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THERMOGRAVIMETRIC INVESTIGATIONS DURING THE SYNTHESIS OF SILICA-BASED MCM-41

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Abstract

MCM-41 material was synthesized starting from hydrogel containing colloidal fumed silica, sodium silicate, cetyltetramethylammonium bromide (CTMABr) as surfactant, and distilled water as solvent. These reactants were mixed to obtain a gel with the following composition: 4 SiO_2:1 Na_2O:1 CTMABr:200 H_2O. The hydrogel with pH=14 was hydrothermally treated at 100°C, for 4 days. Each day, the pH was measured, and then adjusted to 9.5–10 by using 30% acetic acid solution. Thermogravimetry was the main technique, which was used to monitor the participation of the surfactant on the MCM-41 nanophase, being possible to determine the temperature ranges relative to water desorption as well as the surfactant decomposition and silanol condensation.

Keywords: hydrothermal synthesis, MCM-41, thermogravimetry

Introduction

Since researchers from Mobil reported the discovery of a new family of silica-based mesoporous molecular sieve materials, known as M41S in 1992 [1, 2], there has been an increasing interest in using these materials as adsorbents, heterogeneous catalysts, catalyst supports, and nanocomposite [3–5]. The MCM-41 is the most important member of this family. It presents ordered crystallographic channels, and disordered atomic arrange, similar to that of amorphous silica. The formation of the MCM-41 phase occurs according to the liquid crystal template (LCT) mechanism, in which tetrahedral SiO_4 species react with the surfactant template under hydrothermal conditions. The applications of this material can be limited by its structural stability, it is thus important to investigate new synthesis procedures to improve the thermal stability. The synthesis of these material uses the ordered micelles of surfactant molecules as the template to array inorganic species into regular structures. Many studies deal with the thermal stability and characterization of MCM-41 [6], however our work is about the determination of kinetic parameters for water desorption, surfactant decomposition and silanol condensation processes. To reach this goal, the synthesis conditions with pH-adjustment were optimized by thermogravimetry. TG analysis of

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mesostructured samples provides valuable information on the resulting materials, we employed also this technique to monitor the pH-adjusted synthesis of MCM-41.

Experimental

The silica-based MCM-41 was synthesized starting from silica gel (Aldrich), sodium silicate solution containing 27% SiO_2 and 14% NaOH (Aldrich), cethyltrimethylammonium bromide – CTMABr, $C_{16}H_{33}(CH_3)_3NBr$ (Aldrich) and distilled water. For the pH adjustment 30% acetic acid in ethanol solution was used [7]. The chemicals were mixed in order to obtain gels with the following molar composition: 4 SiO_2:1 Na_2O:1 CTMABr:200 H_2O.

The procedure used to obtain 2 g of calcined MCM-41 was: (i) 0.567 g of silica, 2.8 mL of the sodium silicate solution and 10 mL of water were placed into a 100 mL teflon beaker and stirred at 60–70°C for 2 h in order to obtain a clear solution; (ii) a solution prepared from 2.214 g of cethyltrimethylammonim bromide and 12 mL of distilled water was added to the above-mentioned mixture and aged for 1 h at room temperature. The hydrogel was placed into 45 mL teflon-lined autoclave and heated at 100°C for three days. Their pH was measured each day and adjusted to 9.5–10. Before the pH adjustment, a small sample was collected, dried at room temperature and analyzed by thermal analysis (TG). The final samples were washed with 25 mL of 2% HCl/EtOH solution and subsequently calcined at 550°C for one h in nitrogen and for an additional hour in air. The calcination temperature was reached at a heating rate of 2.5°C min^{-1}. The typical MCM-41 structure was characterized by X-ray diffraction, BET surface area and thermogravimetry. The material was obtained with BET surface area of ca 700 m^2 g^{-1} and total pore volume of 0.68 cm^3 g^{-1}. These values are characteristic of MCM-41.

Thermogravimetric analysis was carried out in Mettler equipment, TGA-851 model, using nitrogen as gas carrier flowing at 30 mL min^{-1}. The sample was heated from room temperature up to 1000°C, at a heating rate of 10°C min^{-1}. For the most well-synthesized MCM-41 sample, the kinetic parameters relative to the water desorption, surfactant decomposition and silanol decomposition were determined.

Results and discussion

The silica-based MCM-41 materials were synthesized using silica gel. In these cases, the pH adjustment was done during the hydrothermal synthesis according to the procedure reported elsewhere [7]. The pH-adjusted synthesis was monitored by thermogravimetry in order to obtain information in different stages of the MCM-41 formation. In this way it is possible to optimize the time necessary for the hydrothermal treatment of the gel allowing to stop the process in the time required for the incorporation of the surfactant in the structure.

The initial pH values of the hydrogel was extremely basic (pH=14). After one day, this value decreased to ca 11–12, evidencing that the hydroxyl concentration in the synthesis gels decreased during hydrothermal process due to the self-assembly of silica species. In order to control the self-assembly process the pH was successively adjusted and maintained about 9.5–10 during the synthesis [8]. The pH was checked each day, and three adjustments were required for good quality MCM-41 material.

Figure 1 shows TG curves for MCM-41 samples collected after the pH adjustments, showing four mass losses. The mass loss steps are located in the following temperature ranges: i) from 25 to 170°C (thermodesorption of physically adsorbed water); ii) from 170 to 270°C (surfactant decomposition); iii) from 270 to 530°C (residual surfactant decomposition and silanol condensation – ca 40%), and iv) from 530 to 740°C (residual silanol condensation – ca 8%). It was observed that after the first pH adjustment, about 13% of water was desorbed. For the second and third pH adjustment, this amount was practically constant, i.e., about 2%. For the surfactant decomposition, after the second and third pH adjustments, about 40% of mass loss was measured, which was greater than the corresponding mass loss for the sample after the first pH adjustment. This indicates that the amount of self-assembled $CTMA^+$ cations with silica species during the second and third day of the synthesis is greater in comparison to the amount self-assembled during the first day, which is in agreement with the earlier data for MCM-41 materials [9]. The amount of the silanol groups in the samples, determined in the temperature range from 340 to 800°C, was equal to 4.8 mmol g^{-1}. This value is in agreement with literature [8] in which 4.4 mmol g^{-1} of silanol groups in the temperature range from 500 to 800°C for silica-based MCM-41 was reported.

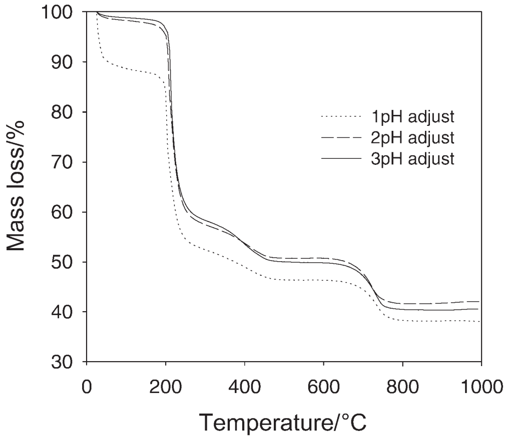

Fig. 1 TG curves for unwashed MCM-41 samples synthesized with pH adjustment using silica gel

In Fig. 1, a well defined mass loss is observed due to surfactant decomposition. This is the main step in the thermal decomposition of CTMABr-MCM-41, which can be used to preview if the material was obtained with typical MCM-41 structure. From DTG curves (Fig. 2), it is clearly verified that the reactivity of silica is reflected by the shift of the surfactant removal step towards higher temperatures. For the MCM-41 sample taken after successive pH adjustments, the temperature corresponding to the maximum decomposition rate of the surfactant was shifted from 202 to 206 and next to 212°C (Fig. 2). Also, a shoulder on the DTG curve at ca 218°C was observed for the samples after the first and second adjustments, and disappeared after final pH adjustment. Thus, it is possible to optimize the synthesis condition. The higher temperature of DTG for surfactant decomposition is related to the quality of the material.

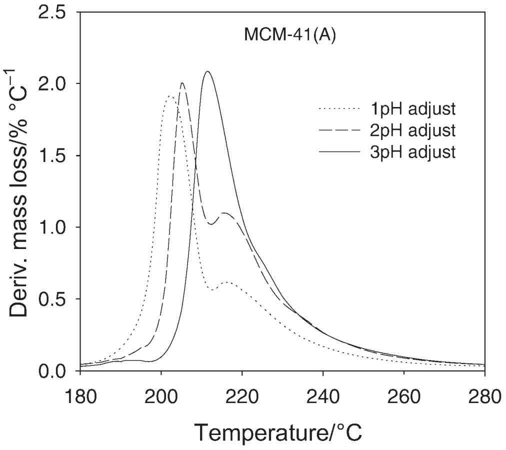

Fig. 2 DTG curves for MCM-41 in the temperature range of surfactant decomposition

The current study of the self-assembly of silica and surfactant species under controlled pH conditions indicates that pH plays an important role in this process. It was reported elsewhere [10] that in the pH range from 10 to 12 some phase transformations from hexagonal via cubic to lamellar mesostructures can occur with increasing silica/surfactant ratio. At pH=12 the lamellar phase is mostly formed [11]. However, at pH=10, as reported by Ryoo *et al.* [10], a high quality MCM-41 mesostructures can be obtained.

Thermogravimetry was the main technique, which can be used in a satisfactory way to monitor the effective participation of the surfactant on the nanostructured MCM-41 phase, making possible to determine the temperature ranges relative to water desorption (30 to 170°C), and mainly the temperature for surfactant decomposition (160 to 340°C) and silanol condensation (340 to 550°C).

Conclusions

The multistage TG or DTG curves indicate a clear dependence on the preparation time in the autoclave or the number of pH adjustment, respectively, necessary to obtain a good quality silica-based MCM-41 nanostructured material.

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