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INFLUENCE OF SILICA RESOURCE FROM RICE HUSK ON STRUCTURE OF HZSM-5 ZEOLITE

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ABSTRACT

HZSM-5 zeolites were successfully synthesized by hydrothermal treament using silica from rice husk and glasses water. The samples were characterized by XRD, IR, SEM, TEM, BET and ^{27}Al-NMR methods. Characterization results revealed that HZSM-5 material synthesized from rice husk silica has crystallinity and acidity as high as HZSM-5 sample synthesized from glasses water. HZSM-5 material synthesized from rice husk silica not only has the conventional pores system as shown structure of HZSM-5 sample synthesized from glasses water, but also has mesoporous system with kinetic diameter in range of 10-50 nm. This multi-porous system is expected to increase significantly the catalytic activity of synthesized material in the reactions with the present of large molecules .

Keywords: *Rice husk silica, ZSM-5, multi-porous system.*

I - INTRODUCTION

ZSM-5 zeolite is one of the most used catalysts because it has high thermal-hydrothermal durability and is suitable material for the catalyst, adsorption processes, especially for the cracking reaction [1]. ZSM-5 zeolite is synthesized by many different methods. Silica resource for ZSM-5 zeolite preparation is plentiful as TEOS, Ludox which are expensive [2]. Moreover, traditional ZSM-5 zeolite with small pore diameter of 5 — 6 Å is limited in the reactions with large molecules.

Rice husk is the milling byproduct of rice and is a major waste material of the agricultural industry. In Vietnam, annual rice husk quantity is 5 million tons [3]. However, rice husk has little or no commercial application. Therefore, the reusing of rice husk with high value is of great interest of many researchers. Rice husk main compositions are metal oxides, where the SiO_2 content is over 20% and so considered to be a very good quality of silica source [3, 4, and 5].

In this study, we report the results of the synthesis and characterization of HZSM-5 zeolite using silica derived from rice husk and compared with HZSM-5 zeolite using silica from glasses water.

II - EXPERIMENT

1. Materials

a) Silica-source preparation

Silica-source for the synthesis of ZSM-5 was extracted from rice husk by using solution NaOH 1% at 80°C for 30 minutes.

b) HZSM-5 preparation

Raw materials.

Silica-source: extracted solution from Vietnamese rice husk, aluminum source: $Al_2(SO_4)_3.18H_2O$ (China), tetrapropylamonium bromua (TPABr) (German), Distilled water

Synthesis

ZSM-5 material was synthesized by hydrothermal crystallization using TPABr as template. The obtained gel was crystallized at 170°C for 24 hours. The gained solid product from crystallization process was washed to 7, dried at 100°C and calcined at 550°C for 5 hours to remove all the template. Then, product was ion exchanged with NH_4NO_3 2 M, washed, dried and calcined again to form HZSM-5.

Characterization methods

Infrared spectrum (IR): The sample was wafered with KBr as ratio of 1mg (sample)/100mg (KBr) and measured by IR spectrum using Impact 410 (German) instrument at room temperature in the range of 400 - 1300 cm^{-1}. XRD pattern was analyzed on Siemens D500 instrument (German) under the following conditions: CuK_α radiation (λ = 1,5406 Å), U = 30kV, I = 25 mA, Scanning angle $2\theta = 0,1^0 - 30^0$, Scanning rate: $0,2^0$/minute, Measurement temperature: 25°C. The presence of aluminum within the framework has been disclosed through ^{27}Al Solid state magic angle spinning (MAS)-NMR method. Spectrum was obtained with a Bruker MSL 400 spectrometer for ^{27}Al (at 104.3 MHz). Scanning Electro microscopy (SEM) was carried out on a Jeol JSM-7500F, sample was dispersed into ethanol, dried, mounting on a thin plate and coated by a flimsy gold layer. High-resolution transmission electro microscopy (TEM) was performed on a Philips Tecnai-10 microscope at 100 kV. The specimens for TEM observation were prepared by embedding the samples in epoxy resin and ultramicrotoming and mounting on a copper grid. Nitrogen adsorption/desorption isotherms: The BET surface area and pore volume were measured by Nitrogen adsorption/desorption isotherms using ASAP 2010 equipment (Micrometrics-USA). The sample was treated in vide pressure at 120°C for 4 h and at 350°C for 9h.

III - RESULTS AND DISCUSSION

1. IR spectra of HZSM-5

Figure 1 presents IR spectrum of HZSM-5 synthesized from rice husk silica comparing to that of HZSM-5 synthesized from glasses water in the range of 400 - 1300 cm^{-1}. From observed spectrums, we can see that the IR spectrum of HZSM-5 synthesized from rice husk silica sample completely agree with that of one synthesized from glasses water sample. There is no stranger phase occurring in the spectrum of the synthesized material. This result demonstrates that the synthesized materials have MFI structure. The peak at 550 cm^{-1} contributes to the fluctuation of 5-1 rings in ZSM-5 structure and it is typical for the crystalline status of the material. According to [8], the crystallinity of the synthesized material is 100% if the intensive ratio of 550 cm^{-1} to 450 cm^{-1} peaks is 0.8. The calculated value of the intensive ratio of 550 cm^{-1} to 450 cm^{-1} in our case is 0.8 confirming that the crystallinity of the synthesized material can reach approximately 100%.

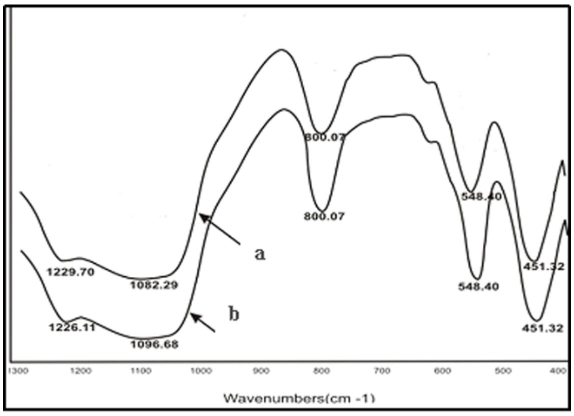

Fig. 1: IR spectra of ZSM-5 zeolite
(a) synthesized from glasses water;
(b) synthesized from rice husk

2. Powder X-ray diffractional patterns

Figure 2 presents the XRD patterns of HZSM-5 materials synthesized using different silica sources. The XRD pattern of materials indicates that no impurities phase or amorphous materials were presented. In addition, the intensity of typical maximum diffractions occurring at $2\theta = 5 - 10^0$ and $2\theta = 20 - 25^0$ of synthesized materials is equivalent to that of

ZSM-5 standard sample with typical MFI structure [6]. From this result, we can consider that the HZSM-5 material synthesized using silica from rice husk has very high crystallinity (approximately of 100%) as HZSM-5 material synthesized using silica from glasses water. This conclusion completely agrees to that from IR method.

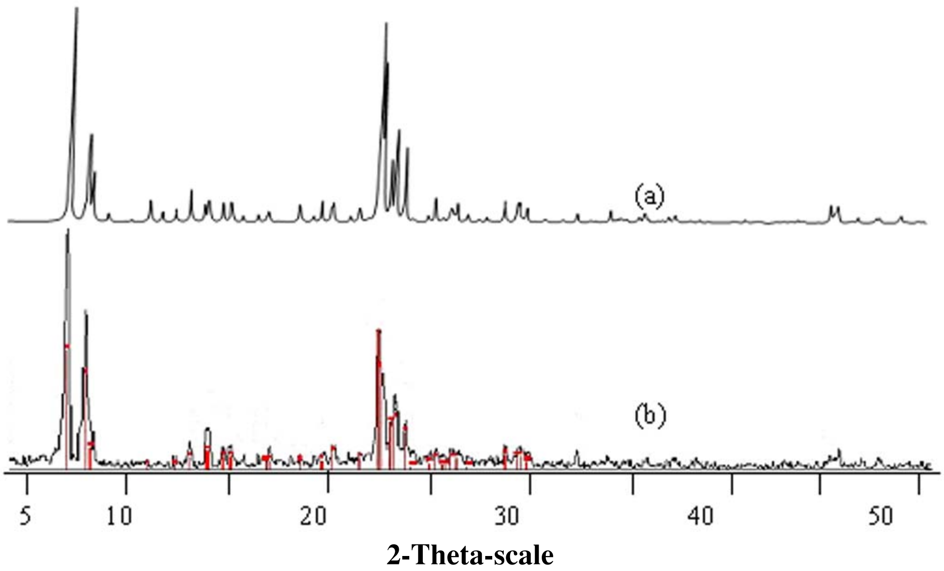

Figure 2: XRD patterns of (a) HZSM-5 synthesized from glasses water
(b) HZSM-5 synthesized from rice husk

3. Nuclear magnetic resonance ^{27}Al NMR method

The exits of Al^{3+} ion in zeolite framework relates with the acidity of material (due to Al^{3+} ion tetrahedrally coordinated in zeolite). From obtained result, the acidity of material can be indirectly measured via the determining of Al^{3+} distribution in the zeolite framework. In order to determine the distribution of Al^{3+} ion of synthesized material, the ^{27}Al-NMR method was used. Figure 3 shows the ^{27}Al-NMR of HZSM-5 material synthesized from rice husk.

It is similar to HZSM-5 material synthesized from glasses water, the ^{27}Al-NMR spectrum of the HZSM-5 material synthesized from rice husk gives rise to a resonance at 55 ppm with high intensity due to aluminum in a tetrahedral environment, which is typical for zeolitic framework aluminum [7,8]. This proves that almost of aluminum used in synthesis process are presented in zeolite framework. However, the ^{27}Al-NMR of HZSM-5 material synthesized from rice husk shows one resonance at 0ppm with very low intensity and it is negligible in comparing to the intensity of resonance at 55ppm. According to references [7,8], this resonance is attributed to Al^{3+} which is not presented in zeolite framework indicating that almost of used aluminum were corporated in the zeolite framework. These result showed that HZSM-5 synthesized from rice husk have high acidity similar to HZSM-5 material synthesized from glasses water.

4. SEM and TEM images of HZSM-5 synthesized using silica from rice husk

The SEM image of HZSM-5 is presented in figure 4 showing that the HZSM-5 crystals were formed with well ordered size of 0.5 - 0.7 μm. The similar result can be obtained from the SEM image of HZSM-5 showing that the synthesized material has well ordered size of 0.5 - 0.7 μm.

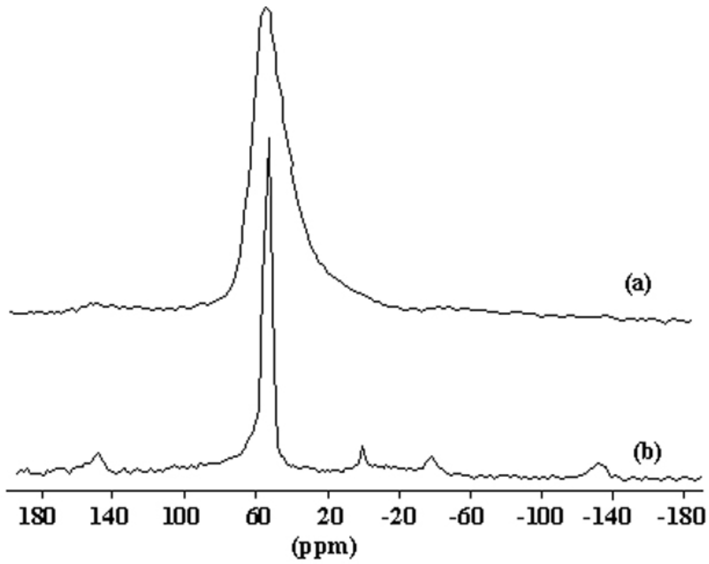

Fig. 3: ^{27}Al-NMR spectrum
(a) HZSM-5 synthesized from glasses water; (b) HZSM-5 synthesized from rice husk.

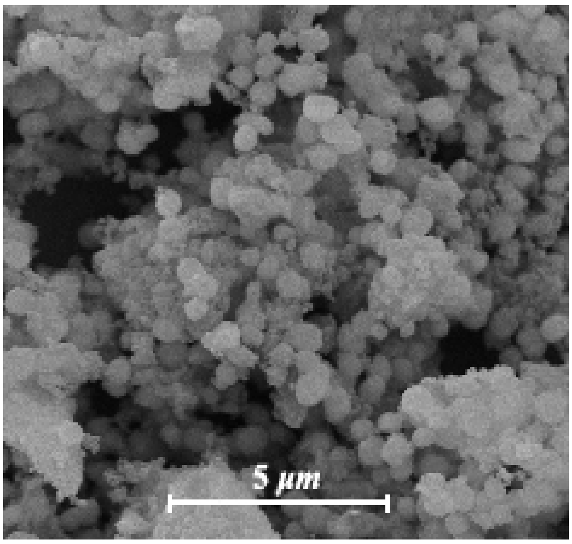

Fig. 4: SEM image of HZSM-5

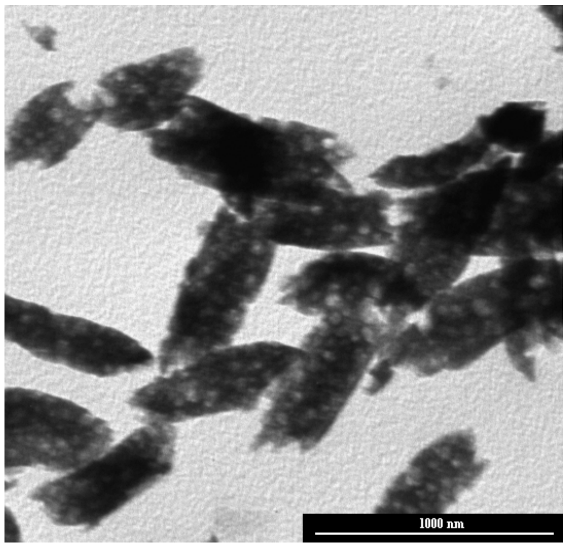

Fig. 5: TEM image of HZSM-5

In addition, there observed a very interesting feature, i.e., a pore system with disordered size in the structure of HZSM-5 material having the pore size in range of 10 - 50 nm. This could be explained that the carbon presenting in the treated rice husk is continued to be removed in the calcination process. The removal of carbon formed special mesoporous system of the synthesized material.

5. BET characterization of HZSM-5 synthesized using silica from rice husk

The exits of mesostructure of the "HZSM-5" sample was also observed by N_2 adsorption/desorption isotherms. Fig. 6 shows appearance of a wide hysteresis loop at P/Po of 0.5. This is a typical shape characteristic of mesoporous structure [8].

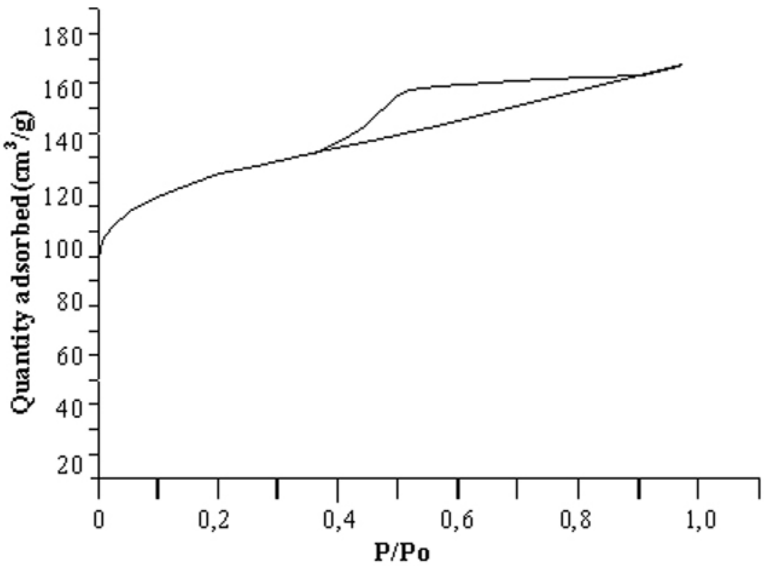

Fig. 6: N_2 adsorption/desorption isotherms

IV - CONCLUSION

HZSM-5 material was successfully synthesized from rice husk silica. The characterization results show that the synthesized material has the crystallinity equivalent to that of the standard sample. Besides the conventional pores system exiting in zeolite structure, there is another pores system having diameters in the range of 10 - 50 nm (mesoporous system). This is due to the burning of organic compounds left remaining in the material during the calcination process. This mesopours system might increase the catalytic activity of synthesized material. The results are opened up a new research way to use rice husk as the silica source for of catalysts preparation. The more detailed research results will be published in the near future.

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Nghiên cứu ảnh hưởng của nguồn silic tỏch từ vỏ trấu tới cấu trỳc vật liệu zeolit ZSM-5

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