

Synthesis and modification of MCM-41 with PEI using hydrothermal techniques in autoclave and microwave reactor

Yasmin T. Barboza^{a,b}, Marília R. Oliveira^b, Silvia M. Egues^{a,b}, Juliana F. De Conto^{a,b}

^a Tiradentes University (UNIT), Postgraduate Program in Process Engineering (PEP), Av. Murilo Dantas, 300, Aracaju-SE, Brazil, ZIP Code 49032-490.

^b Study Group on Colloidal Systems (NUESC)/Institute of Technology and Research (ITP), Av. Murilo Dantas, 300, Aracaju-SE, Brazil, ZIP Code 49032-490.

Abstract

The ordered mesoporous silica MCM-41 stands out due to its characteristics such as high surface area and pore volume. In this work, its synthesis is presented in two ways: via microwave and autoclave reactor. Microwave synthesis significantly accelerates the process by reducing reaction time, thanks to the rapid and uniform heating provided by microwaves, resulting in more adjustable pore sizes and larger specific surface areas. Additionally, this study performed the one-pot synthesis and modification of amine-modified MCM-41 using a microwave reactor and compared it to conventional synthesis in an autoclave reactor with post-synthesis impregnation modification. This study is pioneering, presenting promising results for one-step modification and synthesis, yielding a surface area almost three times larger than the conventional method. Physicochemical characterizations (BET, XRD, and FTIR) revealed surface areas of 1147 and 852 m² g⁻¹ for the silica synthesized using microwave and autoclave methods, respectively. Microwave technology proved effective, demonstrating that it is possible to obtain MCM-41-type silica in just 30 minutes while maintaining physicochemical properties. These results highlight the potential of this technique to optimize mesoporous silica synthesis processes, with important implications for future applications.

Keywords: MCM-41, Microwave irradiation, *One-pot* modification.

1. Introduction

The synthesis of MCM-41 is carried out using conventional methodologies, such as hydrothermal treatment in an autoclave, which involves high temperatures and long reaction times (100 °C for 24h). The hydrothermal synthesis method offers advantages in the production of mesoporous materials, such as control over the ordered structure and pore size, well-defined morphology, thermal stability, high purity, and uniformity. This occurs because the process takes place in a closed system under pressure and temperature. However, this synthesis method, though effective, can be time-consuming and energy-intensive [3, 4].

Alternatively, the use of microwaves offers advantages over conventional synthesis, such as reduced energy consumption, shorter reaction times, and highly uniform, rapid, and volumetric heating rates. This technique also allows for efficient control over the pore size distribution and particle diameter, as well as a higher quantity of silanol groups on the

silica surface, enhancing its use in catalysis and adsorption applications [9].

In their studies, Oliveira *et al.* [9] report that during the process, microwave energy uniformly heats the material and is directly distributed within it, unlike conventional heating, where heat is first applied to the walls of the container and then transferred to the material. Consequently, the rapid and controlled heating and reaction conditions provided by microwaves can lead to the formation of thermodynamically stable and efficient crystalline structures that would not easily be obtained through conventional heating methods.

However, to further enhance the efficiency of materials in adsorption processes, such as selectivity and adsorption capacity, surface modifications can be performed. The incorporation of organic functional groups on the silica surface is seen as a promising approach, as it increases the selectivity and adsorption capacity of organic compounds compared to unmodified silicas. This can be explained by the fact that silica has free silanol groups (Si-OH) on its surface, favoring the

anchoring of organic functional groups on the material's surface [6, 1].

Numerous studies on the modification of silica with amine groups have been conducted due to the high demand for efficient CO₂ capture solutions [1, 15-18]. Therefore, developing materials with modified surfaces that are highly selective and have a high adsorption capacity through accelerated processes is of utmost importance, not only for academic research but also for industry. This is because the significant reduction in energy and time costs in the preparation of these materials can yield considerable benefits.

Thus, this work aims to compare the textural and structural properties of mesoporous MCM-41 silicas synthesized using autoclave and microwave irradiation, followed by their modification with PEI (polyethyleneimine). Such a comparison is essential to identify the best approach for producing ordered mesoporous MCM-41 silica, with the goal of optimizing its properties and synthesis time for future technological applications.

2. Methodology

Synthesis of MCM-41 in Autoclave

The synthesis of MCM-41 was adapted from the procedure described by Grun et al. [8]. First, 1.4 g of CTAB was dissolved in 60 mL of water, followed by the addition of 4.75 g of ammonia and, slowly, 5 g of TEOS, under stirring for 1 hour at room temperature. This reaction mixture was subjected to hydrothermal treatment in an oven at 110 °C for 24 hours. After filtration, washing, and drying at 110 °C for 8 hours, the material was calcined at 550 °C for 6 hours to remove the surfactant. The resulting material was designated MCM-41-AC.

To perform the modification with PEI, 0.3 g of MCM-41 silica was placed in an oven at 100 °C overnight. Then, a PEI solution in methanol (0.165 g of PEI and 2.4 g of methanol) was prepared and stirred for 10 minutes. Subsequently, 0.3 g of MCM-41 was added to the solution, and stirring continued for 30 minutes. After the reaction, the material was dried in an oven for 8 hours at 80 °C. The resulting material was designated MCM-41-PAC.

One-pot Synthesis of Amine-Modified MCM-41 in Microwave Reactor

The methodology was based on the work of Oliveira *et al.* [9]. In this study, the reaction mixture (same as the autoclave synthesis) was heated in a microwave at 40 °C for 30 minutes with 300 W power. Afterward, the mixture was filtered, washed with distilled water, and dried at 110 °C for 8 hours. The material was calcined at 550 °C for 6 hours to remove the surfactant and was designated MCM-41-MW.

To perform the modification with PEI, the MCM-41 synthesis via microwave irradiation was repeated as described above, but at the end of the microwave heating, the supernatant was removed, and the PEI solution in methanol (0.165 g of PEI and 2.4 g of methanol) was added. This mixture was again heated in the microwave for 10 minutes at 40 °C. After the reaction, the material was filtered, washed with 100 mL of methanol and 100 mL of hexane, and dried in an oven for 8 hours at 80 °C. The resulting material was designated MCM-41-PMW.

Characterizations

The N₂ adsorption/desorption isotherms were measured at -196 °C using a NOVA 1200e – Surface Area & Pore Size Analyzer from Quantachrome Instruments. The specific surface area (ABET) was determined using the Brunauer-Emmett-Teller (BET) model. Pore distribution and volume analyses were carried out using the Barrett, Joyner, and Halenda (BJH) models. XRD analyses of the adsorbents were performed using a Shimadzu XDR-7000 diffractometer. FTIR spectra were collected on an Agilent Technologies-5975 (Bruker) spectrometer in the spectral range of 4000-650 cm⁻¹. Thermogravimetric analyses (TGA) of the synthesized materials were conducted using a HITACHI STA7200RV analyzer, with measurements taken from room temperature up to 800 °C.

3. Results and discussion

The data on the textural properties of the synthesized silicas are presented in Table 1. When both methodologies are compared, it is observed that the silicas synthesized by microwave irradiation (MCM-41-MW and MCM-41-55OP) exhibit higher surface area values than the silicas synthesized in the autoclave (MCM-41-AC and MCM-41-55P). When comparing the pure silicas with the modified ones, the functionalized materials show significantly

smaller surface areas, indicating that the pores were partially filled due to the modification.

Furthermore, the pore volume obtained from the samples synthesized by the two methodologies can also be highlighted. The silicas obtained via microwave irradiation present a higher pore volume than those synthesized in the autoclave, which is an important result as it relates to the material's adsorption capacity. It is suggested that this material may have greater accessibility and capacity in its pores, corroborating the effect of microwave irradiation, as this influences more uniform pores, internally altering the silica structure [13].

Table 1. Textural analysis and elemental analysis of MCM-41 silicas synthesized via microwave and autoclave.

Samples	A _{BET} (m ² g ⁻¹)	V _p (cm ³ g ⁻¹)	%C	%H	%N
MCM-41-AC	852	0.28	1.05	1.65	0.12
MCM-41-PAC	11	0.01	18.52	4.80	9.71
MCM-41-MW	1147	0.06	0.93	0.14	0.18
MCM-41-PMW	58	0.04	20.65	4.90	1.50

The results of this study, demonstrating a surface area of 1147 m²/g and a pore volume of 0.06 cm³/g for silicas obtained via microwave irradiation, show a distinct profile compared to other studies. Oliveira et al.'s work, which used microwaves for 30 minutes, reported a lower surface area of 760 m²/g but a significantly higher pore volume of 0.77 cm³/g.

It is noteworthy that the synthesis of MCM-41 silica in an autoclave required a longer reaction time, yet the surface areas obtained were similar or even lower than the MCM-41 silicas synthesized in this work. A possible explanation for this is that microwave irradiation heats rapidly and uniformly, making the hydrothermal treatment in a microwave reactor faster and more efficient compared to the autoclave process. This reduces synthesis time while maintaining the quality of the textural properties [9, 13]. This trend is observed in both the unmodified samples and those modified with PEI. Furthermore, elemental analysis shows an increase in the MCM-41-PAC, but not in the MCM-41-PMW, possibly due to the presence of CTAB.

Figure 1 shows the diffraction profile of pure and PEI-modified MCM-41 silicas obtained by hydrothermal autoclave and microwave irradiation

methods. As shown in Figure 1, all samples exhibit the main signal on the (100) reflection plane, characteristic of ordered mesoporous silica. These results confirm the formation of ordered porous materials, as the angular values of the main signal are within the allowed range of 0.5 to 3 degrees [11].

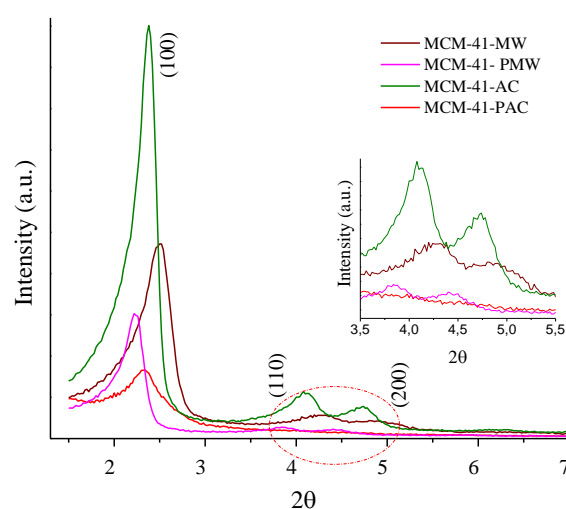


Fig. 1. X-ray diffraction profile of MCM-41 silicas synthesized via microwave and autoclave methods.

However, in addition to the main signal, MCM-41 silica exhibits secondary and tertiary signals corresponding to the (1-1-0) and (2-0-0) reflection planes, as can be observed in the MCM-41-MW, MCM-41-AC, and MCM-41-PAC samples. However, in the MCM-41-PMW sample, these signals are not evident, which may be related to possible residual surfactant in its pores or the high amount of PEI on the surface. It is also worth noting that the modified samples (MCM-41-55OP and MCM-41-55P) show a slight shift in the angle of these signals, indicating a possible structural change due to the anchoring of amine on the silica surface. In agreement with the XRD results, Figure 2 presents the FTIR spectra of the MCM-41 silicas. The vibrations of bands corresponding to the silica-forming groups. In the range of 800 to 1300 cm⁻¹, the characteristic bands of Si-O-Si and Si-O-H groups are observed. The presence of N-H bonding bands from amines in the MCM-41-55OP and MCM-41-55P samples is noticeable in the region of 1700 to 1500 cm⁻¹, confirming modification in both silicas. In the range of 2855 and 2928 cm⁻¹, two bands are observed that are more prominent in amine-impregnated silicas, attributed to the

asymmetric and symmetric stretching vibrations of CH groups.

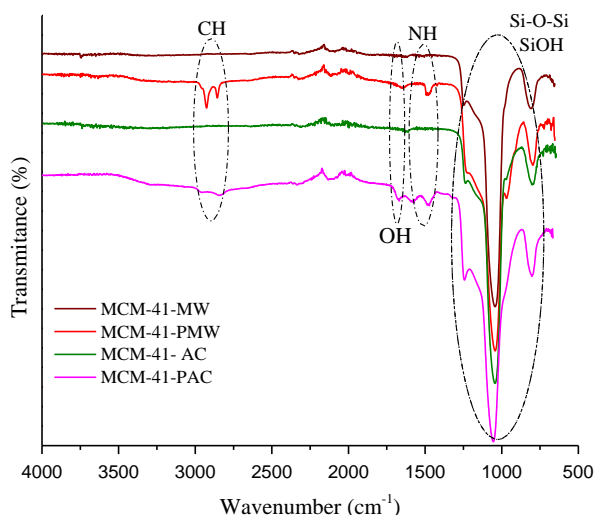


Fig. 2. FTIR spectrum of MCM-41 silicas synthesized via microwave and autoclave methods.

In the MCM-41-PMW sample, these vibrations are even more pronounced, possibly due to the presence of CTAB residues, as calcination was not performed [2, 14]. The region around 1672 cm^{-1} indicates the presence of O-H groups, which are associated with adsorbed water and silanol groups [7, 12].

4. Conclusion

The microwave-assisted synthesis demonstrated promising results compared to the conventional synthesis, not only allowing for a shorter reaction time but also achieving materials with a larger surface area. With a synthesis time of 30 minutes, a surface area of $1147\text{ m}^2/\text{g}$ was obtained, compared to 24 hours of synthesis yielding a surface area of $852\text{ m}^2/\text{g}$. The physicochemical characterizations confirmed the effectiveness of the synthesis. Additionally, it is important to highlight the results obtained from MCM-41-55OP, as this innovative methodology, not yet reported in the literature, shows promising results in terms of surface area, being nearly 3 times greater than the results obtained by conventional impregnation (MCM-41-55P),

providing an efficient alternative in the synthesis of porous materials.

5. References

- [1] CECILIA, J. A. *et al.* E. Functionalization of hollow silica microspheres by impregnation or grafted of amine groups for the CO₂ capture, *International Journal of Greenhouse Gas Control*, 52, p. 344 – 356, 2016.
- [2] OLIVEIRA, M. R. *et al.* Rapid synthesis of MCM-41 and SBA-15 by microwave irradiation: promising adsorbents for CO₂ adsorption. *Journal of Sol-Gel Science and Technology*, v. 105, n. 2, p. 370–387, 31 dez. 2023.
- [3] MEHDIPOUR-ATAEI, S., & ARAM, E. (2023). Mesoporous Carbon-Based Materials: A Review of Synthesis, Modification, and Applications. *Catalysts*, 13(1), 2. doi:10.3390/catal13010002.
- [4] SU, Y., CHEN, Y., & WANG, D. (2023). Advances in Hydrothermal Synthesis of Functional Mesoporous Silica Materials: From Basic Research to Industrial Applications. *Microporous and Mesoporous Materials*, 351, 111637. doi:10.1016/j.micromeso.2022.111637.
- [5] JELLA G.; BARATH T.; RAVINDRAN S. Applications and Future Trends in Mesoporous Materials. *Engineering materials*, p. 235–258, 14 nov. 2021.
- [6] KISHOR, R.; GHOSHAL, A. K. APTES grafted ordered mesoporous silica KIT-6 for CO₂ adsorption. *Chemical Engineering Journal*, v. 262, p. 882–890, fev. 2015.
- [7] ERGÜN, A. N. *et al.* Synthesis of mesoporous MCM-41 materials with low-power microwave heating, *Chemical Engineering Communications*, 200, p. 1057–1070, 2013.
- [8] GRUN, M. *et al.* Novel pathways for the preparation of mesoporous MCM-41 materials: control of porosity and morphology, *Microporous and Mesoporous Materials*, 27, p. 207 – 216, 1999.
- [9] OLIVEIRA, M. R. *et al.* Effect of microwave irradiation on the structural, chemical, and hydrophilicity characteristics of ordered mesoporous silica SBA-15, *Journal of Sol-Gel Science and Technology*, 94, p. 708–718, 2020.
- [10] MUCHAN, P.; SAIWAN, C.; NITHITANAKUL, M. Investigation of adsorption/desorption performance by aminopropyltriethoxysilane grafted onto different mesoporous silica for post-combustion CO₂ capture, *Clean Energy*, 4, p. 120 – 131, 2020.
- [11] ZHAO, D. Y. *et al.* Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores, *Science*, 279, p. 548 – 552, 1998.
- [12] YANG, G. *et al.* A facile approach to synthesize MCM-41 mesoporous materials from iron ore tailing: Influence of the synthesis conditions on the structural properties, *Applied Clay Science*, 111, p. 61 – 66.
- [13] DE CONTO, J. F. *et al.* Synthesis of silica modified with 1-methylimidazolium chloride by sol-gel method: A comparison between microwave radiation-assisted and conventional methods, *Journal Non-Crystalline Solids*, 471, p. 209 – 214, 2017.
- [14] OLIVEIRA, M. R. *et al.* One-Pot synthesis and surfactant removal from MCM-41 using microwave irradiation. 2023.
- [15] KULKARNI, V.; PANDA, D.; SANJAY KUMAR SINGH. Direct Air Capture of CO₂ over Amine-Modified Hierarchical Silica. *Industrial & Engineering Chemistry Research*, v. 62, n. 8, p. 3800–3811, 6 fev. 2023.
- [16] LI, X. *et al.* Amine-functionalized mesoporous silica derived from natural phyllosilicate for efficient CO₂ adsorption. *Applied Clay Science*, v. 256, p. 107433–107433, 1 ago. 2024.
- [17] Anyanwu, JT ; Wang, Y. ; Yang, RT Captura de CO₂ (incluindo captura direta de ar) e dessulfuração de gás natural de sílica bimodal hierárquica enxertada com amina. *Eng. J.* 2022, 427, 131561, DOI: 10.1016/j.cej.2021.131561
- [18] RIHAM SURKATTI *et al.* Comparative analysis of amine-functionalized silica for direct air capture (DAC): Material characterization, performance, and thermodynamic efficiency. *Separation and Purification Technology*, p. 128641–12864