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Structure elucidation of alkaline earth impregnated MCM-41 type mesoporous materials obtained by direct synthesis: An experimental and theoretical study

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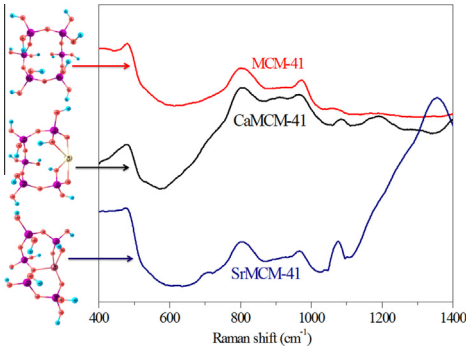
HIGHLIGHTS

- Alkaline earth atoms were embedded into the molecular sieve framework.
- The metal incorporation has promoted the formation of a structure with a center of inversion, active in the Raman.
- The electronic density of oxygen atoms neighbor to the alkaline earth atom has decreased.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, MCM-41 were synthesized hydrothermally and functionalized with calcium and strontium salts by direct method, using the Si/M = 50 molar ratio, in order to elucidate the way as the alkaline earth is incorporated on MCM-41 molecular sieve. The materials were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, nitrogen adsorption–desorption and theoretical calculations by DFT method. Experimental results and computer simulations showed that the alkaline earths were incorporated on MCM-41 through a complex structure, which negatively influences on basic sites formation.

Introduction

Based on the IUPAC definition, the porous materials can be divided into three types, according to the pore diameter: microporous (<2 nm), mesoporous (2–50 nm) and macroporous (>50 nm). Among these materials, zeolites are among the best and most frequently used due to its high crystallinity [1]. However, the use of zeolites as catalysts becomes unsuitable for conversion of large molecules, because of their small pore sizes [2]. Therefore, the synthesis of porous materials with greater pore diameter, has become an important goal and thus in early 1992, a new family of mesoporous molecular sieves, designated as M41S was discovered by scientists from Mobil Oil Corporation [3].

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This family consists of mesoporous materials with different arrangements: hexagonal, cubic and lamellar. According to researchers [4–6], the phase with hexagonal structure corresponds to the MCM-41; the cubic phase, to the MCM-48 and the lamellar phase, to the MCM-50. These molecular sieves may be synthesized from a wide variety of procedures. However, a common feature for almost all syntheses is the presence of a directing agent and a silicon source. The nature of the directing agent, a surfactant, including the length of the carbon chain and the aqueous concentration, molar ratio surfactant/silica, and the reaction conditions (time, temperature and pH) are all critical factors in determining the nature of the product [6–8].

Among the family members M41S, the MCM-41 has received greater attention due to its characteristics be favorable for studies focused on catalysis and adsorption. These features include a hexagonal arrangement of unidirectional mesopores with diameters ranging from 2 to 10 nm, good thermal stability, high surface area and volume of pores [9–11]. However, by not presenting acidic or basic sites, when formed of pure silica, they have low adsorptive and catalytic activity [12,13]. As a result, many studies [14–18] describe the functionalization of these materials with metals to promote the formation of active sites on its surface. In this sense, direct method of functionalization is the most commonly used [19]. In this case, the source of silicon and the precursor of the metallic ion are added slowly to the reaction medium simultaneously or in sequence. By this method, the literature indicates that the metal (M) is incorporated predominantly into the framework of the molecular sieve, forming bonds of the type Si–O–M–O–Si [2,7]. When the metal is an alkaline earth, basic sites are generated on MCM-41 [9,14,16–18], indicating that alkaline earth promotes a increasing in the electronic density of neighbor oxygen atoms. However, there is the possibility of carry out an isomorphic substitution of Si by M atoms, which might to reduce the electronic density of neighbor oxygen atoms.

Within this context, this work aimed to study the functionalization of MCM-41 with calcium and strontium by direct method to elucidate the way as the alkaline earth is incorporated on MCM-41 molecular sieve.

Experimental

Materials

The mesoporous materials were obtained from silica gel (Acros, 100%), sodium hydroxide (Vetec, 99%), cetyltrimethylammonium bromide (CTMABR, isofar and Vetec, 98%), calcium nitrate tetrahydrate (Isofar 98%), strontium nitrate (Vetec, 98%), acetic acid (Vetec, 30%) and deionized water.

Synthesis

The mesoporous material of pure silica (MCM-41) was synthesized hydrothermally according to the procedure described in the literature [3,20], with adaptations. For the synthesis of MCM-41, it was used the silica gel, NaOH, the structural directing agent (CTMABr) and the solvent (deionized water). The synthesis gel was prepared in the following molar composition: 1CTMABr, 2NaOH, $4SiO_2$, $200H_2O$. The synthesis was based on the preparation of two solutions, where the first containing the silicon source, sodium hydroxide and half of the deionized water; the second, the directing agent and the other half of the deionized water. The first solution was kept under stirring at 60 °C for 1.5 h, while the second was kept under stirring at room temperature (approximately 30 °C) for 0.5 h. Then, the second solution was added to the first and the reaction mixture was kept under stirring for 0.5 h at room temperature. Subsequently, the obtained gel was transferred to a Teflon container of 100 mL and heated at 100 °C for five days, taking place every 24 h, the correction of the pH for 9–10 with acetic acid at 30%, until the same acquired stability. After the mentioned time, the reaction mixture was vacuum filtered, washed with about 100 mL of deionized water and dried at 100 °C in an oven. After drying, the material obtained was calcined at 500 °C under air flow at 100 mL min^{-1}, for 4 h.

The process of functionalization of MCM-41 with calcium and strontium was performed by the direct method, using a procedure similar to that described above for the synthesis of molecular sieve of pure silica. The only difference was the addition of 0.08 mol of the calcium source, Ca $(NO_3)_2$, or strontium, $Sr(NO_3)_2$, into first solution (described above) with the aim to obtain a molar ratio Si/metal equal to 50 in both mesoporous solid functionalized. The samples thus synthesized were termed CaMCM-41, MCM-41 functionalized with calcium and SrMCM-41, MCM-41 functionalized with strontium.

Characterization

Measurements of X-ray diffraction were performed on a Shimadzu equipment, XRD model 600, with Cu Kα radiation source (λ = 1.5406 Å) obtained for 40 kV in filament current of 30 mA. Data were collected at a low angle (1–6°) with a scan speed of 2° min^{-1}.

The adsorption spectra in the infrared region with Fourier transform (FT-IR) were obtained on a spectrophotometer VERTEX 70 in the region of 4000–400 cm^{-1} and a resolution of 4 cm^{-1}. For analysis, samples were diluted in solid KBr, and then pressed (7 tons) to obtain the pellets to be analyzed.

The Raman spectra were obtained on an equipment Brooker Senterra MicroRaman, with excitation and laser power of 532 nm and 20 mW and, respectively. The integration time was of 3 s.

The analysis of nitrogen adsorption and desorption was performed in an ASAP-2420 equipment of the Micrometrics maker. For each analysis were used approximately 30 mg of sample calcined, previously degassed at 300 °C for 3 h. The isotherms were obtained in a range of relative pressure (P/P_0) of 0.01 to 0.99 at the temperature of liquid nitrogen (77 K). The surface area was determined by BET method, the pore volume and average pore diameter by the BJH method.

Aiming to better understand the interaction between the alkaline earth atoms and the structure of the molecular sieve, theoretical calculations were developed by the density functional theory (DFT) using the hybrid functional B3LYP [21,22] in combination with the basis set 6-31+G(d,p). The molecular sieve MCM-41 was simulated with only six tetrahedral silicon atoms. The incorporation of the metal (M = Ca, Sr), in the molecular sieve, was performed by replacing one of the silicon atoms for a metal, initially considering a metallic system bidentated. The electronic and molecular properties as well as the geometric parameters were obtained by the program Gaussian 09 [23]. Calculations of vibrational frequencies were performed to check the minimum power of each system and obtain the infrared and Raman spectra. All calculations were performed in vacuum.

Natural bond orbital (NBO) and second-order perturbation energy stabilization (E2) values were also used to determine the origin of the electron density donation to the metal ion [24–27]. The E2 values are an alternative measurement of the interaction strength between a donor NBO and an acceptor one. This energy represents the estimate of the off-diagonal NBO Fock matrix elements. It can be deduced from the second-order perturbation approach [28]:

$$E2 = \Delta E_{ij} = q_i F^2(i,j)/\varepsilon_j - \varepsilon_i$$