SYNTHESIS of ZEOLITE SOCONY MOBIL–5 FROM RICE HUSK ASH

Đến tòa soạn 20-02-2021

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TÓM TẮT

TỔNG HỢP ZEOLITE SOCONY MOBIL–5 TỪ TRO TRẤU

ZSM-5 là một loại zeolit có hàm lượng silic cao và được sử dụng phổ biến trong các lĩnh vực như: xúc tác, trao đổi ion và hấp phụ. Tro trấu, nguồn silica tự nhiên phong phú với hàm lượng SiO_2 vô định hình cao, thích hợp cho quá trình tổng hợp ZSM-5. Trong nghiên cứu này, SiO_2 đã được điều chế thành công từ tro trấu và được sử dụng làm tác chất phản ứng để điều chế ZSM-5. Các yếu tố chính ảnh hưởng đến quá trình tổng hợp ZSM-5 bao gồm tỷ lệ mol SiO_2 / Al_2O_3, nhiệt độ phản ứng và thời gian phản ứng đã được khảo sát. Kết quả phân tích XRD và SEM cho thấy ZSM-5 được tổng hợp thành công với cấu trúc tinh thể và kích thước tinh thể trung bình 3-5 μm. ZSM-5 là một zeolit có kích thước mao quản trung bình và có nhiều tiềm năng ứng dụng trong thực tế.

Từ khóa: *Phương pháp thủy nhiệt, tro trấu, silica, ZSM-5.*

1. INTRODUCTION

Zeolite is a material based on aluminum and silicate of the alkaline or the alkaline earth metals. Currently there are several hundred types of zeolite derived from natural or synthetic sources [1-3]. Zeolite socony mobil–5 (ZSM-5) is a medium pore zeolite (a pore dimension of 0.54 - 0.56 nm) with a high silica content [4-7]. ZSM-5 is widely used for catalysis, ion exchange, adsorption due to the high surface area, great thermal stability, acidic activity, and molecule sieving capacity [1, 2, 4-8].

There are several methods to prepare ZSM-5 including hydrothermal treatment, colloidal pretreatment method, ultrasound-assisted alkali-treatment method, and microwave-assisted heating [7, 9-12]. Hydrothermal reaction is the most effective option to prepare ZSM-5 [1]. The reaction is based on precursors of SiO_2, Al_2O_3, and tetrapropylammonium bromide (TPABr). TPABr is often used as a template for the synthesis of ZSM-5 [1, 8]. Due to the economic and environmental aspects, the researchers have sought to take advantage of SiO_2 sources from nature instead of using synthetic chemicals [1, 13-15]. SiO_2 derived from natural silica sources for the preparation of ZSM-5 include fly ash, rice husk ash, and kaolin [1, 2, 10-13, 16, 17]. Studies show that the main factors influencing the ZSM-5 crystallization process include SiO_2/Al_2O_3 molar ratio, reaction temperature, and reaction time [14, 16, 18].

Rice husk ash is a by-product of the agricultural processing industry and is abundant in Vietnam, especially in the Mekong Delta [19-21]. Currently, a part of rice husk ash is used as a source of plant mineral supplements [15, 17]. The major component of rice husk ash is amorphous SiO_2 and is often used as an adsorbent [2, 17, 19-23]. Therefore, the application of SiO_2 derived from rice husk to synthesize ZSM-5 can reduce the cost of the commercial production as well as minimize environmental pollution caused by rice husk ash [2, 14, 16, 18]. In this study, SiO_2 prepared from rice husk ash was used as a precursor in the preparation of ZSM-5. The effects of reaction factors on ZSM-5 synthesis were investigated.

2. MATERIALS AND METHODS

2.1. Materials

Sodium hydroxide (NaOH), hydrochloric acid (HCl), tetrapropylammonium bromide $(CH_3CH_2CH_2)_4N(Br)$, sodium hydroxide were purchased from Aldrich Sigma. A locally collected source (at Cai Rang District, Can Tho city, Vietnam) of rice husk ash was obtained for the preparation of SiO_2.

2.2. Methods

2.2.1. Preparation of silicon dioxide from rice husk ash

Silicon dioxide was extracted from rice husk ash using alkaline solvent [24]. Rice husk ash (20 grams) was added to 200 mL of 6 M NaOH at 95 °C for 4 hours. After filtration, the obtained solution was reacted with 4 M hydrochloric acid at pH 3 for 4 hours. After the reaction, the precipitate was filtered and washed several times with distilled water and ethanol before drying at 60 °C for 24 hours. Finally, the solid powder was calcined in air at 550 °C for 2 hours to obtain silica. The obtained silica powder was characterized by X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR).

2.2.2. Preparation of ZSM-5

ZSM-5 zeolite was synthesized by a hydrothermal method [18]. Silica powder was dispersed into water to form a silica suspension. The solutions of aluminum hydroxide and sodium hydroxide were added to the silica suspension at room temperature in the following molar ratios:

(1) Na_2O: Al_2O_3 : SiO_2: TPABr : H_2O
3.12: 0.162: 2.835: 0.185: 100
to give ZSM-5 of SiO_2/Al_2O_3 = 17.5

(2) Na_2O : Al_2O_3 : SiO_2: TPABr : H_2O
3.12: 0.162: 6.48: 0.185: 100
to give ZSM-5 of SiO_2/Al_2O_3 = 35

(3) Na_2O : Al_2O_3 : SiO_2: TPABr : H_2O
3.12: 0.162: 11.34: 0.185: 100
to give ZSM-5 of SiO_2/Al_2O_3 = 70

After that, the mixture was reacted in a hydrothermal reactor (Teflon-coated autoclave) at a reaction temperature of 200 °C and a reaction time of 24 hours. To investigate the effect of the reaction temperature, SiO_2/Al_2O_3 molar ratio of 35 was kept constant and the reaction temperatures were carried out at 120, 170, and 200 °C for 24 hours. To investigate the effect of the reaction time, SiO_2/Al_2O_3 molar ratio of 35 was held constant and reaction times were changed at 8, 12 and 24 hours at 200 °C.

2.2.3. Characterizations of silica and ZSM-5 zeolite

The crystalline phase of silica and ZSM-5 zeolite was investigated by X-ray diffraction (XRD, D8 Phaser, Bruker, Germany) over 2 theta (2θ) range from 10° to 70° with a scanning speed of 0.05°/min using CuKα radiation (λ= 1.5406 Å). The surface morphology of ZSM-5 zeolite was observed under a scanning electron microscope (SEM, Hitachi, S-4800) at an accelerating voltage of 10 kV after gold coating. The formation of silica was observed by Fourier transform infrared spectroscopy (FTIR, FTS-3500, Bio-Rad, USA) using KBr pellets with the scanned spectra of 4000 – 400 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1. Preparation SiO_2 from rice husk ask

Figure 1 shows the results of the characteristic analysis of silica. Figure 1a shows the major chemical bonding groups of silica were identified. The absorption bands at 3500 and 1640 cm^{-1} were due to the H – O – H stretching and bending modes of water adsorbed on the silica. Peaks appeared at 800 cm^{-1} and 473 cm^{-1} due to stretching and bending modes of bulk Si-O-Si [25]. The peaks at 3366 cm^{-1} and 955 cm^{-1} were indicated for the SiO-H asymmetry stretching vibration and bending vibration. The XRD results (Fig. 1b) of silica showed that the broad peak at 2θ from 18° to 30° was indicated to amorphous silica with the maximum diffraction peak at 2θ of 22.5° [13, 22, 25]. The XRD pattern without noise peaks showed that the obtained silica was high purity and completely amorphous.

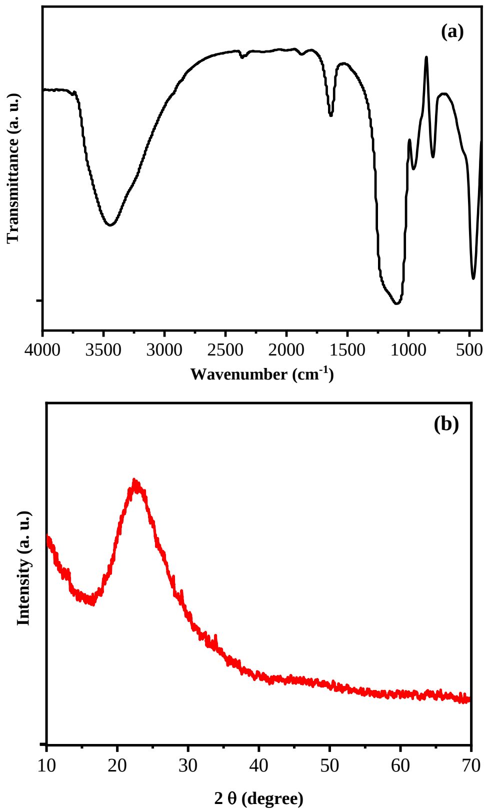

Figure 1. Characteristic of silica: a) FTIR spectrum; b) XRD pattern

3.2. Effects of factors on ZSM-5 zeolite synthesis

3.2.1. Effect of Si/Al ratio

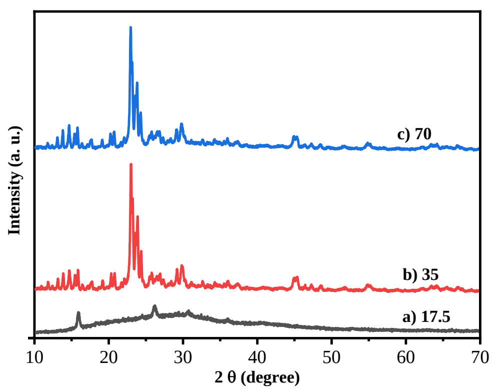

Figure 2. X-ray diffraction spectra of the samples (ZSM-5) synthesized at 200 °C of reaction temperatures, 24 h of reaction time with different SiO_2/Al_2O_3 molar ratios: a) 17.5; b) 35; and c) 70

Figure 2 shows XRD patterns of ZSM-5 obtained from the synthesis with different Si/Al molar ratios. As the molar ratio of Si/Al increases, characteristic peaks of ZSM-5 presented with a Si/Al molar ratio higher than 35 (Figure 2b-c). The characteristic peaks of ZSM-5 were at the scanned angles of 2θ = 14°, 14.2°, 15.1°, 16°, 23.4°, 24.2°, 25.6°, and 30.2° that were corresponded to (101), (111), (102), (112), (131), (022), (051), (313), (323), and (062) planes, respectively. The results were compatible with previous research results and were completely indexed to the structure of ZSM-5 zeolite [12, 14, 16, 18]. Therefore, a molar Si/Al ratio of 35 was chosen to investigate the effects of temperature and reaction time.

3.2.2. Effect of reaction temperature

Figure 3 depicts the XRD spectra of ZSM-5 zeolite synthesized with different reaction temperatures. The reaction temperature is proportional to the reaction rate. Therefore, when the reaction temperature was increased from 120 °C to 200 °C, characteristic diffraction peaks of ZSM-5 appear corresponding to diffraction angle 2θ = 14°, 14.2°, 15.1°, 16°, 23.4°, 24.2°, 25.6°, and 30.2° that were corresponded to (101), (111), (102), (112), (131), (022), (051), (313), (323), and (062) planes, respectively. The results were totally indexed to the structure of ZSM-5 zeolite [12, 14, 16, 18]. Therefore, the temperature of 200 °C was chosen to investigate the effects of reaction time.

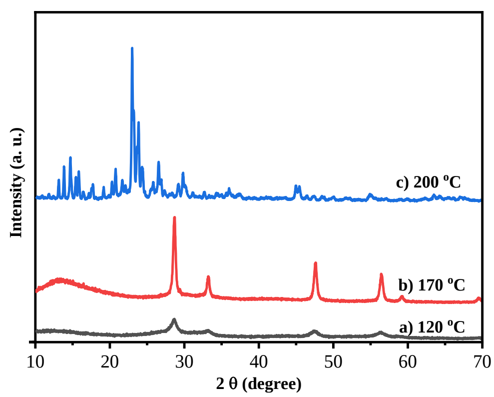

Figure 3. X-ray diffraction spectra of the samples (ZSM-5) synthesized at 24 h of reaction time, 35 of SiO2/Al_2O_3 molar ratio with different reaction temperatures: a) 120 °C, b) 170 °C, and c) 200 °C.

3.2.3. Effect of reaction time

Figure 4 shows the XRD patterns of ZSM-5 were synthesized at different reaction times. The reaction time was related to the conversion to ZSM-5. In other words, the time could affect the crystallization process of ZSM-5. When the reaction time increased from 8 to 24 hours, the characteristic peaks of ZSM-5 appeared fully with a reaction time of 24 hours (Figure 4c). In Figure 4c, the characteristic peaks of ZSM-5 presented corresponding to diffraction angle 2θ = 14°, 14.2°, 15.1°, 16°, 23.4°, 24.2°, 25.6°, and 30.2° that were corresponded to (101), (111), (102), (112), (131), (022), (051), (313), (323), and (062) planes, respectively. The results were totally agreed with the structure of ZSM-5 zeolite [12, 14, 16, 18]. In addition, there were no strange diffraction peaks in the XRD pattern, indicating that the obtained ZSM-5 was pure crystal. Therefore, the reaction temperature of 200 °C was chosen for the synthesis of ZSM-5 zeolite. In summary, suitable conditions to synthesize ZSM-5 from silica obtained from rice husk ash include a reaction temperature of 200 °C, a reaction time of 24 hours and a SiO_2/Al_2O_3 molar ratio of 35.

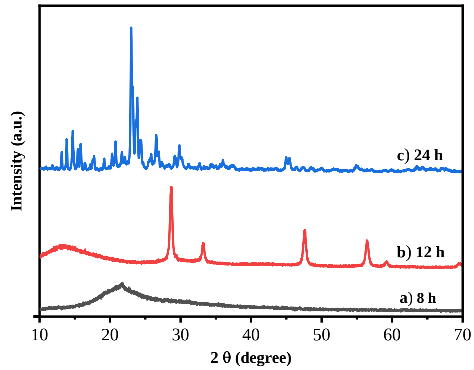

Figure 4. X-ray diffraction spectra of the samples (ZSM-5) were synthesized at at 200 °C of reaction temperatures, 35 of SiO_2/Al_2O_3 molar ratio with different reaction times: a) 8 hours, b) 12 hours, and c) 24 hours.

3.3. Morphology of ZSM-5

SEM images of ZSM-5 zeolites are shown in Figure 5. SEM result shows obtained ZSM-5 zeolite was well crystallized in a cube shape. ZSM-5 zeolites were in uniform size distribution with an average particle size of 3-5 µm. The results were consistent with the previous reports [4, 12, 16]. None of the other shaping components in the SEM image showed that the obtained ZSM-5 was pure, as demonstrated in the above XRD analyses. Therefore, ZSM-5 zeolites were successfully synthesized from silica precursors, derived from rice husk ash.

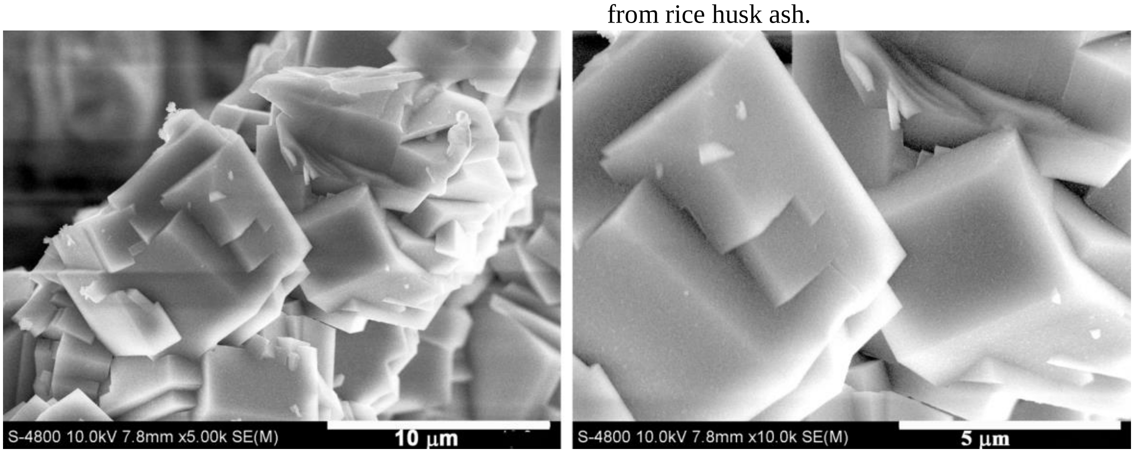

Figure 5. SEM images of ZSM-5 zeolite SEM synthesized at 200 °C of reaction temperatures, 24 h of reaction time, 35 of SiO_2/Al_2O_3 molar ratio with different resolutions

4. CONCLUSION

Silica prepared from rice husk ash was a precursor to the synthesis of ZSM-5 zeolites. ZSM-5 zeolite was successfully synthesized by a hydrothermal method at the reaction temperature of 200 °C, the reaction time of 24 hours, and the SiO_2/Al_2O_3 molar ratio was 35. The obtained ZSM-5 was cuboid in shape with an average particle size of 3-5 μm. The obtained ZSM-5 zeolites would be potential materials for applications as a carrier, catalyst, and adsorbent.

Acknowledgments

This work was financially supported by the "Can Tho University Improvement Project VN14-P6, supported by a Japanese ODA loan", under grant number E6.

Conflict of interest

The authors declare that there is no conflict of interest.

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