



SYNTHESIS OF MCM-41 MATERIAL USING RICE HUSK ASH AS A SOURCE OF SILICON

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Abstract: In the present paper, a synthesis of MCM-41 mesoporous material with a sodium silicate solution prepared from rice husk ash as a silica source using the hydrothermal process is demonstrated. The influence of synthesis conditions on the material structure such as cetyltrimethylammonium bromide (CTAB) concentration, SiO₂/CTAB molar ratio, stirring time, and aging time was investigated. The materials were characterized using XRD, FT-IR, and N₂ adsorption-desorption isotherm measurement. The results show that the material possesses highly ordered hexagonal mesostructure with uniform mesopore size distribution in a large range of CTAB concentration (the mass fraction is from 0.0133 to 0.0481) and the SiO₂/CTAB molar ratio (4–15). The sample with the molar ratio of CTAB: SiO₂: H₂O = 1: 6: 1000 has a high surface area (1074 m²/g) and large pore diameter (33.5 Å).

Keywords: MCM-41, sodium silicate, rice husk ash

1 Introduction

MCM-41 mesoporous material has become familiar to scientists in the catalytic and absorption field since its discovery in the 1990s [1]. The MCM-41 possesses an ordered hexagonal mesoporous structure with a large specific surface area (> 1000 m²/g) as well as exhibits good thermal and hydrothermal properties. Thus, this family of material is suitable for an adsorbent or a support in the catalytic and adsorption field [1, 2]. It can be said that the research on the synthesis and modification of mesoporous material in different directions to produce modified materials with improved adsorption and catalytic properties and many other important applications has attracted the attention of many scientists worldwide. This is proved by a lot of works related to this material (nearly 148,000 articles, according to Google Scholar). Among them, a large number of articles are published in recent years [2, 3, 4]. Although many works have been carried out, the application of this material is still limited. One of the reasons for the moderate applicability of this material is that they are synthesized from pure silicon precursors such as tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS), etc., which are expensive. Therefore, finding low-cost silicon sources in order to replace TEOS, TMOS in the MCM-41 synthesis is one of the practical tasks of scientists. Among low-cost silicon sources of interest, rice husk ash has received a widespread attention since rice husk is an available cheap byproduct and an agricultural waste. So far, there have been several studies on MCM-41 derived from rice husk ash [4, 5, 6, 7]. However, each work only focuses on one aspect of the synthesis process, and there were very few detailed and complete studies. Meanwhile, it is well

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known that the structure of the MCM-41 material is highly influenced by the synthesis conditions.

In this paper, a study of the synthesis of MCM-41 materials using rice husk ash as a silicon source is presented. The influence of CTAB concentration, SiO₂/CTAB molar ratio, stirring time, and aging time on the material structure was investigated.

2 Experimental

Chemicals: Rice husk was collected from Phu Loc District, Thua Thien Hue Province, Vietnam; Cetyl Trimethyl Ammonium Bromide (CTAB) was purchased from Aldrich; sulfuric acid and hydrochloric acid were supplied by Merck, and sodium hydroxide was purchased from Guangdong. All chemicals are of analytical grade.

Preparation of silicon source from rice husk ash: The silicon source (sodium silicate) was prepared according to Hoang Van Duc and Nguyen Thi Anh Thu [8]. Accordingly, the rice husk was washed with tap water and then distilled water. The washed husk was dried and burned to ash. The rice husk ash was further heated at 600 °C for 2 hours, then treated with a 2 M HCl solution for 1 hour at room temperature (30 °C) and a 5 M H₂SO₄ solution for 1 hour under boiling. After being treated with acid, rice husk ash was soaked in a 0.5 M NaOH solution under boiling for 3 hours. The reaction mixture was hot filtered to collect the solution. After cooling, a solution of sodium silicate (10 % SiO₂ content) was obtained.

2.1 Synthesis and characterization of MCM-41 materials

The MCM-41 material was synthesized according to a modified procedure [2]. In a typical synthesis, 1.456 g of CTAB template was dissolved in 72 mL of distilled water at room temperature (30 °C). Then 8.3 mL of sodium silicate solution was added to the CTAB solution with stirring vigorously for 1 hour. The pH was adjusted to 10.5 using a 1 M H₂SO₄ solution; then, the mixture was stirred for another hour. Next, the gel mixture was transferred into a Teflon flask and stirred mildly for 24 hours at room temperature (30 °C) and then aged at 100 °C for 24–72 hours. After that, the precipitate was filtered and washed with distilled water to pH = 7, dried for 24 hours at 100 °C. Finally, the solid was heated at 550 °C for 6 hours to remove the template.

The X-ray diffraction (XRD) analysis was carried out on a D8 Advanced Bruker anode X-ray Diffractometer with CuK α ($\lambda = 1.5406 \text{ \AA}$) radiation. The Fourier transform infrared spectrum (FTIR) was recorded with an IR-Prestige-21 spectrometer (Shimadzu, Japan) within the wave range of 400–4000 cm⁻¹. The transmission electron microscope (TEM) images were obtained from JEOL JEM-2100F and the nitrogen physisorption measurements were conducted by using a Micromeritics ASAP 2020 volumetric adsorption analyzer system.

3 Results and discussion

3.1 Effect of molar ratio H₂O: CTAB

Depending on its concentration in the solution, the template exists in many different forms and they will affect the structural orderliness as well as the crystallinity of the MCM-41 material. Thus, in this study, the influence of CTAB, a structure-directing agent, was investigated and this effect was assessed by changing the molar ratio H₂O/CTAB. The samples were synthesized with molar ratios of CTAB: SiO₂: H₂O = 1: 6: x (where $x = 400, 600, 800, 1000$ and 1500 , corresponding to the mass fraction from 0.0133 to 0.0481). The samples are denoted as M400, M600, M800, M1000 and M1500.

Fig. 1 exhibits the XRD patterns of the MCM-41 samples with different molar ratios of H₂O/CTAB. It can be seen that except for M400 with two characteristic peaks corresponding to the (100) and (110) planes, the remaining samples have a third one, corresponding to the (200) reflection of the MCM-41 material [1, 9]. The narrow peaks with high intensity indicate that the obtained material has high orderliness. This reveals that the hexagonal mesoporous structure of MCM-41 remains in a wide range of H₂O/CTAB ratio. However, the crystal growth rates of the material change slightly as indicated by the half width at half maximum (HWHM, β) (Table 1).

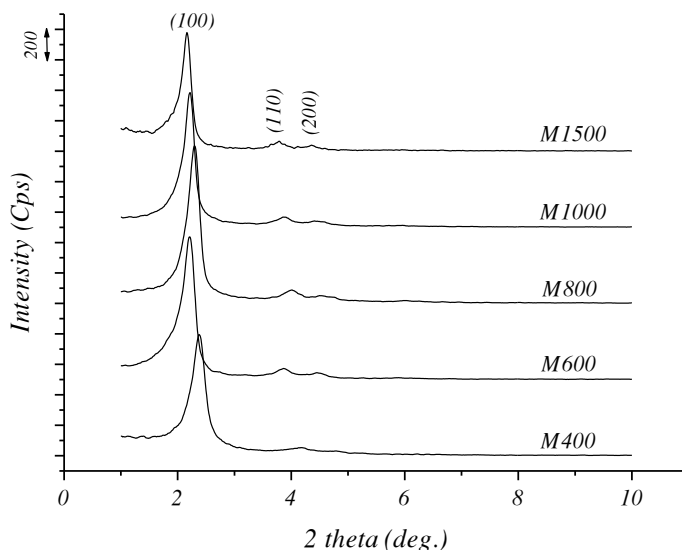


Fig. 1. XRD patterns of the MCM-41 samples with different H₂O/CTAB molar ratios

Table 1. HWHM of the samples with different H₂O/CTAB molar ratios

Samples	M400	M600	M800	M1000	M1500
β (deg.)	0.31	0.29	0.26	0.24	0.27

As can be seen from Table 1, β decreases and reaches a minimum at 0.24 corresponding to the H₂O/CTAB molar ratio of 1000, then it increases to 0.27 at sample M1500. It is known that β is inversely proportional to the size of crystals. Therefore, the M1000 sample exhibits the highest

crystal growth rate. Hence, the molar ratio of $\text{H}_2\text{O}/\text{CTAB} = 1000$ was chosen for the next experiments.

3.2 Effect of molar ratio SiO_2 : CTAB

The material was synthesized with molar proportions of $\text{CTAB}:\text{SiO}_2:\text{H}_2\text{O} = 1:y:1000$ (where $y = 4, 6, 8, 10$ and 15). The samples are denoted as M4, M6, M8, M10, and M15.

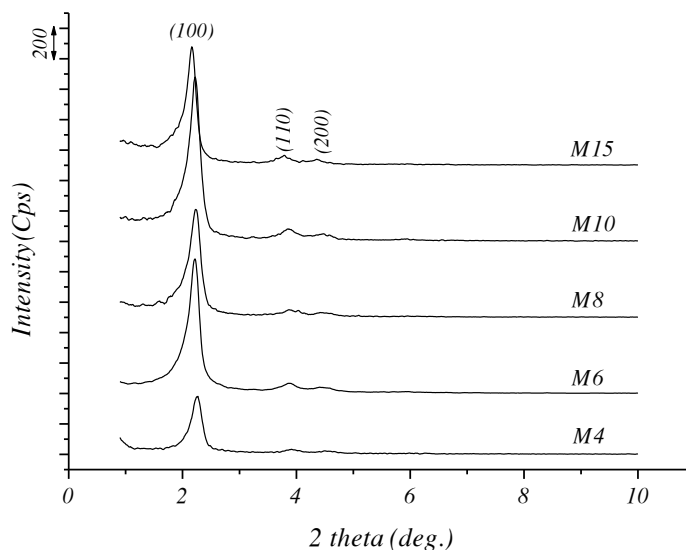


Fig. 2. XRD patterns of the samples with the different SiO_2/CTAB molar ratios

It can be seen from the XRD patterns in Fig. 2 that the synthesized material with different molar ratios of SiO_2/CTAB has typical peaks of MCM-41 material [1, 9]. Except for those with weak peaks, the remaining samples exhibit sharp high-intensity peaks indicating the highly-ordered structure of the material. The β values of these samples are practically the same at around 0.24 deg. indicating the same crystal growth (Table 2). However, when the ratio of SiO_2/CTAB increases, the consumption of sodium silicate is significant leading to the difficulties to adjust the pH because sodium silicate solution provides an alkaline medium. Therefore, the molar ratio of $\text{SiO}_2/\text{CTAB} = 6$ was chosen for the next studies.

Table 2. HWHM of the samples with different SiO_2/CTAB ratios

Samples	M4	M6	M8	M10	M15
β (deg.)	0.24	0.24	0.25	0.24	0.22

3.3 Effect of stirring time

In order to evaluate the effect of the stirring stage in the MCM-41 synthesis (after a strong stirring period of 2 hours), two MCM-41 samples with a molar ratio of gel mixture of CTAB:

SiO₂: H₂O = 1: 6: 1000 were synthesized under no stirring and 24-hour stirring (300 rpm). The samples are denoted as M0h, M24h.

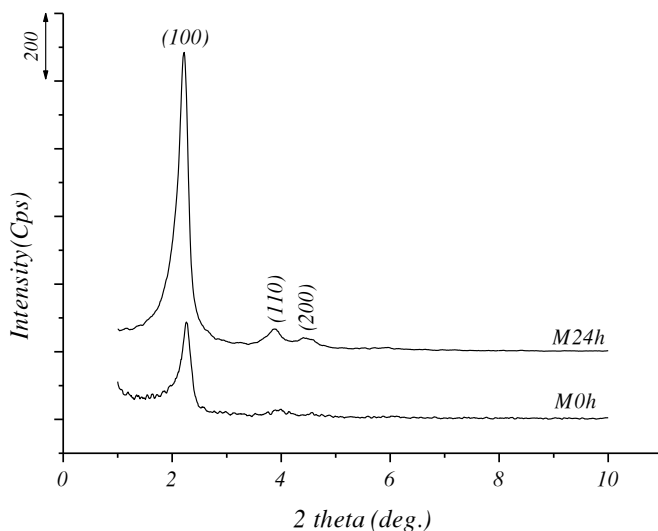


Fig. 3. XRD patterns of the samples with and without stirring

The XRD results presented in Fig. 3 showed that the sample without stirring has only two characteristic peaks assigned to (100) and (110) reflection planes with low intensity. This indicates low structural orderliness of the material. Meanwhile, the 24-hour stirring sample has all three typical sharp peaks of the MCM-41 material with high intensity, and this suggests that this sample has a highly ordered hexagonal structure. Thus, it is advisable to stir the reaction mixture four 24 hours.

3.4 Effect of aging time

According to Kresge [1], MCM-41 is formed according to a “liquid-crystal templating” mechanism. In this process, after sodium silicate is added to the structure-directing agent solution, the silicate anions interact with the polar head groups of the surfactants by an electrostatic interaction and form inorganic walls between the cylindrical micelles. Polymerization and condensation of silicate create an amorphous wall of MCM-41. Therefore, the aging period needs to be investigated to understand the structural stability of the material.

Three MCM-41 samples with a molar ratio of gel mixture of CTAB: SiO₂: H₂O = 1: 6: 1000 were synthesized under 24-hour stirring and aging time of 24, 48 and 72 hours. The samples are denoted as T24, T48, and T72.

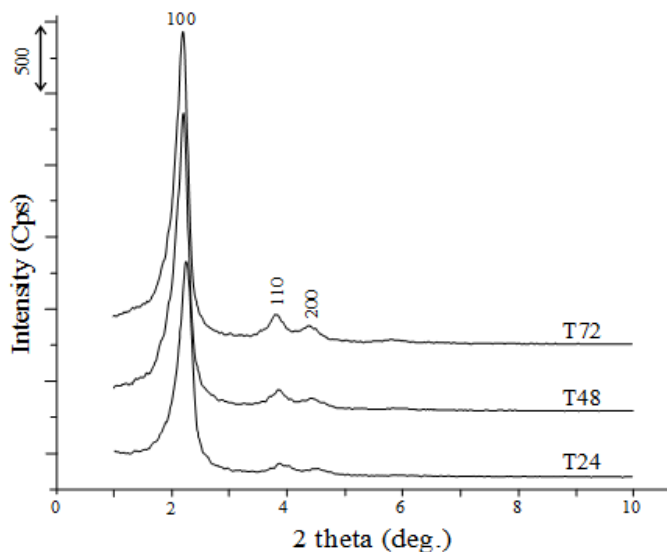


Fig. 4. XRD patterns of the samples with different aging time

Fig. 4 shows the XRD patterns of MCM-41 samples aged at 24, 48 and 72 hours. It is obvious that all samples have three sharp high-intensity typical peaks corresponding to the (100), (110) and (200) planes. It can be concluded that the obtained material has an ordered hexagonal structure. The peak intensity levels out at the 72-hour aging, and the d_{100} values hover around 40 Å. This suggests that the structure of the material is stabilized after 48 hours of aging.

3.5 Characterizations of the synthesized material

The MCM-41 with the molar ratio of CTAB: SiO₂: H₂O = 1: 6: 1000, aged 72 hours was characterized with infrared spectra (FT-IR) (Fig. 5).

It is clear that the synthesized material possesses the characteristic peaks of the MCM-41 material families [5]. The broad peak at 3448.72 cm⁻¹ is ascribed to the stretching vibration of the O-H bond in the hydroxyl groups or of physically adsorbed water. The strong peak at 1643.35 cm⁻¹ is due to the bending vibration of the O-H bond in water molecules. The peaks at 1226.73 cm⁻¹ and 1080.14 cm⁻¹ were assigned to the stretching vibration of the Si-O-Si bond in siloxane. The peak at 964.41 cm⁻¹ is attributed to the stretching vibration of the Si-OH bond in the surface of the silanol groups. The peak at 794.67 cm⁻¹ is associated with the stretching vibration of O-Si-O in the tetrahedral structure. This result is similar to that of previous works [5, 10].

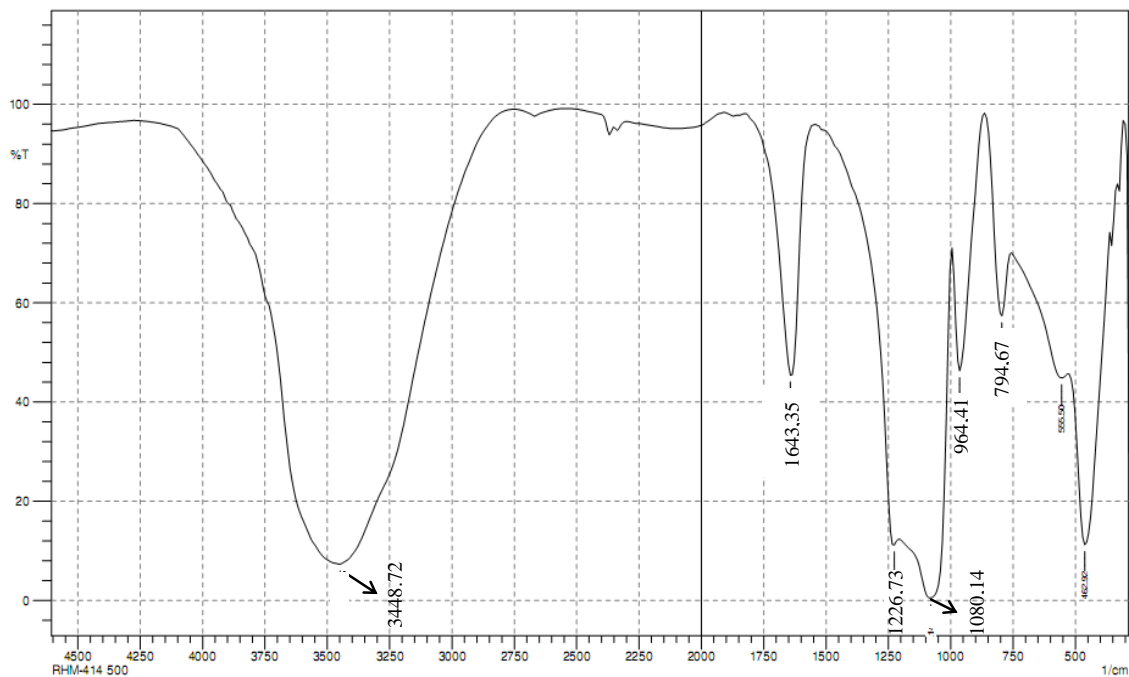


Fig. 5. FT-IR spectrum of the synthesized MCM-41 sample

Fig. 6 displays a TEM image of MCM-41. It can be seen clearly that the hexagonal mesoporous tubes arrange parallelly in the TEM image. This is consistent with the result of the XRD investigation.

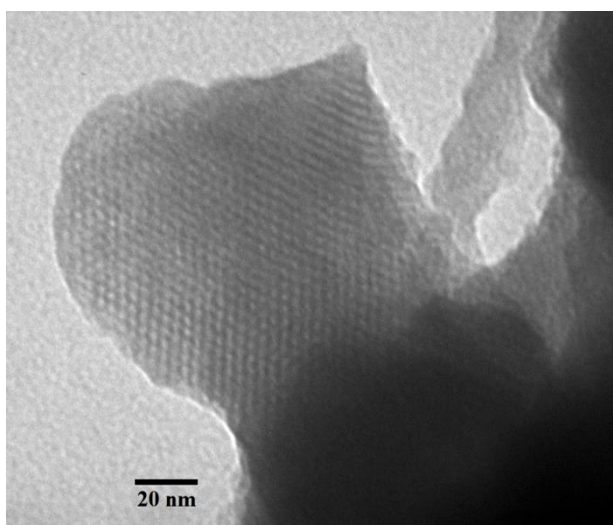


Fig. 6. TEM image of the synthesized MCM-41 material.

The N_2 adsorption-desorption isotherm was used to investigate the textural properties of the synthesized MCM-41 material. Fig. 7a shows that there is a characteristic hysteresis of the

MCM-41 ordered mesoporous material. The isothermal curve is of type IV according to IUPAC classification. The pore-filling step at $p/p_0 \approx 0.3$ and $p/p_0 \approx 0.4$ indicates a mesoporous material with a narrow range of cylindrical pores [9, 11]. The pore size distribution of MCM-41 exhibits a narrow peak (Fig. 7b). It is evident that the mesopores of the obtained material are relatively uniform.

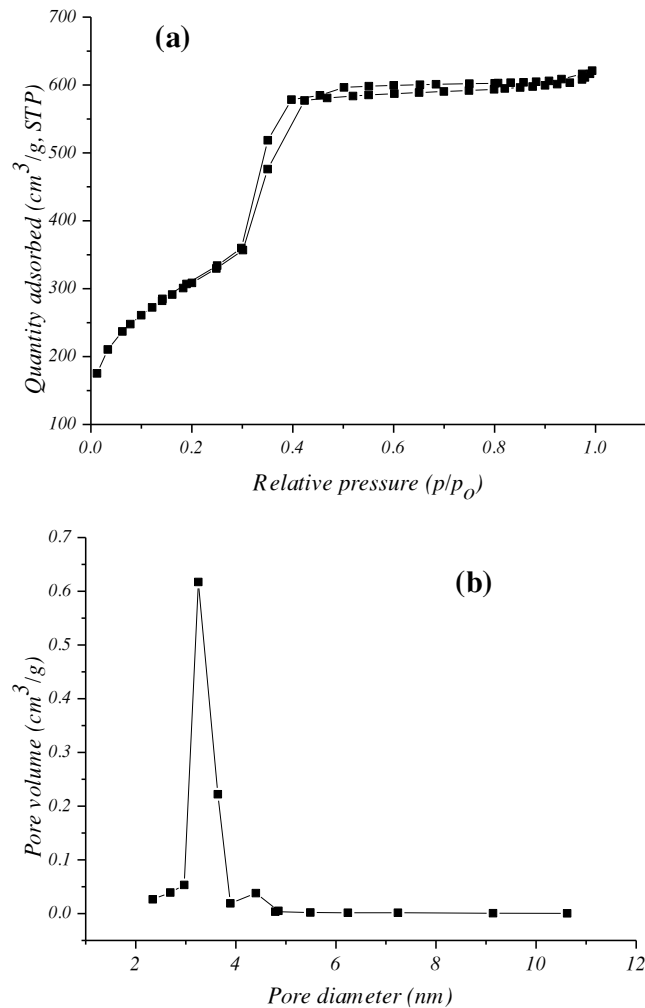


Fig. 7. Nitrogen adsorption-desorption isotherms (a) and pore size distribution (b) of MCM-41 material

It can be seen that the MCM-41 material synthesized with silicon from rice husk ash has a very large specific surface area of 1074.3 m²/g, a wide pore diameter of 33.56 Å, and a thick pore wall of 12.51 Å (Table 3). The same parameters of MCM-41 reported in other works are also shown in the table for comparison. It is obvious that nearly all the properties of the material obtained in this study are similar to or even better than those in the literature.

Table 3. Textural parameters of the synthesized MCM-41 sample

Sample	d_{100} (Å)	a_0 (Å)	d_p (Å)	V_{total} (cm ³ /g)	S_{BET} (m ² /g)	t_w (Å)	Reference
MCM-41	39.9	46.07	33.56	0.94	1074.3	12.51	This study
MCM-41*	37.9	43.80	28.70	0.29	796.0	15.10	[4]
MCM-41*	–	44.14	32.76	–	903.4	11.38	[5]
MCM-41*	–	–	24.30	0.49	602.0	–	[6]
MCM-41*	–	–	36.00	0.49	602.0	–	[7]
MCM-41**	–	–	34.00	0.88	1028.0	–	[3]
MCM-41**	39.6	45.80	27.90	0.77	941.0	17.90	[11]
MCM-41***	40.0	–	–	0.93	1050.0	–	[9]

(*) silicon source from rice husk ash; (**) silicon source from TEOS; (***) silicon source from TMOS; (–) not reported

4 Conclusion

The MCM-41 mesoporous material with the source of sodium silicate from rice husk ash was synthesized in a simple method. The synthesis conditions affecting the structure of the material were investigated. The synthesized material possesses an ordered hexagonal mesoporous structure within a wide range of surfactant concentration (1.33–4.81 % mass), of the SiO₂/CTAB molar ratio (4–15), and of aging time (24–72 hours). The MCM-41 material synthesized with the molar ratio of the CTAB: SiO₂: H₂O = 1: 6: 1000 has a highly-ordered hexagonal structure, very large specific surface area up to 1074.3 m²/g and wide pores of 33.56 Å. These properties of the synthesized MCM-41 material are equivalent to those of MCM-41 from TEOS, TMOS. It can be deduced that the rice husk ash is a suitable silica source for synthesizing MCM-41 material.

References

1. Kresge C. T., Leonowicz M. E., Roth W. J., Vartuli J. C., and Beck J. S. (1992), Ordered mesoporous molecular sieves synthesized by liquid-crystal template mechanism, *Nature*, 359, 710–712.
2. Jafarzadeh A., Sohrabnezhad Sh., Zanjanchi M. A., Arvand M. (2016), Synthesis and characterization of thiol-functionalized MCM-41 nanofibers and its application as photocatalyst, *Micropor. Mesopor. Mater.*, 236, 109–119.
3. Dong C., Li X., Wang A., Chen Y, Liu H. (2017), Influence of nanoscale distribution of Pd particles in the mesopores of MCM-41 on the catalytic performance of Pd/MCM-41, *Catalysis Communications*, 100, 219–222.
4. Adam F., Kueh C. W. (2015), Heterogeneous para-phenylamino sulfonic acid ligand functionalized on MCM-41 derived from rice husk ash: Selective mono-alkylated products of tert-butylation of phenol, *Applied Catalysis A: General*, 489, 162–170.
5. Suyanta and Agus Kuncaka (2011), Utilization of rice husk as raw material in synthesis of mesoporous silicates MCM-41, *Indo. J. Chem.*, 11 (3), 279 – 284.

6. Boonpoke A., Chiarakorn S., Laosiripojana N., Towprayoon S. and Chidthaisong A. (2011), Synthesis of Activated Carbon and MCM-41 from Bagasse and Rice Husk and their Carbon Dioxide Adsorption Capacity, *Journal of Sustainable Energy & Environment*, 2, 77–81.
7. Renuka N. K., Praveen A. K., Anas K. (2013), Influence of CTAB molar ratio in tuning the texture of rice husk silica into MCM-41 and SBA-16, *Materials Letters*, 109, 70–73.
8. Hoang Van Duc, Nguyen Thi Anh Thu (2014), Synthesis of SBA-15 mesoporous material with silica source from rice husk ash, *Viet Nam journal of catalysis and adsorption*, 3(2), 10–16 (in Vietnamese).
9. Lim M. H. and Stein A. (1999), Comparative studies of grafting and direct syntheses of inorganic-organic hybrid mesoporous materials, *Chem. Mater.*, 11, 3285–3295.
10. Yang S., Wu Y., Wu Y., Zhu L. (2015), Optimizing decolorization of Acid Fuchsin and Acid Orange II solution by MnO₂ loaded MCM-41, *Journal of the Taiwan Institute of Chemical Engineers*, 50, 205–214.
11. Qi B., Lou L. L., Wang Y., Yu K., Yang Y., Liu S. (2014). Comparison of different prepared Mn-MCM-41 catalysts in the catalytic epoxidation of alkenes with 30 % H₂O₂, *Micropor. Mesopor. Mater.* 190, 275–283.