Effects of Starting Compositions and Operating Conditions on Synthesis of ZSM-5 from Kanuma Pumice, and the Properties of Catalysts in Alkylation of Toluene with Methanol

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Kanuma pumice admixed with silicon dioxide was subjected to hydrothermal synthesis in a NaOH medium. Conditions for ZSM-5 zeolite synthesis without addition of any organic reagent as a template were examined. Furthermore, the catalytic properties of ZSM-5 from Kanuma pumice in the alkylation of toluene with methanol were compared with those of ZSM-5 prepared from tetra-*n*-propyl ammonium. It was found that ZSM-5 from Kanuma pumice could also be used.

1. Introduction

Not only some soils, but also some clays contain humic substances formed by continuous decomposition of remains of animals or plants, and by reaction with soil or with clay. When weathered pumice from Kanuma, so called 'Kanuma-tsuchi' or 'Kohshitsu-do', which abounds in allophane of mineral clay, is used as a starting material for hydrothermal synthesis of zeolite, ZSM-5 zeolite can be synthesized without addition of any organic reagent as a template¹⁾. It was found that this was due to the synergistic effect of the colloidal properties and humic substances of Kanuma pumice. To ascertain how the synthesis proceeds when the starting composition other than the compositions shown in the preceding paper¹⁾ is used, the authors investigated how the zeolite ZSM-5 synthesis depended on the concentrations of NaOH, SiO₂, Al₂O₃, and H₂O in the starting material and on the operating conditions such as stirring, reaction temperature, and time for zeolitization. The authors further examined the effect of the synthesized ZSM-5 zeolite used as a catalyst in the alkylation of toluene with methanol by comparing it with that of ZSM-5 prepared with tetra-*n*-propylammonium iodide according to the Mobil's method²⁾.

2. Experimental

Materials, synthetic and product identification methods used are the same as those in the preceding paper¹⁾. The starting molar composition (1) was Na₂O: 5.0, SiO₂: 41.0, Al₂O₃: 1.0, H₂O: 940. The amounts of Kanuma pumice (wet), silicon dioxide, sodium hydroxide, and water used were 0.6460 g (0.2535 g-dry), 2.3400 g, 0.4089 g and 14.5667 g, respectively. Starting composition (2) was Na₂O: 3.5, Q₂O: 1.5, SiO₂: 41.0, Al₂O₃: 1.0, H₂O: 940 where Q represented tetra-*n*-propylammonium ion (TPA). The synthesis of zeolites was hydrothermally carried out in a tubular autoclave (SUS 316) of 24-ml with axial stirring of an amplitude of 10 cm per second. Amounts of uncalcined products (Na-ZSM-5) synthesized from starting compositions (1) and (2) by this "amplitude" method at 175°C for 24 hours were 0.5609 and 0.5856 g-dry per 1 g-solid in the starting composition, respectively. The products were designated as P-NaZSM5-AM and TPA-NaZSM5-AM, respectively. Circumferential stirring was further examined in the autoclave placed in a rotating electric furnace to increase the stirring effect. ZSM-5 synthesized from the starting composition (1) by the "rotating" method (200 rpm) at 175°C for 24 hours was designated as P-NaZSM5-RM. The same conditions of measurements for powder XRD reported previously were used for comparison.

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The catalytic properties of the synthesized zeolites, including Na or H type of P-ZSM5-AM, TPA-ZSM5-AM, and P-ZSM5-RM, were examined with respect to the acidity and distribution of their acid strengths, and alkylation of toluene with methanol. The acidity and distribution of their acid strengths were measured by temperature-programmed desorption (TPD) of NH_3 in the following manner: (1) 0.2 g of a sample was placed in a vessel; (2) pretreated in vacuo at 420°C for 1 hour; (3) NH_3 was adsorbed at ambient temperature and the system was evacuated; (4) the bed temperature was increased at a rate of $10^\circ\text{C}/\text{min}$ in a 60 ml/min He stream; (5) the desorbed NH_3 was detected with a TC cell. The alkylation was carried out at 425°C by a pulse method (see below) and He (20 ml min^{-1}) as a carrier gas, and the products were analyzed by gas chromatography. 20 mg of the catalyst placed in a microreactor was pretreated in a 20 ml min^{-1} He stream at 430°C for 2 hours, and $0.7\text{ }\mu\text{l}$ of a pulse of a mixture of equal volumes of toluene and methanol was injected into the microreactor.

3. Results and Discussion

3.1 Influence of Reaction Temperature and Water Content on ZSM-5 Synthesis from Kanuma Pumice

The water content in starting composition (1) was about 95 mole%. The peak intensity ($2\theta = 23.0^\circ$) in powder XRD patterns of the products from this composition (1) at 175°C changed with reaction time as shown in Fig. 1. The crystallinity of ZSM-5 reached a maximum after about 24 hours of reaction; it then slowly decreased with time to the intensity of about 70 (A.U.). At the same time, mordenite and α -quartz were crystallized. When the reaction temperature was raised to 190°C , the transformation of the zeolite phase was more pronounced rapid. The crystallinity of ZSM-5 reached a peak after 36 hours, since mordenite and α -quartz had already appeared after 24 hours because of the high temperature (190°C) involved. Amounts of ZSM-5 and mordenite both decreased with increasing amount of α -quartz, and they finally disappeared after 48 hours. This fact suggests that ZSM-5 appear first as a metastable form and then be successively transformed into mordenite and α -quartz in a more stable phase. When the reaction temperature was lowered to 150°C , the induction period was prolonged from 6 hours to 48 hours, and the crystallinity of ZSM-5 ultimately reached the intensity of 100 after 72 hours. Mordenite and α -quartz did not appear at this temperature.

The results obtained by changing the water

Fig. 1 Changes in Characteristic Peaks in XRD of Products at Varied Reaction Temperatures with Time
Reaction conditions: water content of 95 mol%

key	temperature	products	peak 2θ
$\triangle$ $\blacktriangle$ $\blacktriangle$	190°C	ZSM-5 mordenite α -quartz	23.0° 6.5° 20.8°
$\circ$ $\bullet$ $\bullet$	170°C	ZSM-5 mordenite α -quartz	
$\square$	150°C	ZSM-5

Fig. 2 Changes in Characteristic Peaks in XRD of Products under Varied Water Contents with Time
Reaction conditions: reaction temperature of 175°C

key	water content	products	peak 2θ
$\triangle$ $\blacktriangle$ $\blacktriangle$	93%	ZSM-5 mordenite α -quartz	23.0° 6.5° 20.8°
$\circ$ $\bullet$ $\bullet$	95%	ZSM-5 mordenite α -quartz	
$\square$	98%	ZSM-5	

content in the starting composition at 175°C are shown in Fig. 2. After 24 hours of reaction, the amounts of uncalcined products synthesized with water contents of 93, 95, and 98% were 0.5346, 0.5609, and 0.5041 g-dry per 1 g-solid in the starting composition, respectively. When the water content was increased from 95 to 98%, the induction period increased from 6 hours became to about 18 hours owing to the decrease in the raw material concentration. However, the XRD peak intensity of ZSM-5 reached 100 after 36 hours, and this state was maintained for 60 hours. Neither mordenite nor α -quartz was formed. When the water content was decreased from 95 to 93%, stirring could not be carried out thoroughly due to the resulting higher concentration, that is, an increase in the solid content of the starting material. Consequently, the induction period was longer than was expected; and ZSM-5 was present together with mordenite and α -quartz, and its intensity was as low as 60. α -Quartz became predominant after 72 hours. These results indicated that ZSM-5 was selectively synthesized under mild reaction conditions, but transformed into mordenite and α -quartz under more severe conditions. It was found that ZSM-5 was selectively synthesized by reacting with 95% water content at 175°C for 24 hours.

Fig. 3 Isothermal Phase Diagram of the Products of Zeolite Formed from Kanuma Pumice

Reaction conditions: water content of 95%, temperature of 175°C, time of 24 hours

Key: An: analime, M: mordenite, Z: ZSM-5, P: zeolite P, A: amorphous, α : α -quartz (α -quartz occurred in the dotted line region in Fig. 5)

3.2 Influences of Starting Composition on ZSM-5 Synthesis from Kanuma Pumice

It is known that to synthesize a metastable phase depends greatly upon the starting composition. Effects of molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{SiO}_2$ on the synthesis of zeolites were examined. The synthesis was carried out with water content 95% at 175°C for 24 hours. The product phase diagram is shown in Fig. 3. This is an overall result of about 70 starting compositions with varying $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios from 5 to 100 and $\text{Na}_2\text{O}/\text{SiO}_2$ ratios varying from nearly 0 to 1. The metastable phases besides ZSM-5 in the diagram are three, i.e. those for analime, mordenite, and zeolite P. These phases were identified with those described in the ASTM cards. The blank on the upper right side in the diagram is the region where solid products could not adequately be obtained in an autoclave of 24-ml capacity so as to conduct X-ray diffraction. A tendency for the metastable phases to be transformed successively into ZSM-5, mordenite, and analime by increasing the alkali content at a constant ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ was observed; also a tendency for substantially the same metastable phase to be synthesized even if the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ was varied at nearly a constant ratio of $\text{Na}_2\text{O}/\text{SiO}_2$ was observed. From these facts it can be seen that the synthesized metastable phase depends largely on the ratio of $\text{Na}_2\text{O}/\text{SiO}_2$ of the starting composition rather than on the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$.

Next, the water content was increased from 95 to 98%, and the results depicted in a phase diagram are shown in Fig. 4. The diagram is on the whole extended toward the higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ value than is in Fig. 3. The region where ZSM-5 was synthesized in a single phase has a higher ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ by 35–80 and a wider range of $\text{Na}_2\text{O}/\text{SiO}_2$ ratios. This seems to be attributable to the fact that the metastable phase of ZSM-5 is present even in the region of higher $\text{SiO}_2/\text{Al}_2\text{O}_3$.

Fig. 4 Isothermal Phase Diagram of the Products

Reaction conditions: water content of 98%, temperature of 175°C, time of 24 hours

Al_2O_3 ratios, because the concentration of the starting composition is low; thus, the transformation proceeds slowly as seen in the foregoing section.

On the other hand, a diagram obtained by raising the reaction temperature from 175 to 190°C using the same water content and reaction time as those in Fig. 3 is shown in Fig. 5. A similar tendency to that shown in Fig. 4 is seen in Fig. 5. The phase containing a very small amount of α -quartz is present over a wide region as can be expected from Fig. 1. From the viewpoint of

Fig. 5 Isothermal Phase Diagram of Products
Reaction conditions: water content of 95%,
temperature of 190°C, time of 24 hours

Fig. 6 Changes in Primary Peak ($2\theta = 23.0^\circ$) in XRD of ZSM-5 Synthesized with Varied Revolution per Minute as a Function of the Speed of Revolution (a) and the Reaction Time (b)

Reaction conditions: temperature of 175°C
water content $\square$: 93%, $\circ$: 95%, $\triangle$: 98%
a: after 24 hours, b: at 200 rpm

transformation of the metastable phase, it is quite strange that ZSM-5 is present together with α -quartz. This seems to be ascribable to the faster transformation of mordenite to α -quartz than that of ZSM-5 to mordenite when the reaction temperature is raised, rather than to the accelerated transformation to the stable phase. This is also supported by the fact that the single phase of ZSM-5 can be synthesized at low ratios of $\text{Na}_2\text{O}/\text{SiO}_2$ under more gentle reaction conditions. Kulkarni et al³⁰ has also showed that ZSM-5 can be present together with α -quartz, depending upon synthetic conditions, even when tetrapropylammonium or triethyl-*n*-propylammonium bromide is used as an organic reagent.

3.3 Influence of Stirring on ZSM-5 Synthesis from Kanuma Pumice

Results of the effects of stirring on ZSM-5 synthesis from starting compositions of the following water contents; 93, 95, and 98% at 175°C for 24 hours are shown in Fig. 6a. Amounts of uncalcined products synthesized at 200 rpm from the above water contents were, respectively, 0.5631, 0.5629, and 0.5730 g-dry per 1 g-solid in the starting composition. Changes in crystallinity with time at 200 rpm are shown in Fig. 6b. The crystallinity of ZSM-5 increased with increasing rpm, but the starting materials were thrown onto walls of the autoclave by centrifugal force when rpm exceeded 200. The crystallinity of ZSM-5 then decreased by drop in stirring effect. The

(a)

(b)

Fig. 7 SEM of ZSM-5 Formed from Kanuma Pumice at 200 rpm, (a) Water Content of 95%, (b) 93%

synthesis with 98% water content required 36 hours until the peak intensity reached 100 as shown in Fig. 2, but 24 hours were sufficient at 200 rpm. The synthesis with 93% water content was improved by stirring effect as shown in Fig. 2, though the presence of large quantities of solid matters prevented thorough stirring. The peak intensity exceeded 100 at 150 rpm or more. The peak intensity with 95% water content exceeded 100 at less than 100 rpm. These facts were confirmed as shown in Fig. 6b that even though there was an induction period of 6 hours in all cases; 18 hours was adequate for crystallization. SEM of ZSM-5 synthesized with the water contents of 95 and 93% at 200 rpm exhibited excellent crystallization as shown in Figs. 7a and 7b, respectively. It was found in these SEMs that growth of the crystals proceeded up to a secondary particle.

3.4 Catalytic Properties of Synthesized Zeolites

TPD spectra obtained were characterized by three desorption peaks (l-, m-, and h-peaks at low, moderate, and high temperatures, respectively) on the H type of every zeolite; and by two peaks (l- and m-peaks) on the Na type, as shown in Fig. 8. The l-peak is ascribable to very weakly or physically adsorbed ammonia on zeolites, and if does not depend on the catalyst properties, but rather on the experimental conditions⁴⁾. Thus, the acidity is defined as a total of m- and h-peak areas. Acid strengths can be estimated from the peak maximum temperatures of m- and/or h-peaks. A comparison of these temperatures resulted in the following sequences for the acid strengths of H- and Na-zeolites, respectively:

P-HZSM5-RM = TPA-HZSM5-AM
> P-HZSM5-AM (1)

P-NaZSM5-RM > P-NaZSM5-AM
> TPA-NaZSM5-AM (2)

While a comparison of these areas gave the following sequence for the acidity of each type:

P-ZSM5-RM > TPA-ZSM5-AM
> P-ZSM5-AM (3)

The weak acidity of P-HZSM5-AM can be attributed to the fact that ion exchange had not sufficiently been done for the zeolite from impurity-containing pumice.

Results of the alkylation of toluene with

Fig. 8 TPD of NH₃ on ZSM-5
(a) P-HZSM5-AM, (b) P-NaZSM5-AM,
(c) P-NaZSM5-RM, (d) P-HZSM5-RM,
(e) TPA-HZSM5-AM, (f) TPA-NaZSM5-AM
Nomenclature is shown in the text.

Table 1 Comparison of Alkylation of Toluene with Methanol

Catalyst		Kanuma pumice				Mobil's method	
		Amplitude method		200-rpm Rotating method		Amplitude method	
		P-NaZSM5-AM	P-HZSM5-AM	P-NaZSM5-RM	P-HZSM5-RM	TPA-NaZSM5-AM	TPA-HZSM5-AM
Conversion of toluene (%)		32.8	50.8	35.9	49.1	63.3	46.9
Selectivity to <i>p</i> -/ <i>m</i> -/ <i>o</i> -xylene (%)		100/0/0	33/47/20	70/13/18	39/46/14	39/46/14	27/65/8
Yield of products based on toluene used (%)	<i>p</i> -xylene	22.3	16.4	32.7	16.2	20.7	20.1
	<i>m</i> -xylene	0	23.3	5.9	19.1	24.5	48.4
	<i>o</i> -xylene	0	9.8	8.4	5.8	7.5	5.6
	benzene	0	2.2	0	2.8	3.4	7.5
Others*		77.7	48.3	53.0	56.1	43.9	18.4

Experimental conditions are shown in the text.
Others* contained ethylbenzene, *p*-ethyltoluene, *m*-ethyltoluene and trimethylbenzene.

methanol over different zeolites are given in **Table 1**. In spite of about one-half acidity of TPA-HZSM5-AM on m- and h-peaks, P-HZSM5-AM gave nearly the same conversion of toluene and also nearly the same yield of *p*-xylene as did TPA-HZSM5-AM. P-HZSM5-RM having strong acidity for m- and h-peaks also showed almost the same values as P-HZSM5-AM. These results imply that strong acidity for m- and h-peaks is not necessarily important to this reaction. Despite almost the same conversion of toluene, P-HZSM5-RM and P-HZSM5-AM gave smaller yields of xylene isomers, especially of *m*-xylene than TPA-HZSM5-AM. It is generally known that the basic sites of zeolites are active for alkylation of the methyl group of toluene^{5),6)}. These facts suggest that the yield of ethylbenzene for either P-HZSM5-RM or P-HZSM5-AM be larger than that for TPA-HZSM5-AM. On the other hand, there was a significant difference among the three types of Na-ZSM-5. P-NaZSM5-AM gave half the conversion that TPA-NaZSM5-AM did, but produced only *p*-xylene, indicating its selectivity to *p*-xylene to be 100%. The conversion over P-NaZSM5-RM was nearly equal to that over P-NaZSM5-AM. The selectivity to *p*-xylene for the former catalyst was between that for the latter and that for TPA-ZSM5-AM.

As described above, it was confirmed that the ZSM-5 zeolites synthesized from Kanuma pumice was as effective as those prepared by known methods, including the Mobil's method, for the catalytic alkylation of toluene with methanol to xylene and ethylbenzene, and the zeolites even showed higher selectivity to *p*-xylene than to other xylene isomers. The selectivity depended on the conditions of synthesis of the zeolites which could be also used for other catalytic reactions.

4. Conclusions

When Kanuma pumice was used in the starting composition (1), ZSM-5 could be synthesized owing to the effect of humic substances, but sometimes it could not depending upon the operating conditions. It was found that ZSM-5 could selectively and effectively be synthesized under mild reaction conditions; i.e., at 175°C and for 24 hours; however, it was transformed into

mordenite and α -quartz under more severe conditions. It was also found that the phases of the products obtained depended distinctly on the starting composition; i.e., water content, the ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{SiO}_2$, etc.. Typical results are summarized in the phase diagrams that show relationships between the starting composition and the product. The diagrams clearly show that whether the metastable phase or ZSM-5 is selectively synthesized or not depends largely on the ratio of $\text{Na}_2\text{O}/\text{SiO}_2$ rather than on the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the starting composition. With increasing water content in the starting composition from 95 to 98%, or with increasing reaction temperature from 175 to 190°C, ZSM-5 could be synthesized up to a high ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$, i.e. from 45 up to 90 or 75. The effect of stirring could be increased by the rotating method in place of the amplitude method, and the crystals of ZSM-5 could be grown to secondary particles. A comparison of acid strengths of H and Na types of ZSM-5 gave rise to sequences (1) and (2), respectively, and a comparison of acidities of each type gave sequence (3). The reactivity of toluene with methanol was not significantly different among the H-ZSM-5's synthesized according to different methods. The conversion of toluene over P-NaZSM5-AM was about half of that over TPA-NaZSM5-AM, but the former could produce only *p*-xylene. P-NaZSM5-RM showed the same level of conversion as that of the former and a lower selectivity to *p*-xylene. It was found that ZSM-5 zeolites synthesized from Kanuma pumice are as effective for alkylation of toluene with methanol as those prepared by conventional or known methods.

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要 旨

鹿沼軽石からの ZSM-5 合成における出発組成と操作条件の効果および生成 ZSM-5 の触媒特性

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前報¹⁾では、一組の出発組成について、鹿沼軽石を用いた ZSM-5 ゼオライト (P-NaZSM-5) の合成を検討した。続いて本報では、触媒調製の観点から、 Na_2O 、 SiO_2 、 Al_2O_3 、 H_2O など出発組成の濃度、および、合成時の温度、時間、かくはんなどの操作条件による ZSM-5 合成条件の変化を検討した。

鹿沼軽石などの原料、ゼオライト合成の方法、生成ゼオライトの同定法は、前報と同じであった。出発組成(1)のモル組成 $\text{Na}_2\text{O} : 5.0$, $\text{SiO}_2 : 41.0$, $\text{Al}_2\text{O}_3 : 1.0$, $\text{H}_2\text{O} : 940$ において、反応温度および水分を変化させた時、生成物の XRD における特性ピークは、それぞれ **Fig. 1, 2** のように、時間とともに変化した。いずれの場合も、誘導期間の後に ZSM-5 が出現し、反応の経過とともに、モルデナイト、さらに α -石英へと準安定相が推移していく傾向があった。

つぎに、175°C, 24 時間、水分 95% の合成条件において、出発組成中の $\text{Na}_2\text{O}/\text{SiO}_2$ と $\text{SiO}_2/\text{Al}_2\text{O}_3$ モル比に対する生成物の相図を **Fig. 3** に示す。合成される準安定相は、出発組成の $\text{SiO}_2/\text{Al}_2\text{O}_3$ 比よりも、 $\text{Na}_2\text{O}/\text{SiO}_2$ 比に依存することがわかった。**Fig. 3** の水分を 95% から 98% へ増加した時、得られる生成物の相図を **Fig. 4** に示す。ZSM-5 の得られる領域が高 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 側へ移動した。また、**Fig. 3** の反応温度を 175°C から 190°C へ上昇した時、得られる生成物の相図を **Fig. 5** に示す。ごく少量の α -石英を共存する相が広範囲に存在した。これは、ZSM-5 がモルデナイトへ推移する速度よりも、モルデナイトが α -石英へ推移する速度の方が大きいことに起因していると思われる。

さらに、175°C, 24 時間で、出発組成(1)において水分を 93

%, 95%, 98% として合成した ZSM-5 に対するかくはんの影響を **Fig. 6a** に示す。また、200 回転における結晶化の時間変化を **Fig. 6b** に示す。回転数の増加とともに、また濃度(固型物質)の増加とともに、ZSM-5 の結晶化度は増加した。かくはん効果を増加すると、結晶化の時間を短縮できることがわかった。**Fig. 7** に 200 回転、水分 95%, 93% で合成した ZSM-5 の SEM を示す。

合成した ZSM-5 の触媒特性は、 NH_3 による TPD 測定 (**Fig. 8**) と、トルエンのメタノールによるアルキル化反応の測定 (**Table 1**) によって調べた。使用したゼオライトは、出発組成(1)を振幅法(振幅 10 cm, 60 回/秒)と回転法(200 rpm)で、175°C, 24 時間で合成した ZSM-5 (それぞれ P-ZSM5-AM, P-ZSM5-RM) の Na と H 型である。また、テトラ-*n*-プロピルアンモニウム (TPA) 塩を用いて合成したものの (TPA-ZSM5-AM) についても測定した。H と Na 型の酸強度を比較して、それぞれ序列(1), (2)を得た。酸性度については、両型とも序列(3)を得た。トルエンのメタノールに対する反応性は、各法の H 型において大きな差がなかったが、Na 型においては異なった。P-NaZSM5-AM は、トルエンの転化率については TPA-NaZSM5-AM の半分であったが、*p*-キシレンのみを生成した。P-NaZSM5-RM は、TPA-NaZSM5-AM と同じ程度のトルエン転化率を示したが、*p*-キシレン選択率はむしろ低かった。鹿沼軽石から合成した ZSM-5 は、トルエンのアルキル化について、既知法で調製したものと同程度有効であった。

Keywords

Catalyst preparation, Crystallization, Pumice, Zeolite, ZSM-5