Effect of Humic Substances in Kanuma Pumice on Hydrothermal Synthesis of ZSM-5 Zeolite

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Weathered pumice from Kanuma admixed with silicon dioxide was subjected to hydrothermal synthesis in a NaOH medium. ZSM-5 zeolite was synthesized without addition of any organic reagent as a template by using Kanuma pumice as a starting material. It is suggested that this be possible due to the synergistic effect of the bound water [H$_2$O(+)] holding the Kanuma pumice colloidal and the humic substances in the pumice.

1. Introduction

Weathered pumice from Kanuma, so-called Kanuma-tsuchi or Kohshitsu-do, abounds in allophane1),2), which is one of the amorphous clay minerals and contains abundance of silica and alumina gels. The pumice admixed with alkali and water may adequately be used as a raw material for zeolite synthesis.

Barrer3) has mentioned of clay minerals as silica and alumina sources for zeolite synthesis and, especially, for the zeolites made from kaolin and meta-kaolin. Ottana4) has reported on hydrothermal synthesis of ZK-19 and phillipsite from Lipari pumice in the alkaline and in the saline environment. Burriesci5) has synthesized faujasites from a pumice in the low temperature range of from 85 to 95°C. Yoshida6) has reported the formation of faujasite-type zeolites from the ground Shirasu volcanic glass. In addition, there are reports on the synthesis of zeolite A7), faujasite8), and mordenite8) from allophane; but, there is no report on ZSM-5 zeolite synthesis from clay minerals.

ZSM-5 zeolite was originally synthesized from a reaction mixture that contained a tetrapropylammonium salt (TPA)10). In recent years, beginning with the use of other quaternary ammonium compounds10),12), amines13), alcohols14), etc. instead of TPA, many reports on the examples of organic compounds having many sorts of functional groups, including carboxylic acids, substituted hydrocarbons, etc.10),15), have appeared. Now, the synthesis of ZSM-5 from a reaction mixture composed of no organic species but only inorganic species is presented. For example, alkali or alkaline earth metal hydroxides16), alkali metal chlorides17), and sodium hydroxides18) have all been claimed to be effective for the synthesis.

When natural soil is used as a raw material of zeolite, a great variety of impurities generally cause serious problems; there is another problem associated with humic substances found in the soil. They are organic matters consisting of humic acid, fulvic acid, and humine. Humic acid is not soluble in aq. mineral acid solutions, but soluble in dilute aq. alkali solutions19),20). Fulvic acid is soluble in both types of solutions. Humine is not soluble in weak aq. alkali solutions, but soluble in a solution of about 10% NaOH. Humic acid is a condensation product resulted from aromatic compounds of the polyhydric phenol form and nitrogen-containing compounds, and the acid is an aggregate of amorphous high molecular materials having a mean molecular in the order of 10,000, and having ion exchange and colloid properties, but its chemical structure is unknown. The elemental analysis of humic acid shows that its carbon content is 50~65% and hydrogen content is 4~6%, and the remaining is mostly oxygen. Fulvic acid contains less carbon and more oxygen than humic acid. Moreover, humic acid and others are polymerized or condensed by liberating carbon dioxide and water.

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to give more stable humines. The engineering utility of these soil humic substances has not so far been presented. In this study, the authors have presented how the humic substances in the pumice have influenced the synthesis of ZSM-5 zeolite when Kanuma pumice was used as the raw material.

2. Experimental

2.1 Materials
Kanuma pumice, which is found widely in Tochigi prefecture, Japan, and used as the raw material, is light yellow aggregates from Terauchi district of Mohka city. The raw pumice contains some pyroclastic rocks such as magnetite, augite, hornblende, quartz, etc. Refined Kanuma pumice was obtained after classifying the finely divided raw pumice using a Novel's elutriation apparatus. The chemical composition, TG-DTA curves, powder XRD pattern, and SEM of the refined Kanuma pumice are shown in Table 1, Figs. 1, 2a, and 3a, respectively. The molar ratio of SiO₂/Al₂O₃ of Kanuma pumice is 1.73. In order to have a starting composition for zeolite synthesis high in silica, silicon dioxide, amorphous precipitated silica, has been added.

2.2 Synthesis of Zeolite

2.2.1 P-ZSM-5 Zeolite
The synthesis of zeolite using Kanuma pumice

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Table 1: Chemical Composition of Kanuma Pumice and Properties of Products

<table>
<thead>
<tr>
<th>Composition</th>
<th>Content [wt%]</th>
<th>Specific surface area [m²/g-cat]</th>
<th>P-NaZSM-5</th>
<th>TPA-NaZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adhesion Water [H₂O(−)]</td>
<td>66.52</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ignition Loss</td>
<td>15.62¹</td>
<td>Mean pore diameter of powdered sample [Å]</td>
<td>13.0</td>
<td>13.2</td>
</tr>
<tr>
<td>H₂O(+)</td>
<td>30.70</td>
<td>SiO₂/Al₂O₃</td>
<td>34.3</td>
<td>34.3</td>
</tr>
<tr>
<td>SiO₂</td>
<td>30.65</td>
<td>Na⁺/Al₂O₃</td>
<td>3.15</td>
<td>1.67</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.58</td>
<td>Na⁺ [mol/g-cat]</td>
<td>1.53×10⁻³</td>
<td>1.01×10⁻³</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.92</td>
<td>Yield of 'as made' product [g-dry/1 g-sol. raw materials]</td>
<td>0.5699</td>
<td>0.5856</td>
</tr>
<tr>
<td>CaO</td>
<td>1.18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>1.44</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>1.54</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹) Organic matters (1-40 wt%) are included in this value.
²) This is not the diameter of the micropores in the framework of ZSM-5, but one evaluated by surface area and pore volume which were measured by BET method and vapor pressure method, respectively. The diameter of ZSM-5 known to be about 6 Å.

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Fig. 1 TG-DTA Curves of Kanuma Pumice

Fig. 2 X-ray Diffraction Patterns of Pumice and Products
(a) Kanuma pumice; (b) p-NaZSM-5; (c) TPA-NaZSM-5; (d) Product of starting composition (3)
was hydrothermally carried out by shaking it in an autoclave (SUS 316) of 24 ml at 175° C for 24 hours. Starting molar composition (1) was Na₂O: 5.0, SiO₂: 41.0, Al₂O₃: 1.0, H₂O: 940.

Amounts of Kanuma pumice (wet, 60.8% H₂O), 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. The 'as made' product was separated from the mother liquor by filtration, washed with water to pH=9, and then dried in air at 110° C for 2 hours, and finally calcined in air at 500° C for 16 hours. The Na-ZSM-5 thus produced was designated as P-NaZSM-5. H-ZSM-5 was prepared by cation exchange by adding 25 ml of NH₄NO₃ solution (1 mol l⁻¹) per 1 g of Na-ZSM-5, maintaining the temperature at 80° C for 1 hour and then calcining in air at 450° C for 6 hours. The H-ZSM-5 prepared from P-NaZSM-5 was designated as P-HZSM-5.

2.2.2 TPA-ZSM-5 Zeolite

In order to evaluate P-ZSM-5, the synthesis of zeolite according to the Mobil's method was carried out by using an organic salt (TPA-iodide), aluminium hydroxide, and silicon dioxide in a similar manner as above. The starting molar 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). Amounts of sodium hydroxide, TPA (iodide), aluminium hydroxide, silicon dioxide, and water used were 0.2671 g, 0.8394 g, 0.1548 g, 2.4932 g, and 15.0000 g, respectively. This zeolite is designated as TPA-ZSM-5. The starting molar composition (3) was that of starting composition (2) in which NaOH instead of TPA was used. This also corresponds to starting composition (1) in which Kanuma pumice was not used.

![Fig. 3 SEM of Pumice and Products](image-url)

(a) Kanuma pumice, (b) P-NaZSM-5, (c) TPA-NaZSM-5, (d) Product of starting composition (3), (e) Product using the extracted residual pumice, (f) Product using the extract

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2.3 Characterization of Material and Product

2.3.1 X-Ray Diffraction (XRD)
Powder samples, prepared by lightly pressing the powder into depressions in a glass plate, were examined in random orientation with a Rigaku Gaigaflex 2013.

2.3.2 Scanning Electron Microscopy (SEM)
Powder samples were placed on a brass holder, and were coated with gold. They were examined in an Akashi Sigma I.

2.3.3 Thermogravimetry-Differential Thermal Analysis (TG-DTA)
Powder samples held in a Pt-Rh pan were examined in a Rigaku Thermoflex 8112H in a flow of air (100 ml min\(^{-1}\)) by using alumina as a reference.

2.4 Extraction and Determination of Humic Substances
Extraction of the humic substances contained in Kanuma pumice was carried out by taking into account of the result of preliminary examination according to the Kumada method\(^\text{20}^\text{)}\). One gram of pumice was shaken occasionally with 15.6 ml of NaOH aq. solution (0.1 mol l\(^{-1}\)), and the mixture was heated in a water bath at 85°C for from 10 to 30 minutes. The extract and residue were separated by centrifuging the mixture at 4,000 rpm for 30 minutes. Weight of the humic substances was evaluated as 1.724 times\(^{\text{22}, \text{23}}\) that of carbon which was measured with a Yanaco CHN corder MT-1.

3. Results and Discussion

3.1 Characterization of Zeolites
The amount of uncalcined product synthesized from composition (1) and the weight percentage of uncalcined product to solid in composition (1) was 1.7441 g and 56.1%, respectively; and those in starting composition (2) were 2.1986 g and 58.6%, respectively. Powder XRD patterns and SEM of calcined product from composition (1) are shown in Figs. 2b and 3b, respectively. Those of calcined product from composition (2) are also shown in Figs. 2c and 3c, respectively; this product was identified with ZSM-5 zeolite on the bases of Mobil’s patent\(^\text{10}^\text{)}\) and references\(^{\text{25}-\text{28}}\). The product from composition (1) using Kanuma pumice was also identified with ZSM-5. The powder XRD pattern and SEM of the product synthesized from starting composition (3) are shown in Figs. 2d and 3d, respectively. This product is not ZSM-5.

3.2 Effect of Calcined Kanuma Pumice on Zeolite Synthesis
It is worth noting that, in either case, ZSM-5 can be synthesized without addition of any organic salt or with addition of Kanuma pumice (1.3 wt\%) net) containing a variety of impurities. The successful synthesis of ZSM-5 from the impurity-containing pumice can be attributed to the fact that hydrothermal synthesis includes a purification process of crystallization. In order to investigate another cause, i.e., the bound water and humic substances, the synthesis of zeolite was carried out by using starting composition (1), having and using in place of uncalcined Kanuma pumice, that calcined in air in the temperature range from 110 to 1,000°C for 16 hours. Powder XRD patterns of the products calcined at 110, 250, and 700°C are shown in Figs. 4b, 4c, and 4d, respectively. Variation in intensity of the prime XRD peak (\(2\theta=23.0^\circ\)) as a function of calcination temperature appears in Fig. 5, in which the peak intensities can be roughly identified with three temperature regions, 150−200, 200−700, and 700−1,000°C. It is considered that a substance removed from Kanuma pumice by calcination at temperatures above 150°C is like an organic salt in that it is usually employed in the synthesis of ZSM-5. DTA shows an exotherm peak at 950°C but it hardly shows any weight loss above 700°C. Thus, the transition observed above 700°C is most likely to be a phase change to mullite\(^{\text{28}}\). It seems that the bound water of Kanuma pumice is largely lost in the temperature region of 200−700°C.

Fig. 4 X-ray Diffraction Patterns of Products using the Calcined Kanuma Pumice
(a) P-NaZSM-5 (uncalcined), (b) Product from pumice calcined at 110°C, (c) Product at 250°C, (d) Product at 700°C
Transition at 150–200°C seems to be attributed to the alternation and/or the disappearance of the humic substances. The existence of humic substances and their effectiveness on the synthesis of zeolite, therefore, were examined in detail.

3.3 Investigation and Effectiveness of Soil Humic Substances

The existence of humic substances in Kanuma pumice was confirmed. The results obtained are shown in Table 2. However, the amount of humic substances contained in Kanuma pumice was very small (1.4 wt%). The content of humic substances in starting composition (1) was also very small (198 ppm). On the other hand, the content of TPA in starting composition (2) was 4.5 wt%. It was found that the former (humic substances) was 228 times as effective as the latter (TPA). Therefore, the humic substances in Kanuma pumice were extracted with NaOH aq. solution (0.1 mol/l) for 10, 20, and 30 minutes. The amount of the humic substances contained in the extract and that in the residue are summarized in Table 2. Because humic and fulvic acids were gradually extracted from Kanuma pumice, the humic substances in the residue decreased with increasing extraction time to 61.6%, 48.6%, and 46.8% of the untreated. The results are shown in Fig. 6 when ZSM-5 was obtained by using the respective residues in starting composition (1). Although the humic substances in the residue after 10 minutes decreased to 61.6% of the untreated, the powder XRD pattern of the residue had nearly the same intensity as that of the untreated. This was also proven from SEM of the product after 24 hours as shown in Fig. 3e. But the crystallinity of ZSM-5 synthesized by using the residue which were obtained after extracting for 20 and 30 minutes did not catch up with that of the untreated. These cases seems to be lack in the amount of humic substances. ZSM-5 was not obtained in starting composition (3) as shown in Figs. 2d and 3d. By considering these facts, it was concluded that the humic substances, above their critical concentrations, were necessary for crystal-
lization of ZSM-5.

Effectiveness of the humic substances was also examined by adding the extract obtained after extracting for 30 minutes to original composition (3). The results obtained when the amount of the extract was changed from 45mg to 15mg are shown in Fig. 7. The crystallinity of ZSM-5 increased with increasing amount of the extract. However, the time required for attaining the maximum crystallinity was twice as long; moreover, the maximum intensity was small. This phenomenon seems to be attributable to the lack of critical amount of humic substances, and to the leak of adequate power of humic and fulvic acids. The results of SEM of ZSM-5 obtained after reacting for 48 hours in the presence of 45mg of the extract are also shown in Fig. 3f. It was found that the extract was also effective for crystallization of ZSM-5.

When the humic substances were extracted with a NaOH aq. solution of 0.1mol l\(^{-1}\), silica and alumina were also eluted as shown in Table 2. Amounts of silica and alumina in the extract after 30 minutes were, respectively, 1.44 mg and 2.32 mg per 1 g-dry Kanuma pumice, that is, per 15.6 ml of the NaOH aq. solution. It was concluded that the amounts of silica and alumina in the extract were negligible.

As mentioned above, the experiments with the extract and with the residue led us to the conclusion that the humic substances in the form of humus-clay complex and also bound water contained in Kanuma pumice were effective for synthesis of ZSM-5. It seems that excellent configuration or miscibility of silica and alumina gels, the humic substances, and water, etc. in Kanuma pumice gives a surprisingly good effect even though the amount of humic substances is only 1/228 of that of a strong reagent like TPA.

4. Conclusion

Kanuma pumice admixed with silicon dioxide was subjected to hydrothermal synthesis in a NaOH medium. It is worth noting that ZSM-5 can be synthesized without adding any organic compound from a starting material making up only 1.3 wt% of Kanuma pumice which contains various impurities. The yield of ZSM-5 from Kanuma pumice was almost the same (96%) as that from the Mobil's method. One of the causes of the success in the synthesis of ZSM-5 may be that hydrothermal synthesis includes a purification process of crystallization. The results from the synthesis of ZSM-5 by using calcined Kanuma pumice indicated that there seems to be another cause, that is, Kanuma pumice contains bound water and humic substances. The concentration of humic substances contained in Kanuma pumice was 1.4%. The humic substances were extracted with NaOH aq. solution, and the residue or the extract was used in the synthesis of ZSM-5. The crystallinity of ZSM-5 decreased with decreasing amount of the humic substances in the residue and increased with increasing amount of the extract. These facts showed that the humic substances were effective in the synthesis of ZSM-5. The concentration of the humic substances in the starting material was only 198 ppm and 1/228 of the amount of TPA. Thus, it can be concluded that ZSM-5 is synthesized by the synergistic effect of the humic substances in and the colloidal properties of Kanuma pumice.

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ZSM-5 ゼオライトの水熱合成における鹿沼軽石中の土壌腐植物質の効果

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軽石原料は, 栃木県真岡市内で採取した淡黄色の風化物で, 鹿沼土あるいは根室土とも言われるもので, 粉粋した原土からノール水液(は)装置で火山岩屑を除いたもの(Fig. 3a)を水熱合成に用いた。この鹿沼軽石風化物は, 非晶質な[ZSM-5(2a)]含水アルミノケイ酸塩(Table 1)であるアルミニウムの富み(Fig. 1), 表土下近くに分布していたことから1.4 wt%の土壌腐植物質(Table 1)を含んでいた。土壌腐植物質は, フリシン酸, フロボ酸, ヒルミンなどの成分からなっている。フリシン酸はアルカリ水溶液には溶けが, 酸には溶けない物質である。その元素分析は, 炭素50~60%, 水素4~6%で残りの大部が酸素である。粘土構造は不明であるが, その粒子は多面フェーネル状の芳香族化合物と腐植酸素化合物の負荷体であるし, 平均粒子数が数万程度の無定形分子物質の集まりである。フロボ酸は酸にもアルカリにも溶ける物質で, フリシン酸に比べて炭素含有量が少なく, 酸素も高くなっている。フルミンは, フリシン酸が無炭酸ガスおよび水を放出して重合すると仮に説明して, いっそう安定になったものである。石炭アルカリには溶解しないが, pH0~10程度のNaOH溶液に溶け出る。本報では, この鹿沼軽石を用いてZSM-5 ゼオライトの水熱合成を行い, 腐植物質のゼオライト合成に対する有効性を検討した。

SUS 316 製24mlのオートクレーブで, 175℃, 24 時間振とうしながらゼオライトを合成した。出発モデル構成(1)は, 
Na2O: 5.0, SiO2: 41.0, Al2O3: 1.0, H2O: 940, で, 高シリカにするために非晶質沈殿シリカを用いた。さらに, 軽石, シリカ, NaOH, 水はそれぞれ0.6640g, 2.3400g, 0.4089g, 14.5667gで, 生物質が1.7441gであった。この生物質のXRD, SEM をそれぞれFig. 2b, 3bに示す。テトラプロピリルアミノウレアオーダイドが用いられた結果(TPA-NaZSM-5 のXRD(Fig. 2c), SEM(Fig. 3c))と比較して, 鹿沼軽石を用いた合成生物質をZSM-5と同定し, P-NaZSM-5と称した。なお, 成形(1)で鹿沼軽石もTPAも用いなかった場合には, ZSM-5は生成しなかった(Figs. 2d, 3d)

つきに, ノールした鹿沼軽石を用いて合成した生成物のXRD Fig. 4に, その第1強ピーク(2θ=23.0°)の変化をFig. 5にそれぞれ示す。Table 1, Figs. 1, 5 から, 700~1,000℃の領域はムライトへの相変化, 200~700℃の領域は軽石中の結晶水の消失によるコロイド性の消減, 150~200℃の領域は腐植物質の変質さし消失にそれぞれ起因していると考えた。そして, 鹿沼軽石中のこれらの結晶水と腐植物質がZSM-5の合成に有効であると思われた。

そこで, 鹿沼軽石中の腐植物質をNaOH溶出(0.1 mol l-1)抽出した。抽出残土および抽出液中の腐植物質の量を
Fig. 6に示す。抽出時間の増加とともに, 抽出残土中の腐植物質は減少し, 抽出液中のそれは増加した。まずこの抽出残土を未処理の鹿沼軽石の代わりに用いて, ゼオライト合成した結果をFig. 7に示す。長時間抽出した残土を用いた場合ほど, ZSM-5の結晶化速度と結晶化度が低下した。これと鹿沼軽石を加えるなっくとも, ZSM-5が生成されなかったことから, 腐植物質はZSM-5の結晶化に必要であり, しかもある程度の濃度を要することがわかった。つぎに, 30分間抽出した抽出物を用いて同様にゼオライト合成を行った結果をFig. 7に示す。抽出物の増加とともにZSM-5の結晶化度が増加し, 抽出物もZSM-5の結晶化に有効であることがわかった。ただし, 不純物を含む鹿沼軽石をZSM-5合成に用いることができるの は, 水熱合成が完結するという特製工程を含んでいることも一因であると考えている。

Keywords
Crystalization, Humic substances, Pumice, Zeolite, ZSM-5

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