Synthesis, characterization, and luminescent properties of MCM-41 and AlMCM-41 mesoporous materials containing Eu(III) ions

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Abstract

Nanostructured materials such as MCM-41 modified with rare earth ions have been studied due to their potential for a variety of applications. Rare earth trivalent ions in some solid compounds emit light at characteristic wavelengths due to infra 4f or inter 4f–5d transitions. The MCM-41 and AlMCM-41 mesoporous materials were synthesized by hydrothermal treatment using cetyltrimethylammonium as template, and then calcined at 500°C in presence of air. The obtained materials were impregnated with Eu(III) ions using europium nitrate solution in ethanol with equivalent concentrations of 5, 10, and 15% in mass, followed by calcination at 500°C under nitrogen atmosphere. The Eu-containing products were characterized by thermogravimetric analysis (TGA), X-ray diffraction, and photoluminescence spectroscopy. The emission spectra were recorded at room temperature. For the Eu–MCM-41 and EuAl–MCM-41 samples, intense photoluminescence were observed in the visible region, with maximum intensity centered at 620 nm.

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1. Introduction

Since its discovery in 1992 [1,2] MCM-41 has become the most popular member of the M41S family of mesoporous silicate and aluminosilicate materials. The most interesting feature of MCM-41 with its regular pore system consists of an hexagonal array of one-dimensional shaped pores. The pore diameter of MCM-41 can be varied systematically from 2 to 10 nm [2]. Other interesting physical properties of MCM-41 include a highly specific surface of up to 1500 m² g⁻¹, and a specific pore volume of up to 1.3 ml g⁻¹. Due to its regular structure and pore shape MCM-41 has attracted considerable interest as a model substance for a vast range of applications [3,4] in catalysis, sorption, molecular recognition, electronics, and photochemistry. The properties of the MCM-41 materials can be adjusted by isomorphous substitution of Si by a trivalent cation such as Al resulting in the AlMCM-41 mesoporous material. Recently, there has been considerable interest in the incorporation of the rare earth ions in the mesoporous materials for the obtaining of materials active optically. The rare earth trivalent ions in some solid compounds emit light at characteristic wavelengths due to infra 4f or inter 4f–5d transitions [5].

The 4f electrons of the rare earth ions are shielded by the outer 5s and 5p electrons. However, the intensities of 4f–4f transitions depend strongly on the nature and structure of chemical environment around the rare earth ion. This is due to the factor that these lines are forbidden by Laporte’s rule, and therefore their transitions are subject to second-order mechanisms [6,7]. These properties are interesting for the development of new materials with the capability to produce visible light with narrow lines, and crucial by applications in optoelectronic technology as optical memory devices, lasers, fiber amplifiers, and fluorescence matrix as base for new photonic devices applications [8]. The photoluminescence of the Eu(III) ion, in especially, make them potential candidate for use as luminescent material by provides facilities in the interpretation of the spectral data [9–11]. The Eu(III) has a great advantage because it has non-degenerate ground and emitting states and the 5D0 → 7F0 transition gives information about the site symmetry of host. This property permits possible application as structural probe of the local environment for technology of new optics sensors. In this report, it is presented the first
results of photoluminescence investigation of the Eu(III) ion impregnated in the SiMCM-41 and AlMCM-41 systems. This investigation is mainly directed to the influence of the mesoporous MCM-41 and AlMCM-41 molecular sieves in the luminescent properties of the europium. The samples were characterized by thermogravimetric analysis (TGA), X-ray diffraction, and photoluminescence.

2. Experimental

2.1. Reactant sources and preparation procedures

The samples MCM-41 and AlMCM-41 were prepared by hydrothermal synthesis in an alkali medium following the procedure of Araújo and Jaroniec [12]. Silica sources used were gel silica (Merck) and sodium silicate solution (Riedel de Haën). The cetyltrimethylammonium bromide (CTMABr) template was provided from V etec. Pseudoboehmite (Catapal B—Vista) was used as aluminum source. The pH adjustment was done with 30% acetic acid in solution. For MCM-41, the reactants were combined to obtain a gel with the following molar composition: 1CTMABr:4SiO2 :1Na 2 O:200H 2 O. The hydrogel was introduced in Teflon-lined stainless steel autoclave, which was heated at 100 °C for 120 h. The pH was measured each day and adjusted to 9.5–10. In order to remove the surfactant, the recovered white solid was washed with 2% HCl:EtOH solution and dried at 100 °C overnight. Finally the material was calcined at 500 °C for 1 h in nitrogen and for one additional hour in air. The calcination temperature was reached at a heating rate of 10 °C min−1. AlMCM-41 was prepared in the same way but with addition of the aluminum source to the synthesis mixture in order to obtain the following molar composition: 1CTMABr:4SiO2 :0.04Al 2 O 3 :1.04Na 2 O:200H 2 O. After the synthesis, the calcined MCM-41 and AlMCM-41 mesoporous materials were submitted to a process of impregnation of europium ion in ethanol, using Eu(NO3 ) 3 ·3H 2 O with equivalent concentrations of 5, 10, and 15% in mass followed by calcination at 500 °C for 1h under nitrogen atmosphere. The final samples were assigned as Eu–MCM-41 and Eu–Al–MCM-41, relative to the MCM-41 samples modified with Eu and Eu–Al, respectively.

2.2. Characterization of the samples

Thermogravimetric analysis were performed on thermobalance Mettler-STGA 851, from room temperature up to 900 °C, under nitrogen flowing at 25 ml min−3 and heating rates of 10 °C min−1. X-ray diffraction patterns were recorded on XRD 6000 Shimadzu using Cu Kα radiation, with the diffraction angle (2θ) at range of 5–10°. A scanning speed of 2° min−1 was used. The distance (d0) between pore centers of the hexagonal structure was calculated from the formula [13]:

\[ d_0 = \frac{2d(100)}{\sqrt{3}} \]

The emission spectra were recorded a room temperature with Jobin–Yvon Ramanor U1000 spectrometer, using a argon laser (488 nm, 150 mW) as excitation source.

3. Results and discussion

Thermogravimetric analysis of MCM-41 materials in nitrogen atmosphere show basically three weight losses, as was previously reported [14,15]. The TGA curves for the samples before of calcination step showed three weight losses (see Fig. 1 for MCM-41 and AlMCM-41). The weight loss steps are located in the following temperature ranges: (i) from 30 to 150 °C (thermodesorption of physically adsorbed water); (ii) from 150 to 250 °C (surfactant decomposition); (iii) from 250 to 490 °C and 250 to 620 °C (residual surfactant decomposition and silanol condensation) for the MCM-41 and AlMCM-41, respectively. The thermogravimetric curves of the samples with Eu(III) ions are shown in Fig. 2, for all the
samples there is a mass loss in temperature range from room to 100 °C related to the humidity and a second mass loss related the decomposition of the europium nitrate, where it is verified that as larger the concentration of impregnated europium, minor is the initial temperature of decomposition of the salt.

The X-ray diffraction patterns of the samples are shown in Fig. 3. The diffraction of the AlMCM-41 was the same as those of MCM-41 materials as previously described [16]. For the MCM-41 and AIMCM-41 samples a sharp Bragg peak ascribed to the (1 0 0) reflection of the hexagonal structure of the mesoporous was observed at $\Theta = 1.15–1.13^\circ$, corresponding to $d = 3.8–3.9$ nm. These clear peaks indicated that the long-range order structure was achieved and the regular mesoporous structure was retained after the introduction of aluminum. The Eu-containing samples showed a reduction in the intensity of the (1 0 0) diffraction peak and the $2\Theta$ position shift to a higher value indicating a contraction of the lattice caused by incorporation of Eu(III) ions (see Table 1).

The emission spectra of the samples impregnated with europium are presented in Fig. 4. For the two systems investigated, is observed the presence of a wide band centered in 520 nm, which was attributed to the oxygen vacancy in the silicon tetrahedron, as well as to the presence of superficial defects in the structure of MCM-41 [17].

In the spectra of the Eu-MCM-41 system modified with Eu(III) ion at the concentrations of 5; 10 and 15 wt.% is observed the emissions corresponding to the $^5D_0 \rightarrow ^7F_0 – ^7F_4$ transitions in the range of 450–750 nm, under excitation at 488 nm (argon laser). The format of the band correspond to $^5D_0 \rightarrow ^7F_0$ (Eu $^{3+}$) transition (observed around 578 nm), display only one peak, confirmed in spectrum registered at 77 K (see insertion Fig. 4), we can suggest that in the system the Eu(III) ion possibly occupy only one type of local chemical environment. In addition, the photoluminescence investigation of the $^5D_0 \rightarrow ^7F_1$ transition shows three peaks at ca. 588, 592, and 596 nm, indicating that the Eu(III) ion is found in only one type of local chemical environment [18].

The high intensity of the $^5D_0 \rightarrow ^7F_2$ transition (DEF: transition for forced electric dipole, therefore hypersensitive) in relation to the intensity of the $^5D_0 \rightarrow ^7F_1$ transition (DM: transition for magnetic dipole and almost independent of the crystal field environment) is around the Eu(III) ion. This is characteristic for the occupation the europium ions in silicon mesopore in low symmetry site.

The emission processes observed can be attributed to the phenomenon generated by the light-laser incident in porous Si that photocreates electrons and holes in the structure [19]. These excess carriers subsequently recombine, some of them radioactively emitting light (in large bandwidth), and by energy transfer for the Eu$^{3+}$ ion, resulting in emission leaving of the $^5D_0$ level.

For the EuAl-MCM-41 system, it was not observed the emission corresponding to the transition of the Eu(III) ion. The only emission observed was characteristic to the matrix in the green region, in function of the recombination of carriers confined into the mesoporous silicon (Fig. 4). The carriers generated in this system are usually balanced for Na(I) ions. The presence of sodium ions in the structure of the AIMCM-41 system associated to the effect of the carrier recombinations act in the quenching process of the luminescence Eu(III) ion by complexes non-radiative processes.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a_0$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-41</td>
<td>4.40</td>
</tr>
<tr>
<td>AIMCM-41</td>
<td>4.51</td>
</tr>
<tr>
<td>EuMCM-41 (5%)</td>
<td>4.38</td>
</tr>
<tr>
<td>EuMCM-41 (10%)</td>
<td>4.20</td>
</tr>
<tr>
<td>EuAIMCM-41 (5%)</td>
<td>4.22</td>
</tr>
<tr>
<td>EuAIMCM-41 (10%)</td>
<td>4.18</td>
</tr>
<tr>
<td>Eu/AlMCM-41 (5%)</td>
<td>4.09</td>
</tr>
<tr>
<td>Eu/AlMCM-41 (15%)</td>
<td>4.05</td>
</tr>
</tbody>
</table>

* Percentage in weight of Eu(III) ions impregnated.
of energy transfers in the mesoporous structure. New photoluminescence studies are being developed to explain the mechanisms of energy transfer involved in the non-radiative processes.

4. Conclusions

The mesoporous materials of the type MCM-41 and AlMCM-41 were successfully synthesized through the hydrothermal method at temperature using cetyltrimethylammnonium bromide as template, with pH adjustment in the range 9.5–10 every 24 h, with hexagonal structure. The incorporation of the Eu(III) ion promotes a contraction of the structure verified through the decrease of the distance between pore centers of the hexagonal structure. It is observed that the characteristic photoluminescence of the Eu(III) in the Eu-MCM-41 system, with high intensity of the emission the \( ^{7}D_{0} \rightarrow ^{7}F_{2} \) transition in relation to \( ^{7}D_{0} \rightarrow ^{7}F_{1} \) transition, being indicative that the Eu(III) ions are in low symmetry sites. For the system EuAl-MCM-41, is observed only the characteristic emission of the mesoporous matrix indicating the occurrence of non-radioactive processes of emission, acting in the quenching of Eu(III) ions luminescence. The Eu-MCM-41 system seems to be a promising material for luminescent devices of high resolution and technologies of selective optical sensor.

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