THE EFFECT OF ALKALINE TREATMENT ON THE PROPERTIES OF HIERARCHICAL ZSM-5 PREPARED BY POST-SYNTHESIS DESILICATION

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ABSTRACT

The effect of alkaline treatment on properties of hierarchical ZSM-5 was investigated in this work. The ZSM-5 zeolite was treated by aqueous solution of NaOH with variation concentration of 0.25, 0.5, 1.0 and 2.0 M. The properties of hierarchical ZSM-5 were characterized by XRD, FTIR, SEM, and isothermal N₂-sorption. The XRD analysis shows that all samples consist of ZSM-5 and tridymite phase. The NaOH treatment doesn't have a significant effect on the structural phase but greatly influence the crystallinity. The higher NaOH concentration, the lower the relative crystallinity. FTIR analysis confirms the presence of ZSM-5 structure without any new bonding formation. SEM examination revealed that NaOH treatment could change the morphology of the particles indicated by the formation of the hole and crack in the ZSM-5 particle's surface as a result of desilication. The N₂-sorption shows that increasing NaOH concentration can reduce the particle's surface area. The treatment succeeds to form mesopore in the initial ZSM-5 with a diameter of mesopore lies around 36-38 Å. The presence of micropore and mesopore in all samples confirms the formation of hierarchical ZSM-5 after alkaline treatment using NaOH solution.

Keywords: ZSM-5, Desilication, Hierarchical, NaOH Treatment, Mesopore

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INTRODUCTION

ZSM-5 is recently becoming one of the zeolite families that attract many researchers due to its unique acidity and well-defined microporosity. ZSM-5 has excellent heterogeneous acidity, great thermal and mechanical stability, well shape selectivity and interconnected two-dimensional micropore system which contribute to the usage as a catalyst in petroleum and petrochemical industry¹⁻³. However, the microporous nature of ZSM-5 imposes diffusion limitations for reaction or adsorption process, especially for large molecules. The mass-transfer limitation indirectly affects the catalytic activity, selectivity and lifetime of ZSM-5⁴. Based on these facts, it is desirable to improve the porosity properties of ZSM-5 for various applications. The properties of ZSM-5 could be enhanced by the formation of mesopore in the ZSM-5 particles. This formation of mesoporosity in ZSM-5, that naturally has micropore only, produces the hierarchical ZSM-5. The mesopore could enlarge the particle's surface area and shorter intracrystalline path length⁵. Moreover, this mesopore could optimize the diffusion of large molecules to reach the active site in the ZSM-5⁶.

The formation of mesopore in ZSM-5 resulting hierarchical mesoporous ZSM-5 could be carried out by using bottom-up or top-down process. The bottom-up process is carried out when mesoporosity was introduced to the ZSM-5 particle along with the synthesis process, for example by addition of organic structure directing agent (OSDA). In the other hand, the top-down process involves post synthesis treatment to the previous synthesized ZSM-5 by desilication and/or dealumination process⁷. However, the top-down process is usually applied for preparing mesoporous ZSM-5 as this process is easier to be conducted rather than bottom-up process. Due to its simplicity, the top-down process is also more visible to be conducted in large scale application. One of the most interesting processes in the top-down process is desilication of zeolites using an alkaline solution such as NaOH or KOH, or a weak organic base such

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as tetrapropylammonium hydroxide (TPAOH)⁸. This process could generate larger pore in zeolites particle resulting in hierarchical zeolites. In our case that ZSM-5 naturally has micropores only, the desilication could initiate the formation of mesopore or even macropore. This process could also form the interconnected mesopore system in the particle of zeolite thus increase the diffusion rate of the molecules to the zeolites particles^{6,9}.

The desilication process using NaOH solution on several zeolites has been reported by several researchers. Matias et al. (2011) reported that the desilication of TON zeolite (Si/Al=31) using NaOH with different concentration could create the mesopores with pore diameter about 20 nm. However, this alkaline treatment also gave a slight decrease in Brönsted acidity but a significant increase in Lewis acidity. Unfortunately, this desilication did not have influence in the catalytic activity¹⁰. Sadowska et al. (2013) also reported that the desilication of highly siliceous ZSM-5 using NaOH solution could be more effective in the surface zone of the particle than in the bulk. They also revealed that the increase of temperature used for desilication process could increase the extraction of Si as well as Al thus it could produce increasing of the volume and surface of the mesopore¹¹.

Those previous reports show that desilication is also potential to be further developed to prepare mesoporous ZSM-5. The further understanding of the alkaline solution parameter and its effect on the mesoporosity is still also crucial. Thus, in recent study, we focus on the effect of NaOH concentration to the mesoporosity and properties of ZSM-5. The concentration could influence the amount of Si that is extracted from ZSM-5 so it also influences the formation of mesopore in the ZSM-5 particles. The process of desilication process and their effect is discussed in detail.

EXPERIMENTAL

Material and Methods

The materials used in this study were NaOH pellets (Merck, Germany), commercial ZSM-5 (Pingxiang Naike Chemicals, China), Whatmann No.40 filter paper, ammonium acetate (Merck, Germany) and oxalic acid (Merck, Germany). Aqua DI (deionized water) was taken from a Millipore Milli-Q system and used within 1 week.

General Procedure

Parent ZSM-5 Preparation

The commercial ZSM-5 was directly used without further purification. Prior to modification of ZSM-5 with the post-synthesis desilication process, the commercial ZSM-5 was dried at 105 °C for 1 hour in the oven to remove excessive adsorbed water. The samples were then characterized using XRD to analyze the phase and crystallinity of commercial ZSM-5.

Desilication of ZSM-5 by Alkaline Treatment

Modification of hierarchical ZSM-5 with alkaline desilication was started by stirring NaOH solution at 500 rpm and heating to a constant temperature of 65 °C. The variation of NaOH concentration used was 0.25; 0.5; 1; and 2 M. After stirring, ZSM-5 was put into NaOH solution for 30 minutes with solid and liquid ratio of 33 g/L. After 30 minutes of stirring, the mixture of ZSM-5 and NaOH solution was quenched by cooling the mixture in ice water bath to reach room temperature. After that, the solution was filtered using Whatmann number 40 filter paper and washed using aqua DI. The washing process is repeated 3 times. Then, the obtained ZSM-5 was dried at 105 °C for 12 hours. The resulted product was then ion exchanged to form H-ZSM-5. This ion exchange process was carried out by mixing ZSM-5 with NH₄CH₃COO 1 N solution under stirring and refluxed at a constant temperature of 60 °C for 3 hours. The solid and liquid ratio for this process was 1 g over 20 mL of solution. ZSM-5 was then filtered and washed with aqua DI. ZSM-5 was dried in the oven with the temperature of 105 °C for 12 hours. The ZSM-5 was then calcined at 550 °C for 6 hours. The ZSM-5 that has been desilicated and cation exchanged is subsequently called ZSM-5-X with X was NaOH concentration.

Characterization of ZSM-5

The phase purity and crystallinity of ZSM-5 was analyzed using powder X-ray diffraction (XRD) PANalytical X'Pert MPD. The sample was placed in the sample holder. The X-ray irradiation was carried out using CuK α irradiation ($\lambda = 1.54056 \text{ \AA}$) at 2θ of 20 to 100° with a step size of 0.1°.

The crystallinity of the samples was analyzed using Equation 1. The highest peak is used to calculate this relative intensity. The I_{sample} is the intensity of the analyzed sample, and $I_{reference}$ is the intensity of the reference sample.

$$Relativeintensity = \frac{I_{sample}}{I_{reference}} \times 100\% \quad (1)$$

The Infrared analysis was performed to analyze the functional group of ZSM-5. This analysis is performed using Shimadzu Instrument Spectrum One 8400S on fingerprint area.

Scanning Electron Microscopy (SEM) was used to examine the morphological properties of ZSM-5. The analysis was carried out using ZEISS EVO MA. The sample was placed on carbon tape and coated with gold-palladium to increase the conductivity. The imaging process was performed using the Secondary Imaging (SE) detector.

The N₂-sorption was carried out to analyze the specific surface area and porosity of resulted ZSM-5. The analysis was performed using Micromeritics ASAP 2020. The analysis of specific surface area was calculated using Brunauer–Emmett–Teller (BET) adsorption isotherm model, while the analysis of pore diameter was calculated using Barrett–Joyner–Halenda (BJH) model.

RESULTS AND DISCUSSION

X-Ray Diffraction (XRD)

The XRD characterization is performed to analyze the phases that exist in the sample and the crystallinity as well. The diffractogram of the five samples is presented in Fig.-1. From Fig.-1, it is clear that all samples have, indeed, the typical peaks of ZSM-5 as indicated by the presence of peaks at $2\theta = 7.84$; 8.78 ; 22.98 ; 23.20 ; and 23.87° . However, all samples also exhibit additional peaks coming from another phase. Analysis of this additional phase shows that the peaks come from tridymite phase as indicated by peaks at $2\theta = 20.51$; 21.67 ; 23.24 ; 30.02 ; 35.74 ; and 35.98° . This result indicates that all samples consist of two phases, i.e. ZSM-5 and tridymite, where the main phases are still ZSM-5 because the characteristic peaks of ZSM-5 are the major peaks. The comparison between the characteristic peaks of ZSM-5 and tridymite is tabulated in Table-1 to ensure this finding.

Table-1: Characteristic Peaks of ZSM-5 and Tridymite

Samples	ZSM-5 (PDF No. 96-150-5107)	Tridymite (PDF No.96-901-3494)
ZSM-5	7.97; 8.83; 23.00; 23.20; 23.80	20.76; 21.70; 23.20; 29.94; 36.07
ZSM-5-0.25	7.87; 8.74; 22.93; 23.16; 23.79	20.71; 21.64; 23.16; 29.90; 35.55; 39.95
ZSM-5-0.5	7.89; 8.78; 22.77; 23.00; 23.63	20.60; 21.41; 23.40; 30.10; 35.41; 35.79
ZSM-5-1	7.81; 8.76; 22.92; 23.19; 23.82	20.74; 21.57; 23.19; 30.30; 35.91
ZSM-5-2	7.79; 8.74; 22.89; 23.14; 23.77	20.66; 21.55; 23.14; 29.78; 35.89

Figure-1 also shows the difference in intensity between the six samples. In a certain amount of NaOH concentration, the crystallinity of the samples is higher than the untreated (commercial) one. The calculation of relative crystallinity is presented in Table-2. The highest relative crystallinity (as much as 133.230%) appears when the ZSM-5 was treated with 0.25 M of NaOH. This crystallinity is slightly lower reaching 119.592% when the concentration is increased up to 0.5 M. However, these two concentrations still exhibit higher relative intensity than the untreated one. It might be caused by the reduction of tridymite intensity because the Si contained in the tridymite was also dissolved into NaOH solution. Tridymite was also a phase that contains a high amount of silica. The reduction of tridymite intensity affects the relative crystallinity of ZSM-5.

The increasing of NaOH concentration reduces significantly the relative crystallinity of the ZSM-5 as shown in ZSM-5-1 and ZSM-5-2. This reduction is caused by the dissolution of Si from the framework of ZSM-5 into NaOH solution. This Si dissolution occurs in the ZSM-5 surface that in contact with NaOH solution thus the crystal lattice of the ZSM-5 is still maintained^{4,9,12}. The dissolution of Si is predicted to form the additional pores without changing in the ZSM-5 crystal structure as shown by XRD result. Similarly, Li et al. (2014) previously reported that the using of NaOH concentration of 0.1-0.3 M did not

change the crystallinity of zeolites, but when the concentration is higher, the crystallinity would be reduced due to partial dissolution of zeolite particles¹².

Fig.-1: Diffractogram of Commercial ZSM-5 and Hierarchical ZSM-5

Table-2: Relative Crystallinity of Commercial ZSM-5 and Hierarchical ZSM-5

Materials	Relative Crystallinity(%)
ZSM-5	100
ZSM-5-0.25	133.230
ZSM-5-0.5	119.592
ZSM-5-1	69.5103
ZSM-5-2	57.8365

Fourier Transform InfraRed (FTIR)

Figure-2 shows the FTIR spectra of the commercial ZSM-5 and hierarchical ZSM-5 after desilication process. There are absorption bands in wave number of 450 and 550 cm^{-1} which indicate the presence of ZSM-5 crystals with MFI structure. This result in accordance with the previous report^{13,14}. The absorption band at 550 cm^{-1} refers to the vibration of the pentacyl skeleton on the zeolites. The absorption band at wave number 450 cm^{-1} shows the vibration of T-O-T bending as reported by Abello et al.⁴. In addition, the absorption band at wave numbers between 1120-1070 cm^{-1} and 1230-1070 cm^{-1} show the vibration associated with asymmetric T-O-T stretching vibration. The absorption band at 800 cm^{-1} refers to the symmetric stretching vibration of T-O-T¹²⁻¹⁴. These absorption peaks are tabulated in Table-3.

The IR spectra show that there is not formation of new functional groups as indicated by the absence of new bond formation during the desilication process. The desilication process is only a process of dissolving silica inside and outside the ZSM-5 crystals. The results of ZSM-5 FTIR analysis showed that the difference in NaOH concentration does not cause the formation of new functional groups or chemical bonds in the hierarchical ZSM-5.

Scanning Electron Microscopy (SEM)

Figure-3 shows the SEM micrograph of the commercial ZSM-5. As shown in the Fig.-3, it seems that there are several irregular particles besides the typical ZSM-5 particles. The typical ZSM-5 particles are usually indicated by the hexagonal formed particle. These irregular particles are possibly the particles from the tridymite that exist as an impurity. Surprisingly, the impurities phases of tridymite were

diminished by the addition of alkaline concentration as shown in Fig.-4. This is likely due to the dissolution of Si by NaOH solution.

Fig.-2: IR Spectra of Commercial and Hierarchical ZSM-5

Table-3: Spectra IR Data of Commercial and Hierarchical ZSM-5

Wavenumber					Functional Group
ZSM-5	ZSM-5-0.25	ZSM-5-0.5	ZSM-5-1	ZSM-5-2	
1222.9	1220.9	1222.9	1222.9	1217.1	asymmetric T-O-T stretching vibration
1097.5	1097.5	1097.5	1097.5	1099.4	asymmetric T-O-T stretching vibration
796.63	796.63	796.63	796.63	796.63	symmetric T-O-T stretching vibration
543	543.94	545.87	545.87	545.87	vibration of the pentacyl ZSM-5
451	449.43	449.43	455.22	459.07	T-O-T bending vibration

The NaOH treatment on ZSM-5 particle shows the formation of holes and crack in the surface of particles which are getting more massive until the side of the particles are eroded. ZSM-5-0.25 begins to experience slight damage on their particles. However, the irregular particles also begin to be diminished indicating the removal of impurity's particle. The higher NaOH concentration applied, the higher morphology reduction of ZSM-5 particles and the higher removal of irregular particles (impurity's particles). At the concentrations greater than 0.5, it seems that the destruction of ZSM-5 particles is more massive ZSM-5 as indicated by the eroded walls of the ZSM-5 particles. This result is in good accordance with the XRD result that shows the lowest relative crystallinity. The result is also in accordance with Khoshbin and Karimzadeh (2017) that alkali treatment could damage the morphology of ZSM-5 particles¹⁵.

N₂-Sorption

Figure-5 shows the BET isothermal curve of the commercial and hierarchical ZSM-5. Table-4 shows that the increasing NaOH concentration decreases the BET surface area (S_{BET}) of the particles. This decreasing of the surface area is predicted as a result of micropore damage to form mesopores. Increasing the specific surface area of BET (S_{BET}) in ZSM-5-0.25 confirms the dissolution of Si in tridymite and ZSM-5 phases so that it can increase the BET surface area. However, the surface area of ZSM-5-0.5; ZSM-5-1; and ZSM-5-2 decreases. This is caused by the damage of ZSM-5 crystals and an increasing number of mesopores after treatment with more concentrated NaOH solution. This result is in good accordance with the SEM image in Fig.-4 which shows that the damaging of ZSM-5 particles after treatment with concentrated NaOH solution.

Fig.-3: Micrograph SEM of Commercial ZSM-5

Fig.-4: Micrograph SEM of Hierarchical ZSM-5- (a) 0.25; (b) 0.5; (c) 1 and (d) 2

The reduction of surface area due to the formation of mesopore from micropore is confirmed by the presence of a hysteresis loop in the curves. It is clear that Fig.-5 shows the existence of micropores as indicated by the increasing curve at $p/p_0 < 0.1$ in all samples. This data confirms that conventional ZSM-5 has micropores in their particles. Furthermore, there is also mesopore as indicated by the presence of a hysteresis loop in all samples except ZSM-5-2.

The hysteresis loop is a characteristic of Type IV isothermal curves. It is caused by capillary condensation in the mesopore at high pressure^{6,16}. The hysteresis loop also shows a difference in the amount of gas adsorbed and desorbed at the same relative pressure. Several curves show the increasing in mesopore characteristics as indicated by the widening of the hysteresis loop. In ZSM-5-0.25, 0.5 and 1, there is wider hysteresis loop which shows increasing the number of mesopores¹⁷. ZSM-5-2 only shows slight hysteresis loops. However, it also shows the increasing of adsorption at $p/p_0 > 0.9$ indicating the possibility of macropores formation. This BET data revealed that the treatment of ZSM-5 using NaOH solution could increase the mesoporosity of the ZSM-5¹¹. However, at high concentration, such as 0.5 M, the mesoporosity might be tremendously reduced forming macropores.

Fig.-5: Isothermal Curve of N₂-Sorption from Commercial and Hierarchical ZSM-5Table-4: Isothermal N₂-sorption Analysis Data

Material	SBET (m ² /g)	Pore Volume (V)		Average Diameter Pore(Å)
		V Micro (cm ³ /g)	V Meso (cm ³ /g)	
ZSM-5	324.762	0.108	0.042	18.606
ZSM-5-0.25	334.185	0.108	0.056	19.701
ZSM-5-0.5	307.497	0.097	0.065	21.191
ZSM-5-1	173.068	0.062	0.047	25.436
ZSM-5-2	134.929	0.044	0.031	22.338

Pore size distribution analysis is carried out using the BJH method to determine the pore diameter. The BJH method is used for pore distribution analysis for meso-sized pore only. Figure-6 shows the pore size distribution (BJH) with the largest population of pore diameter at 36-38 Å. Increasing population or uniformity of pore diameter with diameters between 36-38 Å occurs in ZSM-5-0.25 and ZSM-5-0.5. However, the ZSM-5-0.25 with mesopore diameter greater than 36-38 Å is not formed.

Decreasing of micropore volume occurs with a higher concentration of NaOH as presented in Table-4. The micro-volume decreases due to the replacement of micropores with mesopores as desilication results. This is evidenced by the increasing of mesopore volume at ZSM-5-0.25, 0.5 and 1.0. Mesopores can grow from micropores which are increasingly enlarged to form mesopores. In addition, the decrease in mesopore volume occurs in ZSM-5-1 and ZSM-5-2 due to damage to ZSM-5 crystal structure^{6,11}. The decreasing of mesopore volume in ZSM-5-2 is also predicted as the result of the formation of macropores as shown by BET curves.

Fig.-6: Pore Size Distribution (BJH) Commercial and Hierarchical ZSM-5

CONCLUSION

The commercial and hierarchical ZSM-5 show that all samples consisted of ZSM-5 and tridymite phase as an impurity. The desilication process did not change in the crystal structure, but the crystallinity of ZSM-5 underwent changes where the highest crystallinity was obtained at NaOH 0.25 M. The difference in NaOH concentration did not cause the formation of new functional groups in ZSM-5 as shown by FTIR analysis. In addition, the increasing NaOH concentration also caused severe deterioration of ZSM-5

particles. Analysis with isothermal N₂-sorption shows that the surface area of the particle decreases as increasing of NaOH concentration. The NaOH treatment also succeeds to form mesopore in the particles as indicated by the presence of hysteresis loop. However, at high concentration, the mesopore is tremendously reduced forming macropore. The pore volume of the mesopore at the particles relies on 36-38 Å.

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