SYNTHESIS OF NB/MCM-48 MATERIAL USING RICE HUSK ASH AS SILICA SOURCE WITH DIFFERENT SI/NB MOLAR RATIOS

Síntese do material Nb/MCM-48 usando cinzas da casca de arroz como fonte de sílica com diferentes relações molares Si/Nb

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ABSTRACT: The large amount of rice produced in Brazil generates a large volume of co-products, such as, Rice Husk (RH) and Rice Husk Ash (RHA). These co-products have amounts of silicon (Si) present in their structure, which can be used to synthesize silica-based materials as zeolites and MCM-type structures. The synthesis of MCM-48 material was carried out at room temperature, using the ionic liquid $[C_{16}MI \cdot Cl]$ as structure-directing agent, depositing the niobium in situ during the synthesis with different molar ratios of Si/Nb (5, 20, 50 and 80). The material obtained was subjected to characterization by X-Ray Diffraction (XRD), Nitrogen Adsorption/Desorption isotherms and Scanning Electron Microscopy (SEM). The results confirm the formation of Nb/MCM-48 materials, in which their properties are consistent with those described in the literature. The deposition of Nb on MCM-48 did not change its structural properties, such as specific surface area and pore distribution for Si/Nb higher than 5. The results obtained demonstrate the success in the synthesis of mesoporous materials Nb/MCM-48 using industrial residues of rice as an alternative source of silicon, and in situ deposition of the niobium metal on the structure.

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RESUMO: Grandes quantidades de arroz são produzidas no Brasil, gerando coprodutos, como a Casca de Arroz (CA) e as Cinzas da Casca de Arroz (CCA). O silício contido nestes coprodutos podem ser utilizados na síntese de materiais à base de silício, como zeólitas e estruturas do tipo MCM. A síntese do material Nb/MCM-48 ocorreu à temperatura ambiente, usando o líquido iônico $[C_{16}MI \cdot Cl]$ como agente direcionador de estrutura, depositando o nióbio *in situ* durante a síntese com diferentes relações molares de Si/Nb (5, 20, 50 e 80). O material obtido ao final do processo foi submetido à caracterização pelas técnicas de Difração de Raios X (DRX), isotermas de adsorção/dessorção de nitrogênio (N_2) e Microscopia Eletrônica de Varredura (MEV). As análises confirmaram a obtenção do material Nb/MCM-48, onde suas propriedades condizem com as descritas na literatura. A deposição do Nb sobre a MCM-48 não alterou suas propriedades estruturais, como área superficial específica e distribuição de poros para relações molares maiores que 5. Os resultados obtidos demonstram o sucesso na síntese dos materiais mesoporosos Nb/MCM-48 utilizando resíduos da indústria de arroz como fonte alternativa de silício e na deposição *in situ* do metal nióbio sobre a estrutura.

Palavras-chave: Síntese Direta. MCM-48, Silício. CCA. Nióbio. Materiais Mesoporosos.

Introduction

Rice is among the five most productive crops in the world, in which its annual production is around 700 million tons (FAO, 2019). However, 20% of rice weight is Rice Husk (RH) (NATARAJAN; NORDIN; RAO, 1998), which is a co-product for industry, used as biomass fuel, generating energy through burning, replacing fossil fuels, and decreasing the CO2 emission (HUANG; LO, 2019). In this process, RH generates Rice Husk Ash (RHA) as residue, which contains a significant amount of silicon on its composition (BHAGIYALAKSHMI et al., 2010). The RHA includes 85% to 98% of amorphous silica on its composition when obtained from a controlled burning process (ENZWEILER; BARBOSA-COUTINHO; SCHWAAB, 2013).

Countless materials use silicon as the main element for the formation of their structures, like zeolites, mesoporous silicas and M41S materials. Typically, for the synthesis of silica-based materials, silicon commercial sources as Tetraethyl Orthosilicate (TEOS), Tetramethylammonium silicate (TMA-silicate), Tetramethyl Orthosilicate (TMOS), sodium silicate and amorphous silica are used, in which most of these precursors are expensive for industrial uses (BAŞGÖZ; GÜLER, 2020; BRINKER; SCHERER, 1990; HSIEH et al., 2017; SHAH et al., 2017). The application of alternative silica sources in the synthesis of silica-based materials decreases production costs and enables the utilization of residues. Different alternative sources of silica have been used by the scientific community in material synthesis, as RHA, coal fly ash, and residues from the sugar industry (BRAGA et al., 2013; MILLER; CUNNIN-

GHAM; HARVEY, 2019; MISRAN et al., 2007; SOUZA et al., 2011).

Materials from M41S family, first reported by Mobil Oil Company (1992) (CHU et al., 1992), embraces three different structures MCM-41, MCM-48 and MCM-50, in which MCM-48 has cubic three dimensional structure, MCM-41 has a hexagonal two-dimensional structure and MCM-50 have lamellar structure (KUMAR et al., 2001; VARTULI et al., 1998). Normally, MCM-type materials are synthesized under hydrothermal procedures. However, these structures can be achieved at room temperature using surfactants as structure-directing agents (KUMAR et al., 2001).

Ionic liquids act as surfactants and structure-directing agents in the synthesis of MCM-type materials through the formation of extended hydrogen bond system in the liquid state (ANTONIETTI et al., 2004). The substitution of commonly used structure-directing agents as cetyltrimethylammonium bromide (CTABr) and tetramethylammonium chloride (TMACl) is interesting due to low vapour pressure of ionic liquids, which decreases the emission of VOCs into the atmosphere (ANTONIETTI et al., 2004; AVELLANEDA et al., 2009)

The synthesis of MCM-type materials using alternative silica sources and ionic liquids as structure-directing agents through one-pot synthesis have a great application potential, reducing costs process steps (ARNALDO; COSTA, 2019; BHAGIYA-LAKSHMI et al., 2010; LOVELL et al., 2014; MISRAN et al., 2007; TEMPELMAN et al., 2016). MCM-48 properties, such as high thermal stability, high surface area, and three-dimensional structure, allows its application in catalysis fields as a support for different materials (HAZARIKA; BARMAN, 2019; LI et al., 2018; ROMERO et al., 2019; SHABAN; ABUKHADRA; HAMD, 2018; TAVAKOLI; MAMAGHANI, 2019).

The niobium is a transition metal with a significant occurrence in the Brazilian territory, and its major application is in the steel industry (ALVES; COUTINHO, 2019). Supported niobium in mesoporous materials could originate a new field of application improving both support and metal properties (FERREIRA et al., 2018; KAO et al., 2020; MÉNDEZ et al., 2017). Niobium has high thermal stability and shows strong metal-support interaction, which justifies its application in catalysis field (LI et al., 2020; PADULA et al., 2020; PERCIANI et al., 2018; SCALDAFERRI; MÁRCIA; PASA, 2019; SHEN et al., 2019; SKRODCZKY et al., 2019; YANG et al., 2019).

Given the above, the present work aimed to obtain through one-pot synthesis Nb/MCM-48 mesoporous materials at room temperature using rice industry waste as an alternative silicon source using different molar Si/Nb ratios (5, 20, 50, and 80).

Materials and Methods

Materials

The chemicals used for Nb/MCM-48 synthesis were: RHA provided by Marina Tecnologia LTDA (Brazil), sodium hydroxide (Vetec), hydrochloric acid (Quimex) ethanol (Synth), ammoniacal niobium oxalate ($NH_4[NbO(C_2O_4)_2(H_2O)_2]$), and the ionic liquid 1-hexadecyl-3-methylimidazolium chloride [$C_{16}MI·Cl$] as structure-directing agent. In order to synthesize the ionic liquid, it was used ethyl acetate (Vetec), acetonitrile (Vetec), chlorohexadecane (Sigma Aldrich), and methyl-imidazole (Sigma Aldrich).

Silica extraction from rice husk ash

The methodology used for the removal of impurities from RHA was carried out as described by Kalapathy et al. (2000). Firstly, the

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RHA was washed using deionized water to remove impurities followed by filtration and then dried at 100 °C for 3 h. 30 g of the washed RHA was submitted to calcination (500 °C during 16 h), followed by acid wash with 300 mL of distilled water with pH previously adjusted to 1 with HCl (6 mol/L). The acid wash was carried out under magnetic stirring at boiling temperature for 2 h. Afterward, the residual material was filtered and dried.

After thermal and acid treatments, the silicon was extracted from 25 g of rice husk ash with 250 mL of NaOH (2 mol/L) in a reflux system for 4 h, resulting in a 0.6 mol/L Na_2SiO_3 solution that was filtered and stored for further utilization. The residual rice husk ash was dried and weighed to evaluate extraction yield.

Synthesis of Nb/MCM-48

The methodology proposed by Kumar and collaborators (2001) for the synthesis of MCM-48 materials was carried out with some modifications. The synthesis proceeded in acid environment in which firstly 2.4 g of C16MI·Cl was dissolved in a 100 mL solution (50 mL of distilled water and 50 mL of ethanol), then, 10 mL of ammonium hydroxide (NH_4OH) was added to the solution and submitted to magnetic stirring for 10 min. After homogenization, the solution was acidified (pH = 1) with HCl 6M and finally, 27 mL of 0.6 M Na_2SiO_3 were added under vigorous stirring. The reaction was carried out under magnetic stirring at room temperature for 2h, and the obtained material was then filtered and washed with distilled water.

For Nb/MCM-48 synthesis, Nb_2O_5 was used as Nb source, originated from calcination of ammoniacal niobium oxalate ($NH_4[NbO(C_2O_4)_2(H_2O)_2]H_2O_n$) in muffle (Fornitec F3 – DM/T), following the heating ramp: 150 °C for 90 min, and 450 °C for 360 min, with a heating rate of 3 °C/min.

The Nb source was added simultaneously with Na_2SiO_3 solution at different Si/Nb molar ratios (5, 20, 50, and 80). Different proportions of niobium were used to verify its influence on structure and synthesis of Nb-MCM-48 using Na_2SiO_3 as silica source.

Equipment and characterization

X-ray diffraction analyses (XRD) were performed on a Rigaku Miniflex II Desktop X-Ray Diffraktometer diffractometer with CuKα radiation (λ = 1.54 Å). The Zeiss scanning electron microscope (model EVO LS25) with metallizer (QUORUM SC7620) was used for the Scanning Electron Microscopy (SEM). The samples were covered with 20 nm gold for the SEM images.

Textural Nitrogen (N_2) adsorption/desorption analysis (Quantachrome NOVA 2200e) were performed at a constant temperature of -196 °C (77 K). The specific surface areas were determined using the BET method (BRUNAUER; EMMETT; TELLER, 1938).

Results and Discussion

Silica extraction from RHA

RHA was submitted to both thermal and acid treatments for silicon extraction through alkaline treatment. The thermal treatment (calcination) resulted in a decrease of 12% of sample mass, referring to organic matter and water. In the acid treatment, was observed a decrease of 2% referring to minerals contained in the sample, as described in literature (KALAPATHY; PROCTOR; SHULTZ, 2000). The resulting material was subjected to silica extraction using sodium hydroxide (2 M), in which a decrease of 60% of sample mass was observed, related to the SiO_2 that interacted with the NaOH, originating the Na_2SiO_3 solution.

The acidification of the Na_2SiO_3 solution causes precipitation of pure silica, which

can be analysed through XRD analysis, as represented in Figure 1. The diffractogram represents an amorphous pattern for the precipitated silica along with peaks related to cristobalite (~32 and ~45 2 θ degrees) (NAYAK; NANDI; DATTA, 2019), such patterns are characteristic of silica obtained from RHA.

Figure 1 - XRD diffractogram for the precipitate silica
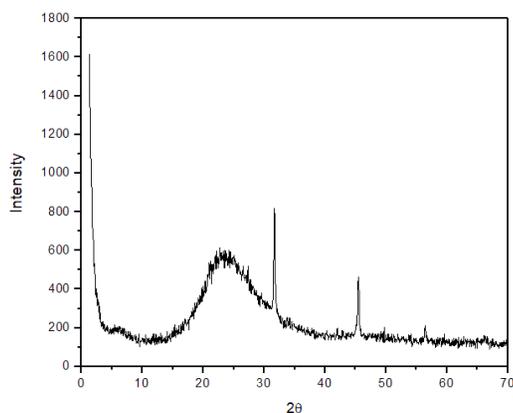
Nb-MCM-48 materials

To obtain the MCM-48 material, using Na_2SiO_3 as silica source, the synthesis was carried out in acid media at room temperature, in which the silicon is found on precipitated form, enabling the material formation, as shown in Figure 2.

The XRD pattern confirms the formation of the MCM-48 material, due to low angle peaks between 2 – 5 2θ degrees followed by an amorphous part, a characteristic pattern for MCM-48 materials (KUMAR et al., 2001).

The Nb incorporation on MCM-48 materials was carried out using niobium oxide (Nb_2O_5), and the obtained results are shown in Figure 3.

Analyzing the diffractogram of Figure 3 (a) related to the Nb_2O_5, it is possible to notice the peaks characteristic to the orthorhom-

Figure 2 - MCM-48 XRD pattern using acid media for the synthesis
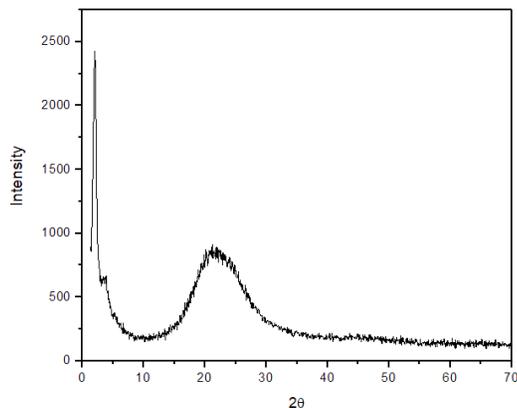
Figure 3 - Diffractograms for Nb/MCM-48 materials, in which (a) represents the pure Nb_2O_5, (b) Si/Nb = 5, (c) Si/Nb = 20, (d) Si/Nb = 50 and (e) Si/Nb = 80
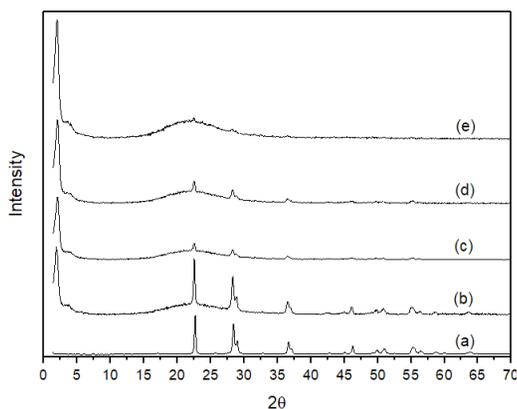
bic phase structure of Nb_2O_5, formed when the material was subjected to calcination at temperatures between 450 °C and 700 °C (R. P. P. ROMERO; P. C. PANTA, 2016). The patterns related to Nb_2O_5 also appears in the diffractograms of synthesized Nb/MCM-48 materials, suggesting that Nb particles are externally deposited on MCM-48 structure, in which a small amount of Nb has possibly been incorporated into the material network, however, more characterization techniques are needed to prove the Nb incorporation into the material network. At low Si/Nb ratios the

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Nb2O5 peaks appear with more intensity, due to higher concentrations of the material and for higher ratios of Si/Nb a decrease in the peaks intensity is seen.

Nitrogen (N2) adsorption/desorption Isotherms

The Nb/MCM-48 materials with different Si/Nb ratios were submitted to nitrogen adsorption/desorption analysis in order to verify the superficial and porous characteristics of the materials. Initially, the pure MCM-48 material was analyzed, so the resulting isotherm is shown in Figure 4.

The obtained MCM-48 isotherms are related to IV(a) type, characteristic of materials from M41S family (JANG et al., 2009) in which the pattern corresponds to materials with mesoporous structures (THOMMES et al., 2015). The phenomenon of condensation and evaporation cause the formation of H1 type hysteresis for MCM-48 materials,

indicating the presence of pores with open cylindrical channels of uniform size and shape (THOMMES et al., 2015).

Figure 4 - Adsorption (●)/desorption (▲) isotherm for pure MCM-48
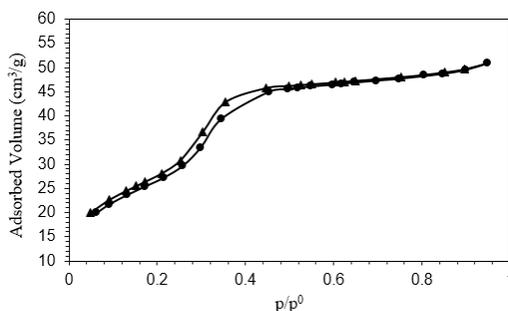
The Nb/MCM-48 materials with different molar ratios were also analyzed, the results are shown in Figure 5.

It is possible to notice that Nb/MCM-48 materials with different molar ratios maintained both isotherms and hysteresis patterns.

Figure 5 - Adsorption (●)/desorption (▲) isotherms for Nb/MCM-48 materials with different molar ratios, where (a) Si/Nb = 5, (b) Si/Nb = 20, (c) Si/Nb = 50 and (d) Si/Nb = 80
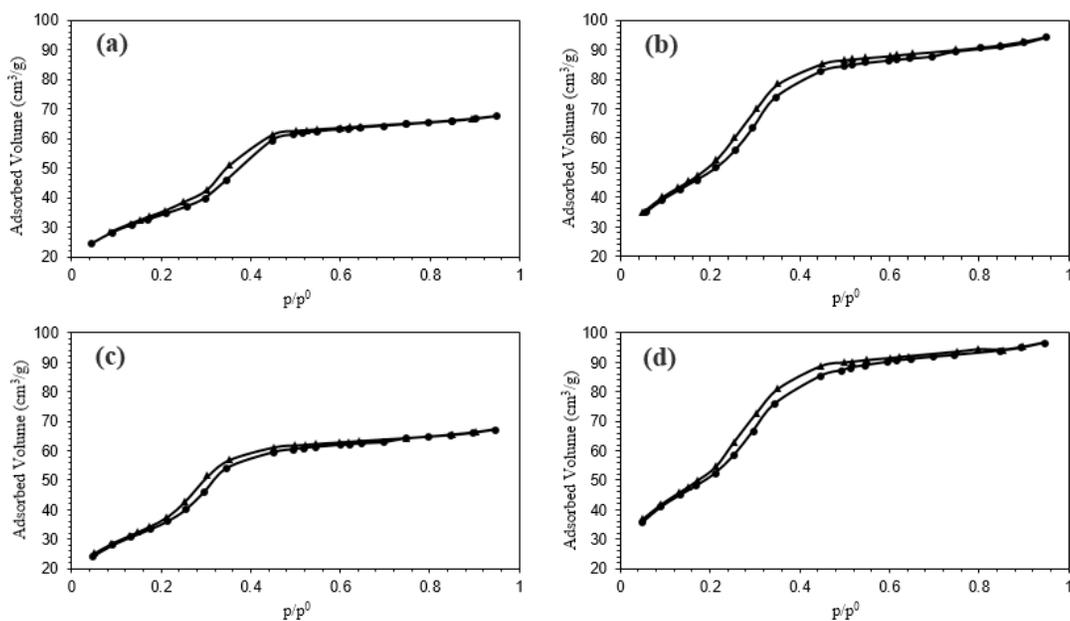
Therefore, Nb incorporation in the MCM-48 material does not modify the material structure, maintaining a mesoporous structure with cylindrical open pores.

The properties of the synthesized MCM-48 along with Nb/MCM-48 materials with different molar ratios are shown in Table I.

Table I - Properties of MCM-48 and Nb/MCM-48 materials with different molar ratios

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)
MCM-48	960	0.33
Nb/MCM-48 (Si/Nb = 5)	590	0.23
Nb/MCM-48 (Si/Nb = 20)	953	0.33
Nb/MCM-48 (Si/Nb = 50)	978	0.33
Nb/MCM-48 (Si/Nb = 80)	944	0.33

Data exposed in Table I shows that for higher molar ratios (Si/Nb=20, 50, and 80) the MCM-48 properties are maintained. However, for the molar ratio Si/Nb = 5 a significant decrease in the surface area and pore volume was observed. That could be caused due to higher Nb_2O_5 that blocks the pore channels, decreasing both surface area and pore volume (WACHS et al., 2000). The pore size remained the same for the different molar relations in the range of 2.2 to 3.2 nm; such values are characteristic for MCM-48 materials (NASCIMENTO et al., 2014).

Scanning Electron Microscopy (SEM)

The obtained MCM-48 and Nb/MCM-48 materials using RHA as silicon source were submitted to Scanning Electron Microscopy (SEM) analysis to verify the material morphology (Figure 6).

As it is possible to be seen in Figure 6, the synthesized MCM-48 presented uniform spherical particles. This result agrees with those found in the literature for MCM-48 using commercial silicon sources (SCHUMACHER; GRÜN; UNGER, 1999).

When comparing the morphologies for both materials, it is possible to verify that the synthesized samples, with or without the addition of Nb_2O_5, show similar morphologies, demonstrating that the Nb_2O_5 does not influence the formation of MCM-48 morphology. In addition, the spherical format of the samples is characterized by the use of ionic liquids as structure-directing agents. All obtained materials are similar to pure MCMs as shown in the literature (BREVET et al., 2016).

Figure 6: Morphology of the obtained materials: (a) MCM-48 using RHA as silicon source and (b) Nb/MCM-48 with Si/Nb = 5

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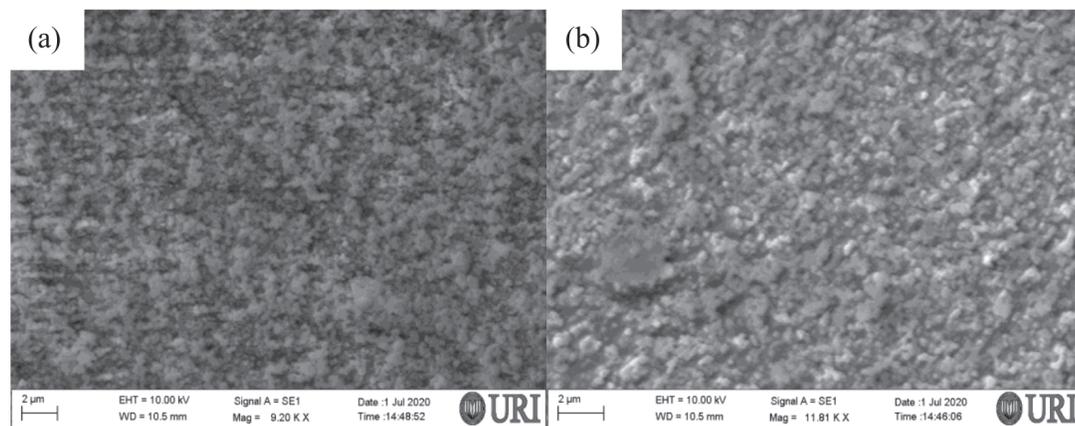
Conclusion

Through the exposed results, it is possible to conclude that the utilization of residues with high concentrations of silicon, as the RHA is a viable source of Na2SiO3 for the one-pot synthesis of Nb/MCM-48 materials at room temperature. The incorporation of small amounts of Nb to MCM-48 materials does not affect its structure. Therefore, it is possible to combine the properties of MCM-48 and Nb materials, creating a new field of application for these materials.

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