



Carbon dioxide adsorption on micro-mesoporous composite materials of ZSM-12/MCM-48 type: The role of the contents of zeolite and functionalized amine



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ABSTRACT

In this study ZSM-12/MCM-48 adsorbents have been synthesized at three ZSM-12 content, and also were functionalized with amine groups by grafting. All the adsorbents synthesized were evaluated for CO₂ capture. The X-ray diffraction analysis of the ZSM-12/MCM-48 composite showed the main characteristic peaks of ZSM-12 and MCM-48, and after the functionalization, the structure of MCM-48 on the composite impregnated was affected due amine presence. For the composites without amine, the ZSM-12 content was the factor determining in the adsorption capacity of CO₂ and for the composites with amine the amount of amine was that influenced in the adsorption capacity.

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1. Introduction

The significant increase in emissions of greenhouse gases in the atmosphere, including carbon dioxide, is accentuating global warming. About 70% of all CO₂ emissions and 60% of all emissions of greenhouse gases are related to the use and production of different forms of energy [1–2]. The search for energy sources that minimize these emissions is of great importance, but also the use of complementary actions and processes to capture greenhouse gases from major sources.

Among various activities that contribute to CO₂ release to the environment are the burning of fossil fuels such as coal, natural gas or oil, and industrial processes such as power plants, oil refining and cement production, iron and steel [1–3].

In this scenario, the abatement of CO₂ emissions from energy sector activities, such as the treatment of gaseous streams, has intensified in recent years. Among the available processes for CO₂ capture, the chemical absorption with amines [1–5] has some disadvantages for being expensive and generate waste in their

recovery. The use of gas-solid selective adsorption of CO₂ has many advantages over absorption with amines, such as easy handling without risk to the environment and recovering the adsorbent material, and can be used more optimized industrial plants [2,6–7].

The search for adsorbents that are competitive for CO₂ capture has led several research groups to design materials of various types, both for applications in which occurs the phenomenon of the physical adsorption as well of the chemical adsorption. Micro and mesoporous molecular sieves, activated charcoals, hydro-talcites, metal organic frameworks, and amines interacting with different oxides are major classes of adsorbents studied for use in the adsorption of CO₂ [2,8–16]. The structural and surface characteristics of these materials are highly diverse.

Among various adsorbent studied, mesoporous materials with silica-based inorganic, such as MCM-41, MCM-48, SBA-15, HMS and MSU has obtained great highlight [2,12–21]. The interest for these materials is in their versatile structures which have pore systems one, two and three-dimensional with diameters that can vary from 15 to 100 Å, and its high specific surface area which can reach 1500 m² g⁻¹. Despite the advantageous structural quality of the MCM-41, the three-dimensional structure of MCM-48 consisting of two systems of independent and inter-connected pores separated by a continuous

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silica wall is potentially more advantageous for catalytic and adsorptive applications compared with one-dimensional pores systems of the MCM-41, because it favors the reagents and products diffusion through the pores, being less prone to blockages [22–23].

Among the microporous materials, zeolites comprise the largest group of microporous molecular sieves and are intensively used for the separation and purification of gases, ion exchange, adsorption and catalysis [2,18,24–25]. The efficiency of zeolites in these processes is due to some of its features, such as strong acidity/alkalinity, thermal and hydrothermal stability, selectivity and adsorption capacity of many adsorbates, etc. In addition to the steric effects, selectivity of zeolites to an adsorbate in particular also depends on the polarity of the molecules. Zeolites X (FAU) and A (LTA) types are widely used in industry due to their stable crystalline structures and due large pore volumes. The zeolite 13X is widely used industrially is an important adsorbent in the purification of gases [2,9,16,18,24–26].

The choice of an adsorbent to be used in the process of separation is based mainly on selectivity, in the adsorption capacity of the solid in relation to one wants to separate and in the regenerability. For the separation of CO₂, the literature indicates that the most suitable zeolitic adsorbents are zeolites of the FAU type, in particular zeolite 13X, which has a pore size greater than the critical molecular diameter of carbon dioxide (>4.0 Å) [2,5,9–10,16,27].

Composite materials containing micro and mesoporous molecular sieves such as zeolites (ZSM-12, ZSM-35 and ZSM-5) and mesoporous materials of the M41S family (MCM-41 and MCM-48), may represent a combination of two inorganic structures whose properties should not be due to the individual characteristics of each component, but rather the final assembly and consequently synergy that can be formed.

A number of studies have been reported in the literature by exploiting the synthesis of composite materials using different methodologies [28–30]. Structures have also been combined in an attempt to obtain more efficient materials from the viewpoint of adsorption and catalysis, especially in relation to hydrothermal stability and accessibility [29–30]. The most significant examples are solids which combine the formation of mesoporous arrangement of the M41S family with the formation of microporous structure type FAU, MFI or BEA [28]. The results obtained for the composite materials of zeolite/M41S type may be promising for application in adsorption and catalysis, in comparison with the adsorbents based in zeolite or M41S materials isolated. The high activity for the processes can occur due to a combination of the strength of the active sites of the zeolite and of the accessibility of these sites in the structure mesoporous of the M41S materials. The combination of high surface area of mesoporous materials of the MCM-48 and MCM-41 type, with the high thermal/hydrothermal stability of zeolites may prove advantageous in the application of composites of these materials as adsorbents for gaseous streams containing water vapor, especially for zeolites with high Si/Al ratio and consequently lower hydrophilic nature [9].

Moreover, the micro/mesoporous composite materials may be efficiently improved for CO₂ capture by inserting amines, which can maximize the chemisorption. This is because, with regard to the treatment of exhaust gas was provided that amines supported maintain high selectivity to the CO₂, and the rate of capture of other components negligible, especially N₂, but without the aforementioned disadvantages associated with the solutions of amines [2,9,17,31–33].

In this study, the effects of the content of zeolite of the ZSM-12/MCM-48 composite and of the changes on the material surface by inserting amino group were studied on the CO₂ capture efficiency.

2. Experimental

2.1. Synthesis of ZSM-12/MCM-48 composite materials

The ZSM-12/MCM-48 composite materials have been synthesized via consecutive methods: hydrothermal treatment aiming at synthesis of the ZSM-12 and MCM-48 materials, in first step, and a mechanical synthesis in the second step in order to obtain the composite material, from the individual materials already calcinated. To obtain the composite materials via mechanical synthesis pre-established mass proportions of microporous components (ZSM-12) and mesoporous (MCM-48) were mixed by grinding in a mortar for 20 min until homogeneous. The grinding was carried out in four steps: a quantity equivalent to $\frac{1}{4}$ of the mass of the microporous material and the amount of $\frac{1}{4}$ of the mass of mesoporous materials (previously weighed in the proportion established) were scattered in a mortar and subjected to manual grinding continued for 5 min. This procedure was repeated three more times, and at each step the weight of the microporous and mesoporous materials was added over the ground material already contained in the mortar. The ZSM-12/MCM-48 composite was obtained with several zeolite contents (25, 50 and 75 wt.%). The materials were denoted as Z12 and M48 (ZSM-12 and MCM-48 adsorbents, respectively), ZM25, ZM50 and ZM75 for 25, 50 and 75 wt.% of loading of ZSM-12 zeolite, where Z=ZSM-12 and M=MCM-48.

In a typical preparation of ZSM-12 zeolite the following starting materials were used: silica gel (Merck, 99%) as silica source, aluminum oxide pseudoboehmite (Vista Chemical, 70%) as aluminum source, methyl-triethylammonium chloride (Sigma-Aldrich, 97%) as organic template, sodium hydroxide (Vetec, 99%) as the alkaline source, and water. These reactants were combined to obtain a synthesis gel with the following molar composition: 20MTEACl: 10Na₂O: 100SiO₂: 2000H₂O: 0.5Al₂O₃. The synthesis procedure [34–35] consisted in mixing of sodium hydroxide and 2/3 of the water necessary for the synthesis under magnetic agitation for 5 min, at ambient temperature to obtain a transparent solution. After this, the solid aluminum source was added to this solution and the system was stirred for 40 min at 70 °C (solution 1). The organic template (MTEACl) was dissolved in the remaining water (1/3) at ambient temperature (solution 2). This solution 2 was added for initial solution 1 and mixed for 20 min at ambient temperature. Silica source solid was added to this system and mixed at ambient temperature for 2 h. After this, the synthesis gel was placed in a stainless steel reactor with internal teflon vessel and heated at 140 °C and at autogenous pressure for 144 h. The resulting solid was filtered, washed with distilled water, dried at 120 °C for 2 h and calcined at 450 °C for 4 h in flowing air using a ramp rate of 5 °C min⁻¹.

For the synthesis of MCM-48 material, the raw chemicals: tetraethoxysilane (Sigma-Aldrich, 98%) as silica source, hexadecyltrimethylammonium bromide (Vetec, 97%) as organic template, sodium hydroxide (Vetec, 99%) as alkaline source and water were used. The chemicals were mixed to obtain a synthesis gel with the following molar composition: 0.55CTMABr: 0.25Na₂O: 1.0SiO₂: 100.1H₂O. The synthesis procedure [36–37] to obtain MCM-48 material was carried out as follows: the CTMABr and NaOH were dissolved in water and kept under magnetic stirring at 40 °C for 30 min. Then the TEOS was added to this solution with stirring and the mixture allowed to age for 40 min at 40 °C. The gel was placed into teflon-lined autoclave and heated at 120 °C for 24 h. After that time, the autoclave was allowed to cool at ambient temperature. A white precipitate was recovered by filtration and washed with water. After drying at 100 °C for 2 h, the template was removed by calcination in flowing air at 450 °C for 2 h using a ramp rate of 5 °C min⁻¹.

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