Synthesis of ZSM-5 zeolite from lignite fly ash and rice husk ash

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Abstract

The lignite fly ash from the Mae-Moh power plant, Thailand, and rice husk ash were used as raw materials for ZSM-5 zeolite synthesis. Factors affecting the yield of ZSM-5 zeolite synthesized from fly ash, i.e., the SiO2/Al2O3 mole ratio, the presence of tetrapropyl ammonium bromide (TPABr, the structure-directing material for ZSM-5 zeolite synthesis), the holding temperature and time, and the initial pressure were investigated. It was found that without TPABr only zeolite P could be synthesized at SiO2/Al2O3 mole ratios of 2.8–200. In order to synthesize ZSM-5 zeolite, sodium silicate solution was added to adjust the SiO2/Al2O3 mole ratio in raw ash. The yield of ZSM-5 zeolite was as high as 59 wt.% when following conditions were used: SiO2/Al2O3 mole ratio, 40; the holding temperature, 210 °C; the holding time, 4 h and the initial pressure, 4 bar. The catalytic performance for CO2 hydrogenation reaction of the ZSM-5 zeolite was preliminary tested and compared with that of commercial one. It was observed that there was no significant difference in the catalytic performance between these two catalysts.

Keywords: Fly ash; ZSM-5 zeolite; Rice husk ash; CO2 hydrogenation

1. Introduction

In Thailand, low quality lignite is found predominantly. Approximately 74% of coal produced are supplied to power station as energy source. The major problem in coal-fired power generation is that the plenty of solid waste so-called fly ash (of about 30% of raw
coal) is produced [1]. Previously, almost all the fly ash was disposed by landfill, which became increasingly expensive and caused an environmental problem. Therefore, fly ash utilization was considered by many investigators. Fly ash can be mainly used as building materials according to its pozzolanic properties [2–4]. However, due to the fluctuation of demand, the alternative utilization of fly ash as the raw material for zeolite synthesis was focused.

The synthesis of zeolites from fly ash can be classified into direct and non-direct synthesis. For the direct synthesis [5–13], fly ash was hydrothermally treated with an alkaline solution. At the temperature lower than 100 °C, zeolites P, X and Na–P1 were obtained with 2–4 M NaOH solution while hydroxy sodalite and zeolite Y were obtained with 4–10 M NaOH solution. At the temperature higher than 120 °C, zeolite Na–P1, hydroxy sodalite and analcime were obtained with 4–10 M NaOH solution.

For the non-direct synthesis [14,15], silica and alumina were firstly extracted from fly ash with hot alkaline solution and this resulted in the mixture of silicate and aluminate extracts. These extracts were used as the starting material for faujasite synthesis at as low a temperature as 60–90 °C and at a synthesis period of 2–5 days.

In this work, the direct synthesis of ZSM-5 zeolite using the Mae-Moh lignite fly ash as the main raw material was focused. However, the SiO2/Al2O3 mole ratio in the raw fly ash is too low to synthesize ZSM-5 zeolite (SiO2/Al2O3 mole ratio=2.8). In order to obtain the appropriate SiO2/Al2O3 mole ratio, the sodium silicate solution was added to adjust the mole ratio of raw fly ash. From the economic point of view, the sodium silicate solution prepared from rice husk ash was used instead of the commercial ones because there is an abundant supply of rice husk in Thailand. The factors affecting the ZSM-5 zeolite yield, i.e., SiO2/Al2O3 mole ratio, the presence of tetrapropyl ammonium bromide, temperature and initial pressure were investigated. In all cases, the most suitable condition that gave the maximum yield of ZSM-5 zeolite was focused.

2. Experimental

2.1. Raw feed and reagents

Lignite fly ash obtained from the Mae-Moh electric power station, Thailand, was ground and sieved to the diameter of lower than 0.074 mm. The sample was dried at 105 °C for 1 h and kept in the desiccator before use. Chemical compositions of fly ash were examined by X-ray Fluorescence Spectroscopy (XRF: Philips, PW 1400). Physical characteristics were analyzed by X-ray Diffraction Spectroscopy (XRD: Philips, PW 1830/40, Cu-α radiation) and BET surface area analysis (Quantachrome, NOVA 1200).

Sodium silicate solution (Na2Si3O7; 4 wt.% NaOH; 27 wt.% SiO2) was used to adjust the SiO2/Al2O3 ratio of fly ash mixture. First, rice husk was treated with 1 M HCl for 2.5 h. The treated rice husk was washed thoroughly with distilled water, dried at 120 °C and pyrolyzed in oxygen atmosphere at 600 °C for 1 h. The residual ash with about 99.6 wt.% silica was dissolved in NaOH solution to obtain a desired composition of sodium silicate solution.

Tetrapropyl ammonium bromide (TPABr; C12H28BrN) of 98% purity from Fluka Chemicals was used as a structure-directing substance for ZSM-5 zeolite preparation.
2.2. Synthesis of ZSM-5 zeolite from lignite fly ash

Batch experiments were carried out to determine effects of the SiO$_2$/Al$_2$O$_3$ mole ratio, the presence of TPABr, the temperature and the initial pressure on the yield of crystalline ZSM-5 zeolite. The characteristics of products were determined by XRD and Scanning Electron Microscopy (SEM: Jeol, JSM-5600 LV). The yield of ZSM-5 zeolite was obtained by converting the peak intensity of ZSM-5 zeolite from XRD analysis to weight of zeolite using of standard curved. The product yield was reported as wt.% of pure ZSM-5 zeolite in the solid product.

2.2.1. Effect of SiO$_2$/Al$_2$O$_3$ mole ratio and the presence of TPABr

In this series of experiments, 3 g of lignite fly ash was mixed with 50 cm$^3$ of 0.001 M NaOH solution and variable amounts of sodium silicate solution. The average SiO$_2$/Al$_2$O$_3$ mole ratio in raw fly ash was about 2.8 (data from XRF). Subsequently, the SiO$_2$/Al$_2$O$_3$ mole ratios were adjusted to 20, 40, 60, 80, 100 and 200 by adding the sodium silicate solution into the fly ash mixture. The TPABr (0.37 g, 20 mol% of alumina in fly ash) was added to the mixture. The 0.5 M H$_2$SO$_4$ solution was used to adjust the pH of the mixture (fixed at 11.0 ± 0.2). With fast synthesis process, the mixture was placed in the autoclave, pressurized at 3 bar by using nitrogen gas (99.99% purity) and then heated up from room temperature to 210 °C within 2 h. During this period, the pressure in the autoclave was autogeneously increased. The temperature was kept constant here for 2 h. By using this process, ZSM-5 zeolite can be synthesized in 4 h. The crude product was then separated from the solution, washed thoroughly with distilled water and dried in the oven at 110 °C for 2.5 h before analysis.

The experimental conditions in Sections 2.2.2 and 2.2.3 were the same as that of Section 2.2.1 unless otherwise indicated.

2.2.2. Effect of temperature

The effect of reaction temperature was examined using the same experimental conditions as those of Section 2.2.1 except the temperature and the holding time. The mixture was heated up from room temperature to 150, 180 and 210 °C with the heating rate of 1.5 °C/min and held there for 2 h. For the study of the effect of the holding time, the synthesis temperature was fixed at 210 °C and the holding time was varied from 0 to 4.0 h.

2.2.3. Effect of initial pressure

The optimum SiO$_2$/Al$_2$O$_3$ mole ratio and temperature determined in Sections 2.2.1 and 2.2.2 were used, and the initial pressures were varied from 1 to 6 bar. The detail of all experimental conditions is shown in Table 1.

2.3. Catalytic performance of ZSM-5 zeolite from fly ash

The catalytic performance of ZSM-5 zeolite synthesized from fly ash was examined in the hydrogenation reaction of carbon dioxide. The experiment was conducted in a catalytic packed bed reactor, made of SUS-316 (id. 7.6 mm). The reactor was 500 mm long, equipped with an infrared furnace. The ZSM-5 zeolite product (powder, 59 wt.% purity)
was packed in the isothermal zone of the reactor (bed length, 4 cm). The reactor was first flushed with N\textsubscript{2} (purity > 99\%) and heated to reaction temperatures (200–500 °C).

Reactant gases (CO\textsubscript{2} and H\textsubscript{2}) were allowed to flow at 50 ml (NTP)/min and the GHSV was approximately 16 h/\text{mol CO\textsubscript{2}}. The mole ratio of CO\textsubscript{2} to H\textsubscript{2} was 1:3 and the operating pressure was fixed at 5 bar. The amounts of CO\textsubscript{2}, CO and all hydrocarbon products were quantitatively analyzed using gas chromatography (Hewlett Packard 5890 series II) equipped with TCD and FID detectors and Porapack Q columns. The experiment was repeated three to five times in each condition.

3. Results and discussion

3.1. Chemical compositions of fly ash

The chemical compositions of fly ash analyzed by XRF are shown in Table 2, in which SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{2}O\textsubscript{3} and CaO are the major components. The X-ray diffraction pattern in

| Table 2 |
|---|---|
| Composition | Amount (wt.\%) |
| SiO\textsubscript{2} | 39.60 |
| Al\textsubscript{2}O\textsubscript{3} | 24.25 |
| Fe\textsubscript{2}O\textsubscript{3} | 12.60 |
| CaO | 10.66 |
| MgO | 2.80 |
| Na\textsubscript{2}O | 1.29 |
| TiO\textsubscript{2} | 0.49 |
| P\textsubscript{2}O\textsubscript{5} | 0.16 |
| Others | 8.15 |
Fig. 1 revealed the major solid compositions in the fly ash was amorphous in nature. The BET surface area of fly ash was 5 m²/g.

3.2. Synthesis of ZSM-5 zeolite from lignite fly ash

3.2.1. Effect of SiO₂/Al₂O₃ mole ratio and the presence of TPABr

Without addition of sodium silicate solution, the SiO₂/Al₂O₃ mole ratio in fly ash is 2.8. In order to obtain SiO₂/Al₂O₃ mole ratios of 20, 40, 60, 80, 100 and 200, lignite fly ash was mixed with 27.4, 59.1, 90.9, 122.6, 154.4 and 313.2 cm³ of sodium silicate solution, respectively. To dissolve the silica and alumina in fly ash, NaOH solution was added to the mixture while the pH of the mixture was controlled at 11±0.2. It was found that without TPABr, at the SiO₂/Al₂O₃ mole ratios of 2.8–200, only zeolite P could be synthesized. The XRD pattern of the zeolite P and amorphous solid products are shown in Fig. 2.

The effects of SiO₂/Al₂O₃ mole ratio (in the range of 2.8–200) and the presence of TPABr on the yield of ZSM-5 zeolite were investigated. The yields of ZSM-5 zeolite obtained from XRD patterns are shown in Fig. 3. The results reveal that without sodium silicate solution, the ZSM-5 zeolite could not be synthesized. It is clear that the SiO₂/Al₂O₃ mole ratio of 2.8 is not suitable for ZSM-5 zeolite synthesis. At the SiO₂/Al₂O₃ mole ratio of 20–100, ZSM-5 zeolite can be synthesized. The maximum yield of 43 wt.% was found at the SiO₂/Al₂O₃ mole ratio of 40.

The SEM photographs of the zeolitic products of various SiO₂/Al₂O₃ mole ratios are shown in Fig. 4. The obtained ZSM-5 zeolite is mainly cubic crystals, accompanying with some flake-like structure. As the SiO₂/Al₂O₃ mole ratio increases from 20 to 40, the cubic crystals of ZSM-5 zeolite are increased in size from 5 to 8 Å. However, the opposite trend was observed when the SiO₂/Al₂O₃ mole ratio is higher than 40. The smallest size of about 1 Å was found at the SiO₂/Al₂O₃ mole ratio of 100.

From this study, it was noticed that the fast synthesis process without TPABr, even if SiO₂/Al₂O₃ mole ratio was varied, could not produce ZSM-5 zeolite from lignite fly ash.
In addition, irrespective of the SiO$_2$/Al$_2$O$_3$ mole ratio, the addition of TPABr of approximately 20 mol% of alumina in fly ash still could not promote the ZSM-5 zeolite formation.

Since the maximum yield of the ZSM-5 zeolite was obtained at a SiO$_2$/Al$_2$O$_3$ mole ratio of 40, this mole ratio was then used in the following experiments.

![Fig. 2. XRD patterns of zeolitic products obtained from synthesis experiments without the presence of TPABr at SiO$_2$/Al$_2$O$_3$ mole ratios of (a) 20, (b) 40, (c) 60, (d) 80, and (e) 100 (Δ, Zeolite P; Initial pressure: 3 bar, holding temperature: 210 °C, holding period: 2 h).](image)

![Fig. 3. Yields of ZSM-5 zeolite obtained from various SiO$_2$/Al$_2$O$_3$ mole ratios with TPABr (Initial pressure: 3 bar, holding temperature: 210 °C, holding period: 2 h).](image)
3.2.2. Effect of temperature

The yields of the ZSM-5 zeolite obtained at temperatures ranging from 150 to 240 °C are shown in Fig. 5 and the SEM photographs of the products at 150 and 180 °C are shown in Fig. 6. At the temperature of 150 °C, the unknown amorphous solids of irregular shape and crystalline were found. It was noticed that the ZSM-5 zeolite could not be produced under this low temperature. The XRD pattern of the product obtained at 180 °C is shown in Fig. 7, which revealed that ZSM-5 zeolite (16 wt.%) and zeolite P were formed. At 210 °C, only ZSM-5 zeolite was found (43 wt.%). In accordance with the XRD result, the SEM photograph of the product at 180 °C indicates the presence of the cubic crystals of ZSM-5 zeolite and the needle-like crystals of zeolite P, while only the cubic
Fig. 5. Yields of ZSM-5 zeolite obtained from various holding temperatures (SiO₂/Al₂O₃ mole ratio: 40, initial pressure: 3 bar, holding period: 2 h).

Fig. 6. SEM photographs of treated products obtained from synthesis at holding temperatures of (a) 150 °C, (b) 180 °C, and (c) 210 °C (SiO₂/Al₂O₃ mole ratio: 40, initial pressure: 3 bar, holding period: 2 h).
crystals of the ZSM-5 zeolite were found at 210 °C. The reason is that the formation of metastable phases of zeolites depend on temperature, and then the most stable phase will continue to grow and be detected finally [16]. Not only the temperature, but the holding time and the initial pressure also play an important role on the formation of the specific metastable phase of zeolite.

For the study on the effect of the holding time, the synthesis temperature was fixed at 210 °C and the holding time was varied at 0, 1, 2, 3 and 4 h. The yields of the product crystals shown in Fig. 8 notify that the longer the holding time, the greater the yield of ZSM-5 crystalline zeolite. As the holding time increased, the alkaline solution could more thoroughly dissolve silica and alumina from the fly ash. These silica and alumina in the alkaline solution are the sources of precursors for ZSM-5 zeolite formation and growth.

![Fig. 7. XRD pattern of zeolitic products obtained from synthesis temperature of 180 °C (O=ZSM-5 zeolite, Δ=Zeolite P) (SiO2/Al2O3 mole ratio: 40, initial pressure: 3 bar, holding period: 2 h).](image)

![Fig. 8. Yields of ZSM-5 zeolite obtained from various holding periods (SiO2/Al2O3 mole ratio: 40, initial pressure: 3 bar, holding temperature: 210 °C).](image)
Therefore, the longer holding time used (in this study, 4 h) the higher yield of ZSM-5 zeolite could be obtained.

### 3.2.3. Effect of initial pressure

The effect of the initial pressure of inert gas on the yield of ZSM-5 zeolite was determined in the range of 1–6 bar. The yields of the ZSM-5 zeolite obtained at various initial pressures are shown in Fig. 9. It should be noted that all the XRD patterns of the products confirm the existence of only ZSM-5 zeolite. The ZSM-5 zeolite yields are gradually increased with the increase of initial pressure up to 4 bar (13 wt.% at 1 bar and 43 wt.% at 4 bar) and then decreased (31 wt.% at 5 bar and 26 wt.% at 6 bar). The initial pressure has a significant effect on the ZSM-5 zeolite synthesis. This is because the synthesis process takes place at high temperature under steam saturation condition. The increase of the initial pressure thermodynamically enhances the solubility of silica and alumina in fly ash in the alkaline solution and consequently the rate of formation of the ZSM-5 zeolite. However, at the initial pressure above 4 bar, the yield of ZSM-5 zeolite tends to decrease. This may be due to the competitive formation of different metastable phases of zeolite during the crystalline formation stage, which resulted in the formation of different phases of zeolite [16].

### 3.3. Hydrogenation of carbon dioxide over ZSM-5 zeolite from fly ash

The catalytic performance of ZSM-5 zeolite synthesized here was preliminary tested and compared with a commercial ZSM-5 zeolite (SiO$_2$/Al$_2$O$_3$ ratio, 40; surface area, 670 m$^2$/g). The average results are shown in Table 3. With both catalysts, CO$_2$ conversions are gradually increased with the increase of reaction temperature (from 2–3 mol% at 200 °C to 28–30 mol% at 500 °C). In order to investigate the effect of thermal reaction, the reaction was tested under the same operating condition with an inert sand bed. It was
found that the conversion of CO2 over the sand bed at 500 °C was lower than 5 % and methane was the major product.

The CO2 conversion of the synthesized ZSM-5 zeolite and the commercial one were comparable. The products were mainly CO, methane and ethane. However, higher yields of C2–C3 were obtained with the synthesized ZSM-5 zeolite. At 500 °C, the C2–C3/CH4 ratios were 0.3 with the synthesized ZSM-5 zeolite and 0.15 with the commercial one. It was suggested that metal oxide impurities remained in the synthesized ZSM-5 zeolite seem to have a little effect on the catalytic hydrogenation reaction.

4. Conclusions

The alternative utilization of Mae-Moh lignite fly ash and rice husk ash as raw materials for ZSM-5 zeolite synthesis is feasible. The effects of SiO2/Al2O3 mole ratio, the presence of TPABr, temperature and initial pressure on the yield of ZSM-5 zeolite have been investigated using the fast synthesis process (about 2–6 h). Without the addition of sodium silicate solution, ZSM-5 zeolite could not be synthesized. With the presence of TPABr, ZSM-5 zeolite could be synthesized in a range of the SiO2/Al2O3 mole ratio of 20–100. At a holding temperature of lower than 210 °C, several types of zeolites were produced. The maximum yield of ZSM-5 zeolite, 59 wt.%, was obtained at a SiO2/Al2O3 mole ratio of 40, synthesis temperature of 210 °C, holding time of 4 h and initial pressure of 4 bar.

The catalytic performance of ZSM-5 zeolite synthesized from fly ash in the hydrogenation of CO2 is remarkable. The conversion of CO2 was 30 mol% at 500 °C and the products were carbon monoxide, methane, ethane and propane. With ZSM-5 zeolite synthesized from fly ash, higher yield of C2–C3 was produced when compared with the commercial one.

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