



Nb-MCM-Type Mesoporous Material Synthesis Using Ionic Solid as Structure-Directing Agent for In Situ Lipase Immobilization

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Abstract

MCM-41 and MCM-48 with niobium were successfully synthesized using 1-tetradecyl-3-methylimidazolium chloride ($[C_{14}MI]Cl$) as a structure-directing agent. The best Si/Nb molar ratio was chosen ($Si/Nb = 20$) and the CALB enzyme was immobilized in situ in the synthesized Nb-MCM. SEM micrographs showed the formation of very regular spherical agglomerates with a diameter between 0.25 and 0.75 μm . The material presented a surface area of 954 and 704 m^2/g and a pore volume of 0.321 and 0.286 cm^3/g , for Nb-MCM-41 and Nb-MCM-48, respectively. Also, both materials showed a pore size of 2.261 nm. The number of recycles obtained for the CALB enzyme immobilized in Nb-MCM-41 and Nb-MCM-48 was 26 recycles with a residual activity of 49.62% and 16 recycles with a residual activity of 53.01%, respectively. For both materials, enzymatic activity remained stable for 5 months of storage at room temperature and refrigeration. The supports were able to catalyze the esterification reaction at 40, 60, and 80 °C, showing industrial application in reactions that require high temperatures. This methodology allows the preparation of new highly active and selective enzyme catalysts using niobium and $[C_{14}MI]Cl$. Also, the new materials can provide greater viability in processes, ensuring a longer service life of catalysts.

Keywords Nb-MCM-41 · Nb-MCM-48 · Niobium · $[C_{14}MI]Cl$ · CALB

Highlights

- MCM-41 and MCM-48 with niobium and $[C_{14}MI]Cl$ were successfully synthesized
- The best Si/Nb molar ratio chosen was $Si/Nb = 20$
- CALB immobilized in Nb-MCM-41 and Nb-MCM-48 showed 26 and 16 recycles, respectively
- Enzymatic activity remained stable for 5 months for both supports
- The supports were able to catalyze the esterification reaction at 40, 60, and 80 °C

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Introduction

Porous silicate materials have excellent chemical and physical properties, such as high catalytic activity and thermal stability, which generates great industrial interest, with application in catalysis, adsorption, or ion exchange involving processes [1]. The pore size in materials is related to the diffusion speed, being found in the range of micropores, mesopores, or macropores. Currently, new materials are being developed with hierarchical pore structures to improve the diffusive properties of materials, making use of ionic liquids and solids [2].

Researchers have investigated the incorporation of metals in mesoporous networks to increase their catalytic capacity. It was found that the so-called MCM (Mobil Composition of Matter) which are materials belonging to the M41S family [3] can be modified with metals, in order to significantly improve their activity and catalytic selectivity. The modification of molecular sieves, such as MCM-41, through the introduction of transition metals, is called “redox sieves.” Molecular sieves are porous metal oxides and can have different compositions and pore sizes. Acting as a support, they offer useful properties, such as high surface area. Mesoporous metallic solids can reach a range of 700–1500 m²/g, and have a hydrophobic or hydrophilic behavior, electrostatic interactions, and mechanical and chemical resistance [4–6].

The structure-directing agent shapes the pores of each material, causing the appearance of different shapes, depending on the material. For this reason, three types of mesoporous molecular sieves of the M41S family of silicates are obtained through different formation routes, being the hexagonal (MCM-41), cubic (MCM-48), and lamellar (MCM-50) phases [5, 7]. However, the preparation of these solids requires a template, and for this reason, ionic surfactants and an ionic organization mechanism are used as structure directing agents [8].

Ionic liquid and/or ionic solid (depending on the cation and anion) can act as a structure and/or mold directing agent, which aims to induce crystallization of crystalline structures that could not be formed without their presence. The advantage of use ionic liquids in the structure construction is by the increase in the space limits of microporous holes, contributes to the stability of the material, and makes its crystallization thermodynamically possible. In addition, ionic liquids present properties as low flammability, low vapor pressure, and unique solubility for organic and inorganic materials where its solubility allows it use for lipase-catalyzed reactions, as shown in the literature [9–11]. Generally, ionic liquids and solids are composed only of ions, defined as salts whose melting point is less than 100 °C, and are used in several applications due to their characteristics [2, 12].

Recently, the impregnation of metals in molecular sieves have been reported [13], and niobium oxides (Nb₂O₅) and their derivatives have been gaining attention and are known as compatible catalysts for several organic reactions [14]. This highlight comes because of the special properties of niobium, such as stability and strong interaction of the support with the metal. Guerrero-Pérez [15] also highlights niobium as an active component of many catalytic systems by investigating industrial catalysts modified with niobium in the last decade, showing an incorporation of this metal in mesoporous molecular sieves, such as MCM.

Méndez and co-workers [6] carried out a study on the effect of niobium on CoMo/MCM-41 and NiMo/MCM-41 catalysts and applied these materials in order to evaluate the performance in the hydrodesulfurization of dibenzothiophene. The results show that the incorporation of small amounts of Nb (3–5% by weight) resulted in an increase in the catalytic activity of the materials in the hydrodesulfurization of dibenzothiophene and affected its selectivity [6]. Mesoporous materials modified with niobium also have water tolerance and were reusable for glycerol acetalization, where acetalization of glycerol in acetone has been reported for the

generation of solketal (4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane), which is an oxygenated compound useful as a chemical additive and fuel for gasoline, diesel, and biodiesel [16]. However, the catalytic properties of niobium have not yet been fully explored.

In the present study, materials based on mesoporous silicates with high surface area modified with niobium (Nb^{5+}) were analyzed. To test the effectiveness of the support, in situ enzymatic immobilization of *Candida antarctica* B (CALB) enzyme was carried out, subjecting the supported material to operational conditions, thermal reaction, and storage stability. The CALB lipase was chosen for the present study because it has several industrial applications, stability in organic solvents, and has broad specificity for substrates [17, 18]. Despite all the advantages of using lipase as a biocatalyst, the use has some restrictions, such as the impossibility of reuse, costs with product separation, and low thermal and operational stability. Therefore, enzymatic immobilization on different supports has become popular in order to overcome these limitations [19–21]. Thus, the presence of porous structures in the support can help to trap enzymes efficiently, as well as reducing their leaching in the application of the reaction of interest. In this sense, it can also protect enzyme molecules from external denaturing conditions, as reported in the literature [22].

Over the years, the supports for enzyme immobilization as nanofibers, mesoporous materials, polymers, nanomaterials, membranes, and cellulose have been improved by modification on the material structures, leading to better enzyme-supports interactions [23]. The use of mesoporous materials supports possibilities' best interactions with enzymes due to it easily modifications on structure and surface through addition of metals and functional groups [24].

Given the above, the present study aimed to obtain new MCM materials modified with niobium by using the ionic solid 1-tetradecyl-3-methylimidazolium chloride ($[\text{C}_{14}\text{MI}]\text{Cl}$) as structure-directing agent. Nb-MCM-41 and Nb-MCM-48 materials were applied as support for enzymatic immobilization of the CALB lipase. Characterizations of the supports were carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM), and textural analysis of N_2 adsorption/desorption (BET). Besides, the operational, thermal reaction, and storage stability of the produced supports was evaluated.

Materials and Methods

The synthesis of the mesoporous materials MCM-41 and MCM-48 was carried out with different molar ratios of Nb, using the ionic solid 1-tetradecyl-3-methylimidazolium chloride ($[\text{C}_{14}\text{MI}]\text{Cl}$) [25] as a structure-directing agent.

Molar Ratios of Niobium in the Synthesis of MCM-48 and MCM-41

Initially, ammoniacal niobium oxalate ($\text{NH}_4[\text{NbO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]3\text{H}_2\text{O}$) was calcined in a Millenium Digital VRC Electric Oven with heating ramps, 150–90 °C, 450 °C, 360 min, to obtain the niobium oxide (Nb_2O_5) that was applied in the synthesis of the mesoporous materials MCM-48 and MCM-41. These materials were synthesized according to the methodology described by Kumar et al. [26], with changes in the template used. For the synthesis of MCM-48 with niobium (Nb-MCM-48), 2.4 g of the ionic solid $[\text{C}_{14}\text{MI}]\text{Cl}$ were diluted in deionized water (50 mL), under magnetic stirring. Fifty milliliter of absolute ethanol and 12 mL of ammonium hydroxide (NH_4OH , Quimex) were added to the reaction medium, where the system was stirred for 10 min. Then, 3.4 g of tetraethylorthosilicate (TEOS) was added and

the variable amount of niobium oxide, as described in Table 1 for molar ratios Si/Nb = 1, 20, 50, and 80. The reaction was under magnetic stirring (Fisatom, model 754A) for 2 h.

The synthesis of MCM-41 with niobium (Nb-MCM-41) was also carried out according to the methodology described by Kumar et al. [26], with adaptations. For this purpose, 2.4 g of the ionic solid $[C_{14}MI]Cl$ were added to 120 mL of deionized water under magnetic stirring. After complete dilution of the ionic solid, 8 mL of NH_4OH were added to the reaction medium, where it was left under stirring for 5 min. Then, 10 mL of TEOS and the variable amount of niobium oxide, as described in Table 1 for molar ratios Si/Nb = 1, 20, 50, and 80. The reaction was under magnetic stirring for 24 h.

To evaluate the immobilization of the CALB enzyme in these materials and verify the action of niobium, the Si/Nb = 20 ratio was chosen, as it is the second molar concentration with the highest amount of niobium and has been shown to be homogeneous.

Synthesis of MCM-41 and MCM-48 with Si/Nb = 20 in Enzymatic Immobilization

For the synthesis of MCM-48 Si/Nb = 20, 1.2 g of $[C_{14}MI]Cl$ and 25 mL of deionized water were added in a 600-mL Teflon reactor. Subsequently, 25 mL of absolute ethanol and 6 mL of NH_4OH were added, and the mixture was left under stirring for 10 min. Afterward, 1.7 g of TEOS, niobium oxide (Si/Nb = 20), and 0.5 g of liquid enzymatic extract of the free CALB lipase were added and the reaction was under magnetic stirring for 2 h. Finally, the resulting material was washed until pH 9 and dried at room temperature (20–25 °C).

After the immobilization of the CALB enzyme on the MCM-48 support, the esterification activity in the immobilized enzymatic derivatives was determined through the reaction using oleic acid and ethanol in the molar ratio of 1:1, as described in the literature [18]. The enzymatic immobilization of the CALB lipase on the MCM-41 support and activity measurement occurred in the same way as previously mentioned for the MCM-48 support, however, with the formation route and reagents described for the MCM-41.

Morphological Characterization

X-Ray Diffraction

X-ray diffraction analyses were performed on a Rigaku Miniflex II Desktop X-Ray Diffractometer, using $CuK\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$), where the samples with the different Si/Nb ratio were analyzed at a 2θ angle (1.5 to 65°) using an X-ray tube voltage of 30.0 (kV) and current of 15.0 (mA).

Table 1 Mass of niobium used in the different Si/Nb ratios in the synthesis of MCM-48 and MCM-41

Si/Nb (mol/mol)	Nb mass (g) MCM-48	Nb mass (g) MCM-41
1	4.250	12.75
20	0.212	0.638
50	0.085	0.255
80	0.053	0.159

Scanning Electron Microscopy

The samples of the materials synthesized with and without enzyme were analyzed by scanning electron microscopy (SEM). The Zeiss scanning electron microscope (model EVO LS25) with metallizer (QUORUM SC7620) was used. The samples were covered with 20-nm gold.

Textural Analysis

The samples of Nb-MCM-48 and Nb-MCM-41 were initially calcined for 3 h at a temperature of 600 °C and pretreated for 12 h at 100 °C under reduced pressure before the analysis. This pre-treatment was carried out to eliminate possible interferences, such as moisture, organic matter, and the structure director. The analysis was performed at a constant temperature of -196 °C (77 K) [27]. The specific surface areas were determined using the BET method [28].

Enzymatic Stability of the CALB Enzyme in Nb-MCM-48 and Nb-MCM-41

Operational Stability

The operational stability of the supports Nb-MCM-48 and Nb-MCM-41 containing the immobilized CALB enzyme was determined in successive esterification reactions with its reuse. After each batch, the reaction medium (liquid phase) was removed, maintaining the solid phase and adding a new reaction medium. This procedure was performed until the activity fell by half the initial value (50% of residual activity) [27].

Thermal Stability of the Esterification Reaction

The thermal stability of the immobilized MCM-48 (Si/Nb = 20) ratio was achieved by the esterification reaction at temperatures of 40, 60, and 80 °C. For this, the esterification methodology described above was used, changing the reaction temperature.

Storage Stability

The storage stability of the materials was carried out at room temperature (20–25 °C) and refrigeration (5–7 °C), as described by Ficanha et al. [27], for 5 months.

Results and Discussion

XRD Analysis

Figure 1 shows the resulting diffractograms, indicating the peaks corresponding to both MCM-41 and MCM-48 at different Si/Nb molar ratios. It is possible to observe the typical structure pattern, related to these materials [2], as well as the peaks corresponding to the presence of niobium in the synthesized material [29], indicating that the niobium was effectively incorporated into the synthesis of MCM. Still, it is possible to note that the relationship with more niobium (Si/Nb = 1) was the one with the highest intensity of Nb₂O₅ peaks, precisely because it had a higher amount of this element. As expected, by decreasing the niobium ratio in the

samples, it is possible to observe a smaller number of peaks and peaks with less intensity. However, Si/Nb = 1 showed no homogeneity in the synthesis, which may be linked to the higher Nb₂O₅ intensity observed in the sample, depending on the portion analyzed by the equipment. Due to that, the Si/Nb = 20 ratio was chosen to continue the analysis of the present study.

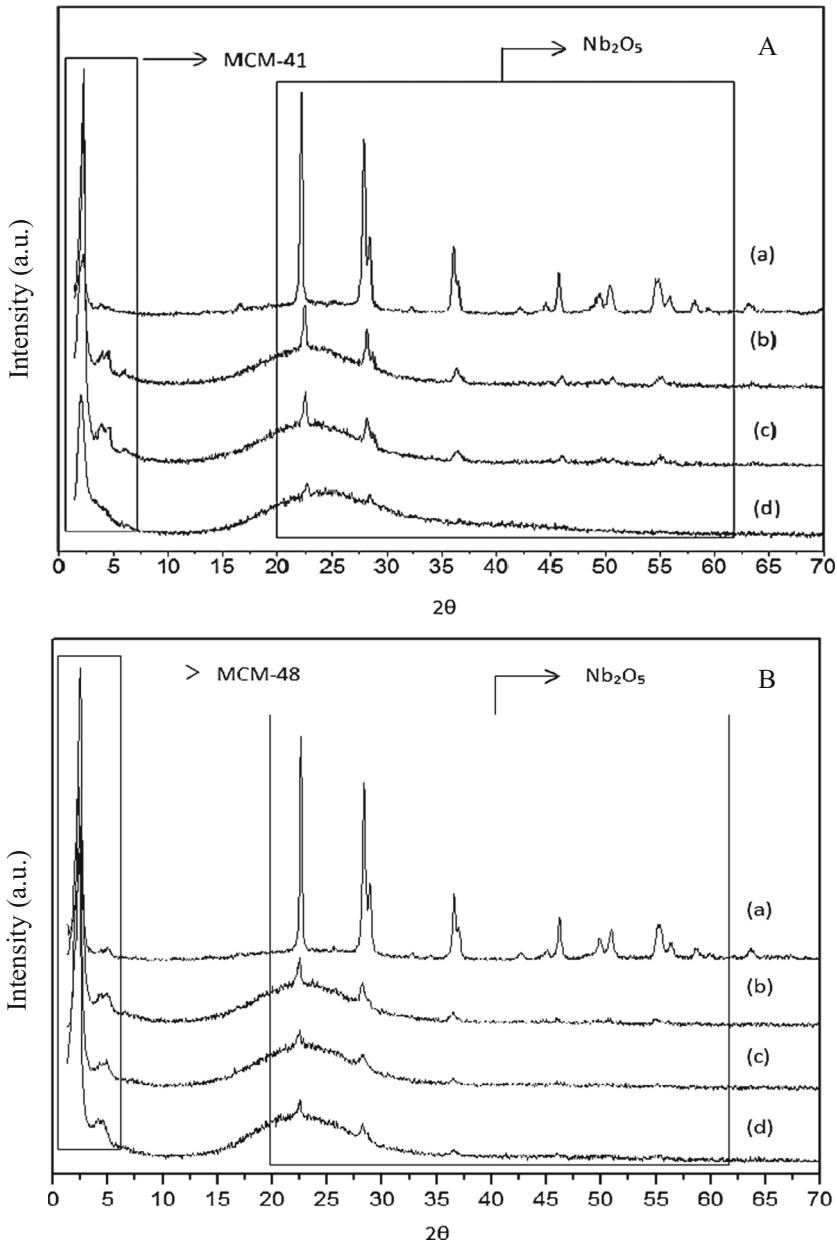


Fig. 1 X-ray diffraction analysis of **A** MCM-41 and **B** MCM-48 with different molar ratios: (a) Si/Nb = 1, (b) Si/Nb = 20, (c) Si/Nb = 50, and (d) Si/Nb = 80

For a better visualization and confirmation of the obtained results, the peaks referring to the niobium in the Si/Nb = 20 samples were approximated and shown in Fig. 2. It is possible to observe a similar peak, with the same tendency for both MCM. This indicates that both MCM-41 and MCM-48 contain niobium in their structure in a similar way, and it is possible to use both mesoporous materials for this purpose.

SEM Analysis

The images obtained by scanning electron microscopy for materials with and without enzyme are shown in Fig. 3. It is possible to observe that mesoporous materials synthesized at room temperature have a spherical shape due to the presence of ionic solid, which in water acts as a surfactant. All materials obtained are characteristic of MCM as observed in the literature [2, 30], and presented a diameter between 0.25 and 0.75 μm .

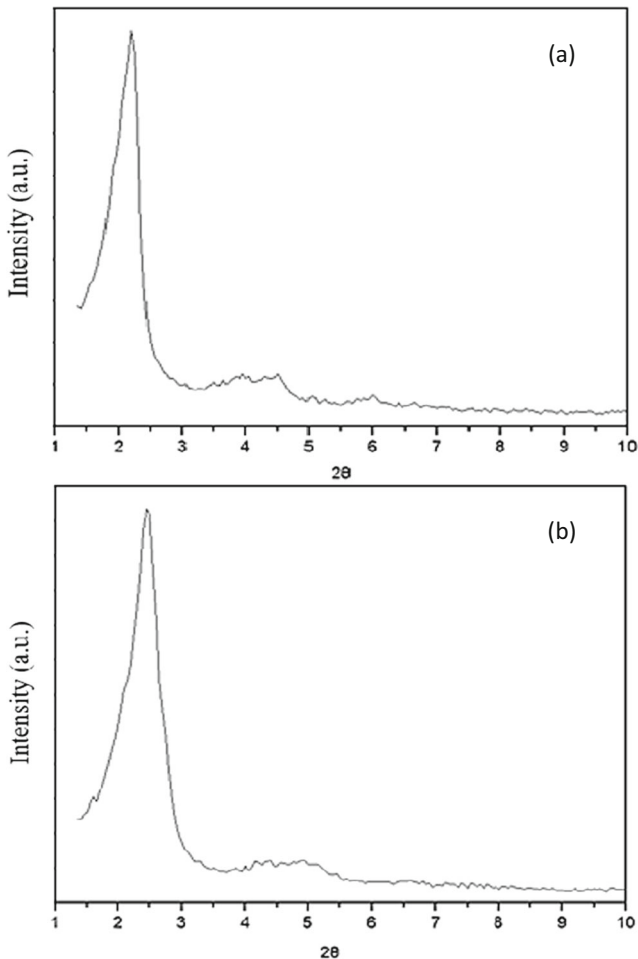


Fig. 2 Amplified X-ray diffraction analysis of (a) MCM-41 and (b) MCM-48 with Si/Nb = 20 molar ratio

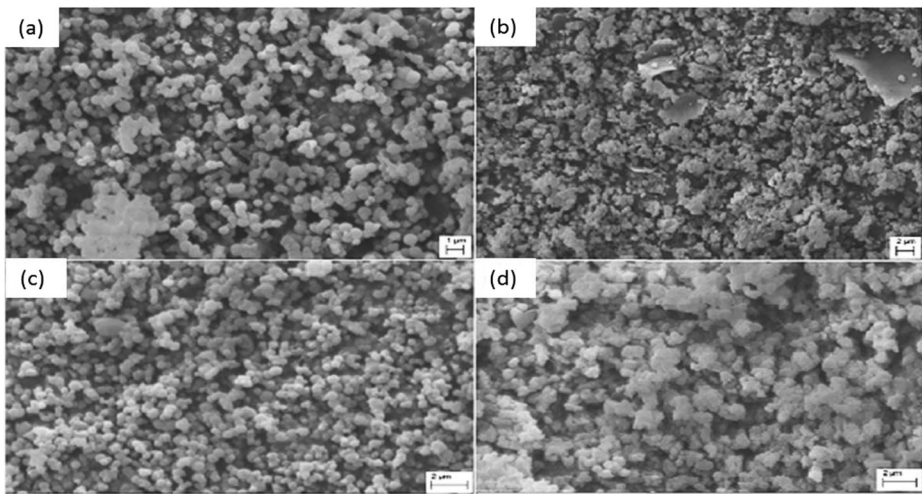


Fig. 3 SEM analyses of the sample Nb-MCM-41 (a) with and (b) without CALB enzyme, and Nb-MCM-48 (c) with and (d) without CALB enzyme

Textural Analysis

Through the textural analysis of N_2 adsorption/desorption, it is possible to observe the isotherms from which important information is obtained, such as volume and pore size, in addition to the surface area of the materials. The isotherms referring to the mesoporous materials of the Nb-MCM type are shown in Fig. 4.

The materials Nb-MCM-41 and Nb-MCM-48 presented isotherms belonging to type IV with hysteresis type H1, according to the International Union of Pure and Applied Chemistry (IUPAC). This classification is common in characterized porous materials since they consist of uniformly compacted spheres or agglomerates in a fairly regular arrangement which, therefore, have a narrow pore size distribution [5, 31]. In Table 2, it is possible to observe the properties of the materials Nb-MCM-41 and Nb-MCM-48, such as pore volume, size, and surface area.

The analyzed materials presented pore volume characteristic of mesoporous materials. In addition, both MCM with niobium showed the same value for the pore size. MCM are known

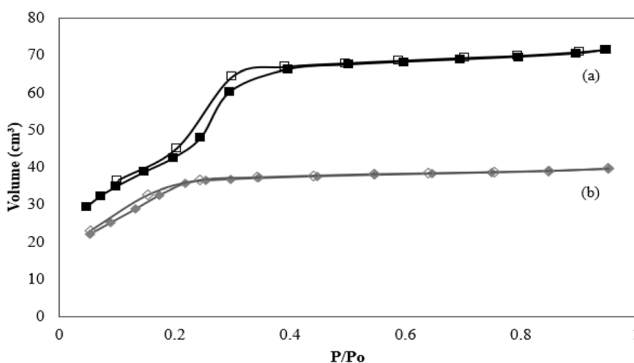


Fig. 4 Adsorption/desorption isotherm for (a) Nb-MCM-41 and (b) Nb-MCM-48

Table 2 Textural properties of the synthesized mesoporous materials Nb-MCM-41 and Nb-MCM-48

	Pore volume (cm ³ /g)	Pore size (nm)	Surface area (m ² /g)
Nb-MCM-41	0.321	2.261	954
Nb-MCM-48	0.286	2.261	704

for their high surface area (ranging from 700 to 1500 m²/g) [3, 7], consistent with the analysis of materials obtained with niobium.

Use of Nb-MCM-41 and Nb-MCM-48 as Support for Enzymatic Immobilization

The supports Nb-MCM-41 and Nb-MCM-48 were used for enzyme immobilization, where the enzyme was incorporated, in situ, into the support through entrapment, during the nucleation process and structural material formation. Before testing the esterification capacity of the enzyme supported on these materials, esterification tests with Nb-MCM-41 and Nb-MCM-48 without the addition of enzymes were carried out on the esterification of oleic acid with ethanol to evaluate the influence of the support on the conversion results. An esterification activity of 150.78 U/g was observed for Nb-MCM-48 and 84.95 U/g for Nb-MCM-41, obtained with the Si/Nb = 20 ratio. The result of the support's influence on the activity measure is important in order to discount the support influence and evaluate the enzyme in isolation. The enzymatic activity of the free CALB lipase was 209.15 ± 4.22 U/mL.

In the stability tests, the esterification value provided by the support without enzyme was discounted and only the results referring to the CALB enzyme are presented. An initial esterification activity of 313.60 ± 15.55 U/g was observed for Nb-MCM-48 and 244.90 ± 19.94 U/g for Nb-MCM-41 with CALB.

Operational Stability

The number of recycles obtained from CALB enzyme immobilized in Nb-MCM-41 and Nb-MCM-48 is shown in Fig. 5. It is possible to observe that Nb-MCM-41 presented the highest number of recycles, showing a residual activity of 49.62% in the 26th recycle. It is also observed that until cycle 23, the support showed 100% residual activity, decreasing after the 24th cycle. Similar behavior was observed for Nb-MCM-48 until the 14th reuse cycle, which showed a residual activity of 100%. However, the residual activity of Nb-MCM-48 decreases to 53.01% of in the 16th cycle.

Battiston et al. [32] studied the immobilization of the CALB enzyme in MCM-48 with the ionic solid [C₁₆MI]Cl (1-hexadecyl-3-methylimidazolium chloride) reporting it reuse up to 10 cycles, showing residual activity of 50%. When comparing the result reported in the literature with that obtained in the present study, the positive influence of niobium with [C₁₄MI]Cl becomes remarkable. In other words, it can be said that niobium helps to protect and prevents leaching of the enzyme into the reaction medium, being possible a significant number of recycles.

Storage Stability

The residual activity at room temperature and in refrigeration of Nb-MCM-41 and Nb-MCM-48 with CALB enzyme remained constant for 5 months (Table 3). For both supports, storage at

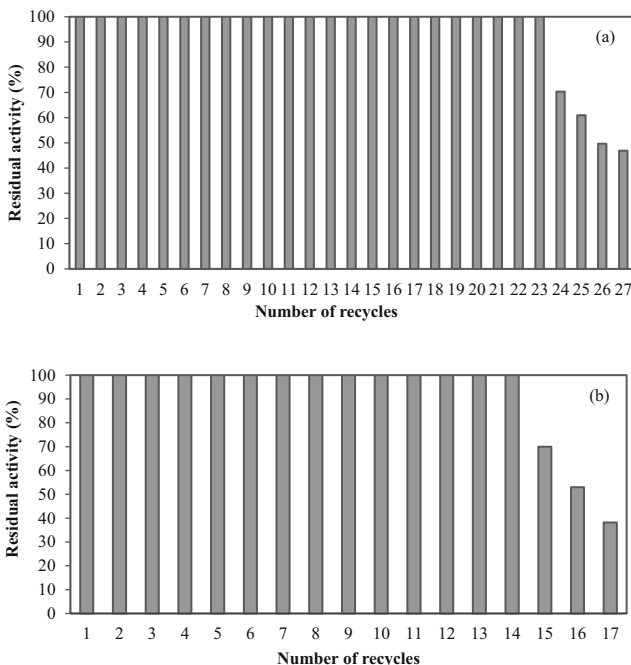


Fig. 5 Operational stability of CALB immobilized in (a) Nb-MCM-41 and (b) Nb-MCM-48

room temperature and refrigeration conditions did not affect enzyme activity. This result demonstrates the effectiveness of the synthesized support, where the support can be stored at room temperature without losing catalytic power and without additional costs.

Studies found in the literature prove the effectiveness of MCM supports with addition of niobium in protecting the wear and denaturing of the enzyme. For the CALB enzyme immobilized in MCM-48 with [C₁₆MI]Cl, 75 days of cold storage were obtained, with an activity obtained of 50.60%, approximately 1.7 times higher than that observed for the free enzyme in the same period (29.96%) [32].

Thermal Stability of the Esterification Reaction

In the literature, it is common to find thermal stability related to storage of materials containing enzymes at different temperatures, temperatures which are often not feasible in industrial terms. In addition, the esterification reaction for the activity measurement occurs at 40 °C [27, 32]. In the present work, the immobilized enzyme was used at different temperatures in the esterification reaction. This result is important for industrial purposes since it measures the

Table 3 Storage stability of CALB immobilized in Nb-MCM-41 and Nb-MCM-48 at room temperature and refrigeration

	Initial refrigeration activity (U)	Initial activity at room temperature (U)	After 5 months in refrigeration (U)	After 5 months at room temperature (U)
Nb-MCM-41	259.0	230.8	258.8	225.5
Nb-MCM-48	324.6	302.6	320.1	301.4

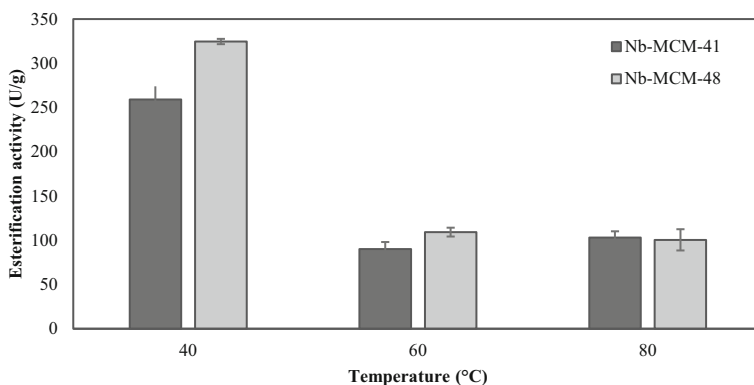


Fig. 6 Enzymatic activity of esterification of CALB immobilized with Si/Nb = 20 in Nb-MCM-41 and Nb-MCM-48 at different temperatures

possibility of applying the enzyme in reactions at 60 and 80 °C, in addition to the 40 °C normally used. Figure 6 shows the values of esterification activity obtained using different reaction temperatures.

The best esterification results were obtained when the reaction was conducted at 40 °C, as expected. However, the supports Nb-MCM-41 and Nb-MCM-48 containing the CALB enzyme showed an attractive esterification activity at 60 and 80 °C, with similar values. For Nb-MCM-48, a greater esterification activity was observed at 40 °C in relation to Nb-MCM-41, when considering the activity presented at 40 °C as 100%. However, Nb-MCM-41 showed a residual activity of 34.75 and 39.82% for temperatures of 60 and 80 °C, respectively, compared to the result obtained at 40 °C (100%). Also, Nb-MCM-48 showed a residual activity of 33.64 and 30.95% for temperatures of 60 and 80 °C, respectively. These results represent a 60.18 to 69.05% decrease in esterification activity compared to the reaction conducted at 40 °C. In addition, the values of esterification activity at 60 and 80 °C were similar, which indicates that this temperature range leaves the enzyme in a stable activity.

Through the results obtained, we can see that the immobilization supports synthesized with the ionic solid $[C_{14}MI]Cl$ and niobium were effective in protecting the enzyme in reactions conducted at high temperatures. This result is important for the application of supports on an industrial scale since they showed good storage stability and a high number of recycles.

Conclusions

The supports Nb-MCM-41 and Nb-MCM-48 synthesized with the ionic solid $[C_{14}MI]Cl$, regardless of the Si/Nb ratio, showed a crystalline network referring to the expected materials; therefore, the amount of niobium used did not interfere in the formation of the mesoporous structure of the materials. The best Si/Nb molar ratio chosen was equal to 20, since the Si/Nb = 1 ratio did not show homogeneity in the reaction. The materials Nb-MCM-41 and Nb-MCM-48 used as support for the immobilization of the CALB enzyme showed a high number of recycles, excellent storage stability, and the possibility of application in esterification reactions at 40, 60, and 80 °C.

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Authors' Contributions IB and MM conceptualized the study. All authors analyzed, interpreted the data, and wrote the manuscript. All authors read and approved the final manuscript.

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Data Availability The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflict of interest.

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