 20 hours reaction time, almost all of the opal-CT, muscovite and smectite were dissolved and ZSM-5 zeolite started to form (Fig. 5(c)). Probably, the degree of supersaturation for the formation of ZSM-5 was satisfied.

Effect of sodium silicate content

In order to synthesize ZSM-5 zeolite, the molar ratio of $\text{Na}_2\text{O} : \text{SiO}_2 : \text{H}_2\text{O}$ needs to be approximately 0.05 : 1 : 50 and the pH around 12 [16]. However, siliceous mudstone contains a large amount of silica (85.85 wt.%) and a small amount of sodium (0.22 wt.%) as shown in Table 1. The

molar ratio of $\text{Na}_2\text{O} : \text{SiO}_2$ for the siliceous mudstone is only 0.0025 : 1. Therefore, it must be modified to 0.05 : 1 by adding sodium. We assumed that the most suitable additive is a sodium silicate solution because it contains large amounts of sodium and silica in an ionic state.

Fig. 6 shows XRD patterns of the precipitates with various weight ratios between the sodium silicate solution (SS) and siliceous mudstone (SM). The other parameters were fixed as reaction temperature = 170 °C, and reaction time = 24 hours. ZSM-5 zeolite was not synthesized at a SS/SM ratio of 0.8 (Fig. 6(a)), however it was synthesized well above 1.0 (Fig. 6).

It seems that at a SS/SM ratio of 0.8, the dissolution rate of the opal-CT was very slow due to the lower availability of sodium ions in the solution. Additionally, a lesser amount of sodium silicate solution could not provide enough Si^{+4} ions. Thus, the degree of supersaturation of silica was not satisfied. At SS/SM ratios above 1.0, ZSM-5 zeolite formed and it was confirmed that the concentration of silica was sufficient for the supersaturation with Si^{+4} ions and it was suitable for the formation of ZSM-5 zeolite.

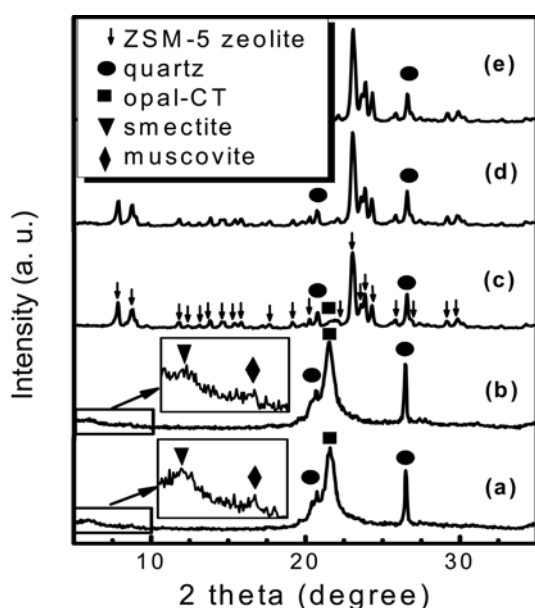


Fig. 5. XRD patterns of precipitates, which were synthesized at various reaction times. Others reaction conditions: reaction temperature = 170 °C and SS/SM = 1.4.

(a) 12 hours, (b) 16 hours, (c) 20 hours, (d) 24 hours, (e) 30 hours.

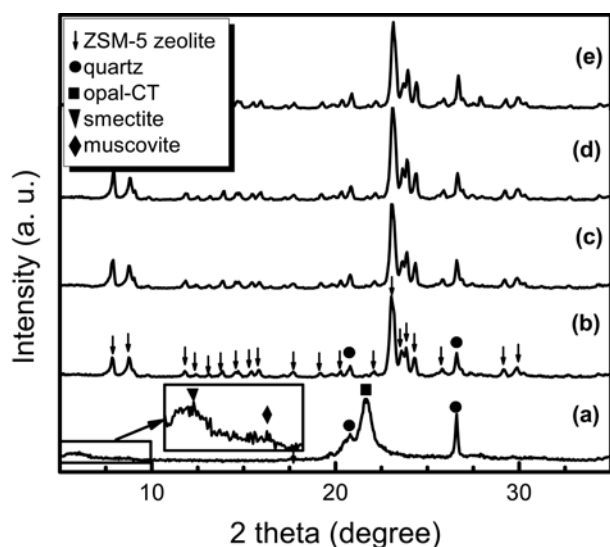


Fig. 6. XRD patterns of precipitates, which were synthesized with various ratios of SS/SM. Others reaction conditions: reaction temperature = 170 °C and reaction time = 24 hours.

(a) SS/SM = 0.8, (b) SS/SM = 1.0, (c) SS/SM = 1.2, (d) SS/SM = 1.4, (e) SS/SM = 1.6.

Effect of calcination temperature

A ZSM-5 zeolite, which was synthesized with a reaction temperature = 170 °C, a reaction time = 24 hours and a SS/SM ratio = 1.2, was used to investigate the effect of the calcination temperature on the BET surface area and thermal stability.

XRD patterns of ZSM-5 zeolites calcined for 4 hours at various temperatures are shown in Fig. 7. The XRD pattern shows no change even after calcination at 300 °C (Fig. 7(a)). However, the intensity of diffraction from crystallographic

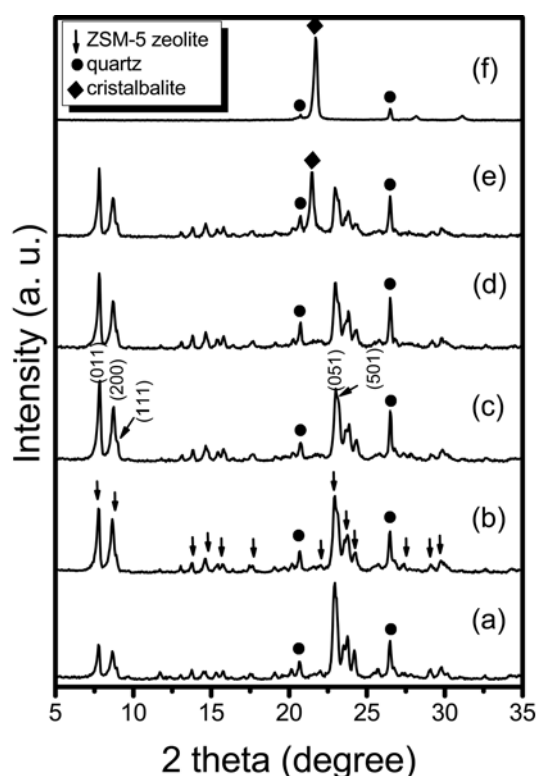


Fig. 7. XRD patterns after calcination. ZSM-5 zeolites were synthesized with a reaction temperature = 170 °C, a reaction time = 24 hours and a SS/SM ratio = 1.2. The calcinations temperature were (a) 300 °C, (b) 500 °C, (c) 700 °C, (d) 900 °C, (e) 1000 °C, (f) 1100 °C.

planes was changed after calcination above 500 °C comparing to the as-synthesized ZSM-5 zeolite (Fig. 7(b)-(e)). The diffracted intensities from (011), (200) and (111) planes were increased, however, the diffracted intensities from (501) and (051) planes were reduced. This is because of the phase transformation from monoclinic to orthorhombic (Fig. 7) [18]. The phase transformation from ZSM-5 zeolite to cristobalite started at 1000 °C (Fig. 7(e)) and was completely transformed to cristobalite at 1100 °C (Fig. 7(f)).

TG-DTA data showed (Fig. 8) a strong exothermic peak at 450 °C due to the decomposition of TPABr in the ZSM-5 zeolite framework [7]. The decomposition of TPABr occurred from 400 °C to 600 °C, and the total weight loss was about 9%.

The effect of the calcination temperature on the BET surface area of ZSM-5 zeolites is shown in Fig. 9. The BET surface area of a ZSM-5 zeolite after calcination at 300 °C ($11 \text{ m}^2 \cdot \text{g}^{-1}$) showed almost no change when compared to that of the as-synthesized zeolite ($10 \text{ m}^2 \cdot \text{g}^{-1}$). It was assumed that no decomposition of TPABr occurred during calcination at this temperature, because the decomposition of TPABr started around 400 °C (Fig. 8). The BET surface area after calcination at 400 °C was $50 \text{ m}^2 \cdot \text{g}^{-1}$, which indicates that a small amount of TPABr was decomposed. However, the BET surface area sharply increased to $324 \text{ m}^2 \cdot \text{g}^{-1}$ after calcination at 500 °C. This is caused by the complete

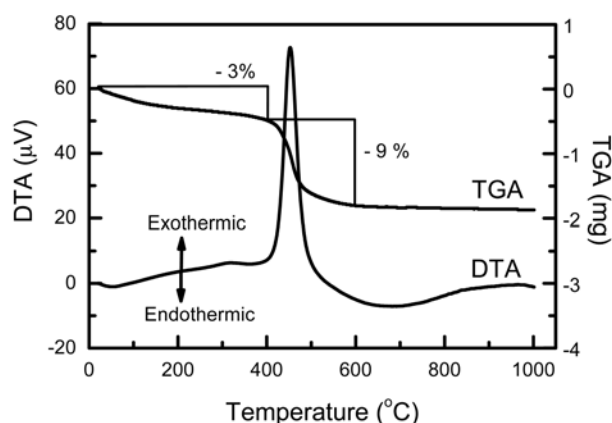


Fig. 8. TG-DTA spectra of a ZSM-5 zeolite, which was synthesized with conditions of reaction temperature = 170 °C, reaction time = 24 hours and SS/SM = 1.2.

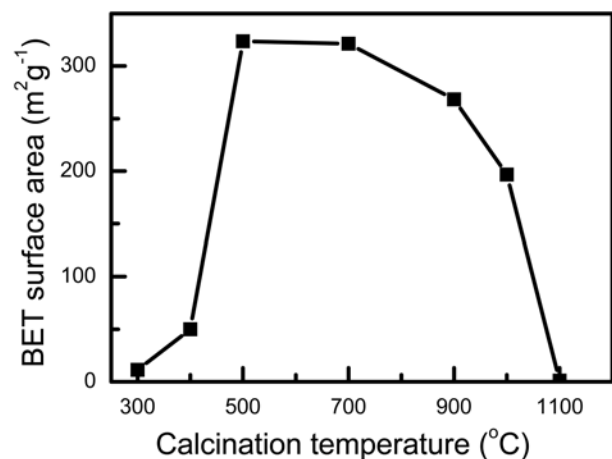


Fig. 9. Effect of the calcination temperature on the BET surface area. ZSM-5 zeolite was synthesized with conditions of reaction temperature = 170 °C, reaction time = 24 hours and SS/SM = 1.2.

decomposition of TPABr and this value was sustained up to 700 °C. Thereafter, the BET surface area gradually decreased with an increase of the calcination temperature to 900 °C, which was due to a sintering effect. A sharp drop in the BET surface area was observed from 900 to 1000 °C. The possible reasons may be due to a sintering effect and a partial phase transformation of ZSM-5 zeolite to cristobalite. At 1100 °C, the BET surface area dropped dramatically to 1 m²g⁻¹ because of the melting of the ZSM-5 zeolite.

The ZSM-5 zeolite synthesized in the present investigation still contains a certain amount of un-dissolved quartz, which is from the raw material. The presence of quartz is believed to be one of the main reasons that the BET surface area was not as high as that for a ZSM-5 zeolite synthesized from pure chemicals.

Conclusions

ZSM-5 zeolite was successfully synthesized by a hydro-

thermal reaction method using siliceous mudstone, a type of natural material. It was formed when the supersaturation of silica was attained by dissolution of opal-CT, smectite and muscovite. The supersaturation conditions varied with the weight ratio of SS/SM, the reaction temperature and reaction time. Within these experimental conditions, the most suitable combination to synthesize ZSM-5 zeolite was SS/SM = 1.2, reaction temperature = 170 °C and reaction time = 24 hours. The particle shape was a faceted-sphere and the median particle size was 5.2 μm. The BET surface area was 324 m²g⁻¹ after calcination at 500 °C and this value was sustained up to 700 °C. The BET surface area was not high compared to that of a ZSM-5 zeolite which was synthesized using pure chemical material due to the existence of un-dissolved quartz from the siliceous mudstone.

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