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Synthesis of aluminosilicate mesoporous material MSU-S from natural resources: Investigating the effects on the structure formation

Nguyen Thi Linh[1,2*], Ngo Ha Son[1,2], Le Van Duong[2,3], Ta Ngoc Don[3], Nguyen Van Khang[4]

[1] Hanoi University of Mining and Geology, 18 Vien street, Duc Thang ward, Bac Tu Liem district, Hanoi, Vietnam
[2] AMCA Research Group, Hanoi University of Mining and Geology, 18 Vien street, Duc Thang ward, Bac Tu Liem district, Hanoi, Vietnam
[3] School of Chemistry and Life Sciences, Hanoi University of Science and Technology, 1 Dai Co Viet, Hanoi, Vietnam
[4] Long Son Petrochemical Co., Ltd, Hamlet 2, Long Son Commune, Vung Tau City, Ba Ria – Vung Tau Province, Vietnam
**Email: nguyenthilinh@humg.edu.vn*

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ABSTRACT

Zeolite seed-based mesoporous aluminosilicate material MSU-S is normally synthesized from pure chemicals. In the study, MSU-S material was synthesized using natural resources such as rice husk, and kaolin in Vietnam. Here, a systematic investigation is conducted to find the relationship between the synthesis conditions (aging time, hydrothermal time, hydrothermal temperature, pH environment) and the formation of mesoporous structure, as well as the material properties. The sample was characterized by XRD, TEM, N_2 adsorption-desorption isotherms, and TGA-DSC. The MSU-S material has been synthesized successfully from rice husk and kaolin. The best conditions are aging time of 24 hours, and hydrothermal conditions at 95°C during 96 hours with pH=9. The MSU-S has an ordered hexagonal mesoporous structure containing zeolite BEA seed. The pore diameter is concentrated at 2.9 nm. The BET surface area is calculated to be 770 m^2/g. Thermal stability is determined to be up to 900°C.

1. Introduction

In the realm of material science, MSU materials denote a class of mesoporous silica developed by researchers at Michigan State University. These substances stand out for their expansive surface areas and well-defined pore architectures, qualities that render them exceptionally suitable for adsorption activities [1]. MSU materials play a pivotal role in adsorption and catalytic processes due to their capacity to accommodate large molecules, including pharmaceuticals, enzymes, and various organic compounds. This is achieved through multiple mechanisms: adsorption, covalent attachment, cross-linking, encapsulation, or entrapment [2]. Their utility extends to catalysis, where they provide a foundation for active catalytic agents. A notable application is the use of vanadium oxide on MSU-1 as a potent catalyst for isobutane dehydrogenation with CO_2 [3]. The substantial surface area of MSU-1 aids in the even spread of vanadium oxide, thereby boosting the catalytic process's efficiency and selectivity. This underscores the importance of MSU materials in elevating the performance of catalytic reactions [4].

Investigations into the synthesis parameters of MSU mesoporous materials are vital, given their broad applicability across various sectors, including catalysis,

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adsorption, sensing, pharmaceuticals, and electrochemistry. These materials are distinguished by their orderly pores and vast surface areas, making them indispensable for numerous scientific and commercial applications.

The synthesis of MSU-type mesoporous materials necessitates meticulous control over several factors: the source of silicon, choice of surfactant, pH levels, ionic strength, and the conditions of aging, such as temperature and duration [5,6]. These elements significantly influence the final material's structure, surface area, pore dimensions, volume, and wall thickness [7].

While MSU materials are typically less structured than other mesoporous substances like MCM or SBA, their synthesis using non-ionic surfactants at a neutral pH leads to the formation of pores with diameters ranging from 2.1 to 8.0 nanometers and wall thicknesses of 1.5 to 4.0 nanometers. Enhancing the synthesis conditions for MSU materials can result in bespoke mesoporous substances with properties tailored for specific uses, thereby improving their functionality and efficiency in practical applications [8,9]. Consequently, continuous research in this domain is imperative for the progression of material science. However, previous research has shown that MSU materials were synthesized totally from expensive pure chemicals resulting in limited applications.

In this study, the synthesis conditions of MSU materials will be investigated and adjusted to develop an effective and suitable MSU synthesis process, utilizing the readily available natural resources in Vietnam such as rice husk and kaolin.

2. Experimental

Material

Rice husk (Vietnam), kaolin (Vietnam), Hydrochloric acid 35 wt% (Xilong), Sodium Hydroxide (Xilong), Tetraethylammonium hydroxide (TEAOH) solution 35 wt% in water (Sigma- Aldrich), Cetyltrimethyl ammonium bromide (CTAB) ≥ 98% (Sigma- Aldrich), Deionized water. Every chemical utilized was directly applied in its received state, with no additional purification conducted.

Raw material treatment

Rice husk, once cleansed of dust, was soaked in a 10% HCl solution overnight, then washed to a pH of 7 and dried. The acid-treated rice husk was calcined at 600°C for 6 hours to yield white rice husk ash, denoted as RHA. Silica was extracted from the RHA by dissolving it in a 1M NaOH solution. The mixture was then reacted at 150°C for 3 hours. After the reaction, the residue was filtered out, collecting the sodium silicate solution (Na_2SiO_3).

Kaolin was treated with a 4N HCl solution at a solid/liquid ratio of 2/3 for 6 hours at 95°C, with continuous stirring. After the reaction, the solids were filtered and washed with distilled water until chloride ions were no longer present, then dried at 105°C. The acid-treated kaolin was then calcined in an air stream at a heating rate of 2°C/min up to 650°C and maintained at this temperature for 3 hours to obtain metakaolin.

Preparation of MSU-S

A mixture of metakaolin and rice husk Na_2SiO_3 was supplemented with water to a specified volume and stirred to create a homogeneous raw material mixture. Subsequently, the mixture was added to TEAOH solution, then the mixture's pH was adjusted to investigated conditions, and the reaction was carried out at room temperature for various aging times. Next, a solution of Cetyltrimethylammonium bromide (CTAB) was added dropwise, with continuous stirring until the solution became transparent and uniform.

Upon completion of the reaction, the entire mixture underwent hydrothermal treatment in an autoclave at 95°C for survey hydrothermal time.

After the hydrothermal reaction, the suspension was filtered and washed with distilled water until a pH of 7 was achieved, yielding a white solid. This solid was dried and calcined at 500°C for 3 hours to obtain MSU-S material in the form of a fine, white, porous powder.

Material characterization

X-ray diffraction patterns at small angles were obtained using a Bruker D5005 diffractometer, employing Cu Kα radiation (wavelength = 1.54056 Å) at a voltage of 40 kV and a current of 40 mA, maintained at 25°C. These patterns were scanned at a rate of 0.025° per second, covering a 2θ range from 0.5 to 10 degrees.

Nitrogen adsorption and desorption isotherms were acquired at the temperature of liquid nitrogen using a TriStar II Plus 2.03 instrument by MicroActive. The BET method was applied to the adsorption isotherms to compute the specific surface areas of the samples, while the BJH method was utilized to determine the pore size distributions from the same isotherms.

Transmission electron microscopy (TEM) images were recorded on a JEOL 200CX microscope operating at an accelerating voltage of 120 kV.

The elemental composition of the raw materials was analyzed using an Energy Dispersive X-Ray Fluorescence Spectrometer, which was set to a cursor energy of 15.494 keV.

The thermal stability of the material was evaluated with thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC). The tests were performed in nitrogen gas flow with a thermo-gravimetric analyzer (SETARAM) with dynamics scans at a heating rate of 10°C/min from room temperature up to 1000°C.

Investigation of synthesis conditions' effects

To optimize the synthesis efficiency of MSU-S, a mesoporous silica material, it is crucial to investigate the impact of various synthesis parameters such as the aging time (20h, 24h, 30h), pH (2 and 9), hydrothermal temperature (60°C, 75°C, 95°C) and hydrothermal time (24h, 48h, 72h, 96h). Each of these factors can significantly influence the structural and functional properties of the synthesized MSU-S. This approach ensures a comprehensive understanding of the synthesis process, leading to enhanced efficiency and material performance.

3. Results and discussion

Rice husk ash

The composition of raw material

To study the chemical composition of the initial rice husk ash and metakaolin materials, the substance is characterized by EDX spectroscopy. The results are presented in Table 1.

Table 1. The composition of materials after treatment

Raw materials	Treatment method	Composition (%) after treatment		Analysis method
		SiO_2	Al_2O_3	
Rice husk	Heat	99%	N.A	EDX
Kaolin	Heat	73%	27%	EDX

N.A: Not Available

Table 1 provides the results of the EDX spectrum, which shows the elemental composition of rice husk ash and metakaolin, primarily consisting of aluminum and silicon. A significant peak on the spectrum indicates a high presence of a specific element. This analysis is essential for understanding the chemical properties of the ash and suggests its potential use in fabricating MSU-S material.

Effect of synthesis conditions

The impact of different synthesis conditions on material structure and morphology were introduced in Figure 1.

Impact of aging time: The XRD results of different materials which were synthesized at different aging time are shown in Figure 1A.

The gel aging time is a critical factor in the formation of TO_4 tetrahedra (SiO_4 and AlO_4^- tetrahedra) and oligomers $(O_3Si\text{-}O\text{-}AlO_3)_n$ (n ≥ 1) from the initial materials. Notably, the MSU-S material synthesized in this study originates from kaolin, a type of clay mineral whose main component is kaolinite, comprising layers of crystal lattice formed from silicon tetrahedra linked to an aluminum octahedral network, resulting in a stable structure, and rice husk ash, which contains silicon existing as polysilicon. To transform metakaolin and rice husk ash into MSU-S mesoporous material, reactions and time are required to break down the structure of kaolinite minerals as well as the polysilicon chains of the rice husk ash. During the gel aging process, in the presence of an organic complexing agent (Co.) and a reactive environment, the crystal lattices of kaolinite minerals are first disrupted, forming SiO_4 and AlO_4 monomers and oligomers $(O_3Si\text{-}O\text{-}AlO_3)_n$ (n ≥ 1), while the polysilicon chains are cleaved to produce oligomers. This stage concludes at a specific time to maximize the quantity of TO_4 tetrahedra and silicon oligomers, that is, to maximize the amount of material for building the mesoporous structure.

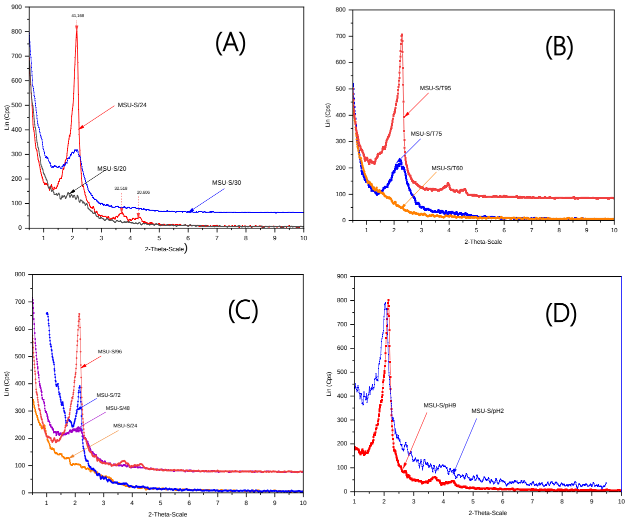

Figure 1. Small Angle X-ray Scattering of the synthesized MSU-S materials at different conditions: (A)-aging time (20h, 24h, 30h); (B)-Hydrothermal temperature (60°C, 75°C, 95°C); (C)-Hydrothermal time (24h, 48h, 72h, 96h); (D)-pH environment (pH=2, pH=9)

XRD results indicate that a short aging time (< 20 hours) is insufficient for the precursor content of TO_4 tetrahedra to construct the mesoporous structure.

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Conversely, prolonged aging leads to the re-condensation of the polysilicon from the rice husk ash, resulting in a shortage of mesoporous building material [10,11]. Studies show that an aging time of 24 hours allows for the orderly formation of mesopores, confirmed by three sharp peaks at 2θ angles of 2.2°, 3.8°, and 4.4°, corresponding to the reflection planes (100), (110), (200) [3, 10].

Impact of hydrothermal temperature

If gel aging time is an important factor in the formation of mesoporous material precursors, then the temperature and duration of hydrothermal crystallization are decisive factors affecting the condensation ability of inorganic precursors (TO_4 tetrahedra) onto the structure-directing micelles. The XRD results of material which undergone different hydrothermal temperature treatment are depicted in Figure 1B.

Hydrothermal crystallization temperature studies at 60°C, 75°C, and 95°C indicate that at temperatures below 95°C, over a duration of 96 hours, the condensation of SiO_4 and AlO_4^- tetrahedra either does not occur or is difficult, hence failing to cover the entire structure-directing micelle tubes. As a result, when treated under calcination conditions, the entire mesoporous structure collapses. These findings are in accordance with previous results related to mesoporous material. Specifically, the temperature during the hydrothermal treatment influences the condensation and growth of inorganic precursors, which in turn affects the size and distribution of the pores formed [12]. At lower temperatures, the condensation of the inorganic precursors may be incomplete or slower, leading to a less uniform pore size distribution and potentially larger pores due to insufficient packing of the structure-directing agents. This can result in a material with a broader range of pore sizes and a less ordered mesoporous structure. Conversely, at higher hydrothermal temperatures, the inorganic precursors condense more efficiently onto the structure-directing agents, leading to a more uniform and narrower pore size distribution. The increased temperature can promote the formation of smaller, more uniform pores, resulting in a material with a higher surface area and a more regular mesoporous structure [13].

The conditions of 95°C and a hydrothermal duration of 96 hours are most suitable for the condensation of TO_4 tetrahedra precursors onto the structure-directing micelles, forming an inorganic-micelle wall thick enough to be stable during the thermal treatment process that creates the mesoporous structure of the material. Moreover, these conditions are also optimal for the uniform and orderly arrangement of the mesopores, with the hexagonal structure of the micelles forming perfectly. The synthesized MSU-S material has an ordered hexagonal mesoporous structure.

Impact of hydrothermal time

The hydrothermal time has a significant impact on the crystallization, structure, and morphology of mesoporous silica materials. The duration of the hydrothermal treatment can determine the extent to which the inorganic precursors condense and organize into a structured framework.

As can be seen in Figure 1C, 96 hours give the best material. Theoretically, extended hydrothermal time enhances MSU material crystallinity, stability, and catalytic potential. It also allows for the self-assembly of a well-defined mesoporous structure and fine-tuning of mesopore size and shape, leading to uniformity essential for various applications [14,15].

Impact of pH

The pH level plays a crucial role in the synthesis of mesoporous aluminosilicate (MSU-S) materials, affecting the efficiency and quality of the final product. A balanced pH environment is essential for the proper assembly of the mesoporous structure and for controlling the size and uniformity of the pores [16,10,17].

In the investigation of pH within the range of acidic and weakly alkaline environments (Figure 1D), it was observed that mesoporous materials formed in both conditions. However, the arrangement of the mesopores in the acidic environment was less ordered compared to that in the weakly alkaline environment. This is attributed to the fact that in the acidic environment, only the polysilicon in the rice husk ash hydrolyzes readily into TO_4 tetrahedra, while the formation of AlO_4^- tetrahedra from kaolinite minerals is more challenging, leading to an imbalance in the ratio of inorganic precursor materials to the amount of structure-directing micelles [6]. In a weakly alkaline environment (pH=9), conditions are favorable for both rice husk ash and kaolin to contribute to the formation of inorganic TO_4 tetrahedra precursors, promoting the orderly development of hexagonally structured mesoporous material [6].

Characteristics of the MSU-S material

XRD result

The XRD result of the final MSU-S material is illustrated in Figure 2.

XRD analysis revealed three peaks at small 2θ angles of 2.2°, 3.8°, and 4.4°, corresponding to the (100), (110), and (200) reflection planes, respectively. Despite the inherently amorphous nature of the material's walls, the orderly arrangement of hexagonally patterned mesopores resulted in an XRD pattern indicative of crystalline behavior. XRD methodology can be considered the best qualitative approach for determining the degree of order as well as predicting the morphology of the average mesoporous material.

The insert image indicates the presence of BEA zeolite crystalline seed on the wall of MSU-S with weak signal peaks at 2θ angles of 14° and 22°.

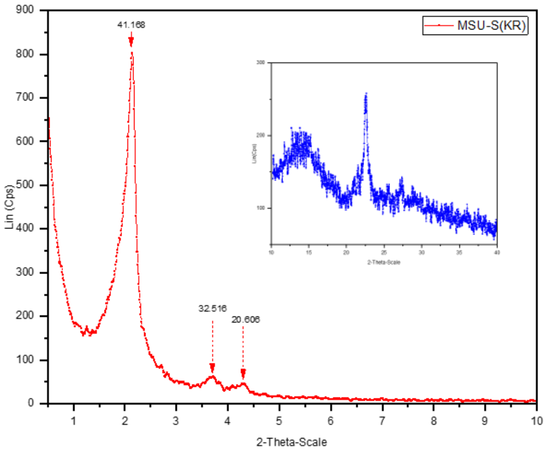

Figure 2. SAXS pattern and XRD (insert image) of MSU-S material

BET result

Figure 3 illustrates the results of the specific surface area and the pore size distribution, respectively, which were analyzed using nitrogen adsorption isotherms conducted at a temperature of 77.3 K.

Type IV hysteresis loops, as classified by the IUPAC, are characteristic of materials with mesoporous carriers. The hysteresis loop appears at P/P0 = 0.45 due to capillary condensation phenomena typical of the mesoporous family. The image reveals that the H2 hysteresis loop exhibits non-uniform adsorption-desorption, possibly due to mesopores with constrictions followed by an expansion, displaying two nearly parallel adsorption and desorption branches indicative of ink-bottle type mesoporous structures. Additionally, the image observation suggests that the hybrid hysteresis loop carries the H4 loop, demonstrating that cylindrical mesopores are interconnected by smaller pores, forming a spatially structured mesoporous system resembling an ink-bottle with the 'main body' being the mesopores and the 'neck' being the smaller pores situated atop and doubly connected to the mesopores. The single-point surface area reaches 786 m²/g, and the BET surface area is calculated to be 770 m²/g. The pore diameter is concentrated at 2.9 nm.

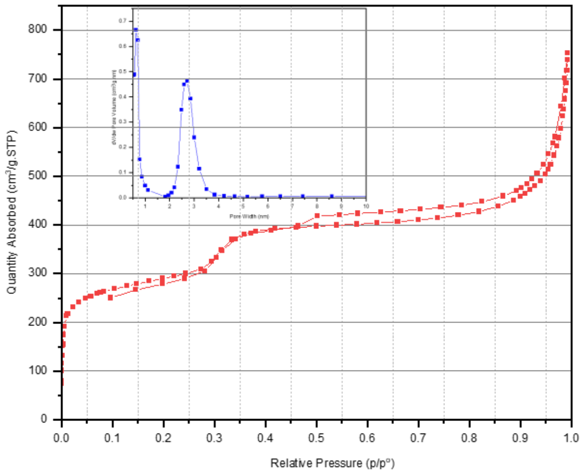

Figure 3. N_2 adsorption-Desorption Isotherms and pore size distribution (insert image) of the synthesized MSU-S material

TEM image

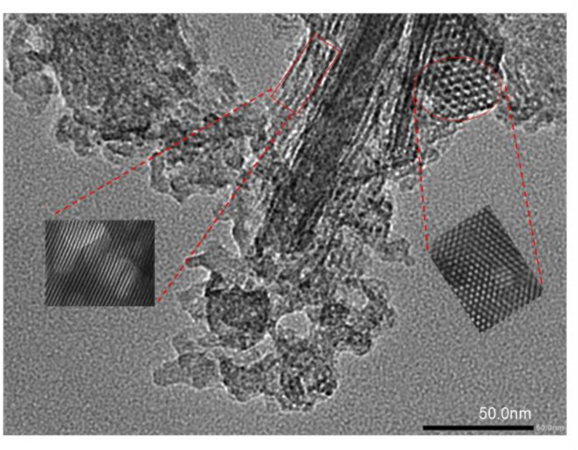

Figure 4. TEM image of the synthesized MSU-S

Figure 4 shows the TEM image of MSU-S material, where the ordered hexagonal structure is observed in the horizontal and vertical planes. The pore diameter was measured and found to be 2.9 nm, which is consistent with the results of the BET analysis and XRD.

Thermal analysis

The results from the thermal analysis schema of the MSU-S are presented in Figure 5. It is observed that the endothermic peaks in the DSC curve and the mass change in the TGA. The curve shows an endothermic peak at 68.5°C. The mass loss at this point is probably caused by the evaporation of surface water. When the temperature rises, an endothermic peak at 247.9°C indicates the decomposition of residue structure directing agents with a mass loss of about 1,39%. An exothermic peak at 946,6°C combined with the TG measurements determined that the structure of MSU-S material begins to break down.

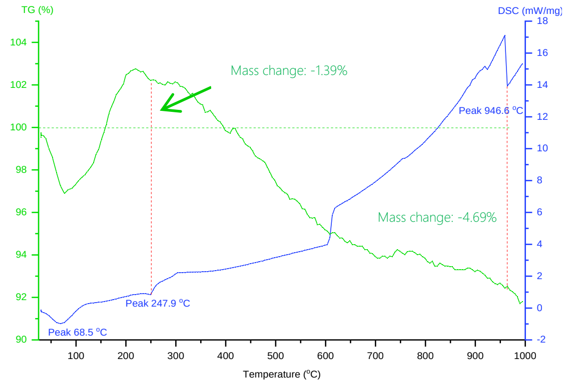

Figure 5. TGA/DSC curves of the synthesized MSU-S

4. Conclusion

In the present research, the MSU-S was synthesized successfully by using silicon and aluminum-containing natural resources such as rice husk and kaolin by a two-step crystalline method. The effects of synthesis conditions for the formation of mesoporous structures are investigated systematically. Additionally, the effects of hydrothermal time, temperature, and pH environment are also crucial conditions for the building and arrangement of pores. We found that the best synthesis conditions are aging time at 24 hours, and hydrothermal conditions at 95°C during 96 hours in a pH environment of 9. The MSU-S has an ordered hexagonal mesoporous structure with a wall containing zeolite BEA crystalline resulting in excellent thermal stability up to 900°C, and the BET surface area is 770 m^2/g with the pore diameter at 2.9 nm. The characteristics of the synthesized MSU-S as a larger specific surface area, suitable pore diameter, and chemical surface nature containing silanol groups are in favor of acidic catalyst and adsorption.

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