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Encapsulation of polymers in CTA-MCM-41 via microemulsion

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ABSTRACT

This work presents the synthesis of a new type of MCM-41 material, based on the polymerization in microemulsion technique. This type of synthesis, which has not been previously reported, uses microemulsion as a means of inserting polymers into the interior of the CTA-MCM-41 channels. The main difference between the traditional synthesis and that described here is in the initial step, involving formation of emulsified polymers derived from the microemulsions. The monomers used in the synthesis were butyl acrylate, butyl methacrylate, and styrene. Samples of monomers and polymers emulsified in aqueous media were characterized by small-angle X-ray scattering (SAXS) and X-ray diffractometry (XRD) was used to determine the degree of organization of the solid samples. These techniques showed the presence of the monomers and polymers in the interior of the cetyltrimethylammonium (CTA) micelles; the shift of the peak corresponding to the (100) diffraction plane to smaller 2θ angles showed that there was an increase in the diameter of the silica channels resulting from the insertion of the polymers. Infrared absorption spectroscopy and elemental analysis were also used to characterize the solids.

1. Introduction

Since the discovery by Mobil of the type MCM-41 mesoporous silicas [1], the synthesis of which employs surfactants to guide the structure, efforts have been made to modify the structure of the channels, for example causing expansion [2] or producing composites [3]. Increasing interest in the synthesis of materials with hybrid organic and inorganic composition has opened up a wide new field of research [4,5]. Of particular interest is the insertion of monomers into the channels of the calcined inorganic matrix, followed by polymerization [6]. The objective is to improve the mechanical and thermal stability of the final material by means of the presence of the inserted polymeric phase [7].

The as-synthesized MCM-41 (designated here as CTA-MCM-41) contains the surfactant in the interior of the channels, and exhibits basic catalytic properties. This is due to the presence of siloxy anions ($\equiv SiO^-$) associated with cetyltrimethylammonium (CTA) cations, as shown in Fig. 1 [8]. The reactions of industrial interest in which these solids can be used are the Knoevenagel condensation [9,10] and the transesterification of vegetable oils [11]. In the latter case, a conversion rate of 65% has been achieved using the silica in the transesterification reaction of canola oil with ethanol. Loss of activity of the catalyst after successive usages has been associated with leaching of the CTA cations from within the silica channels [11,12].

The motivation for the present work therefore arose from the need to stabilize the activity of this catalyst. It was proposed to modify the synthesis by employing a new procedure involving the encapsulation of polymers in the interior of the CTA-MCM-41channels. Since the polymers would be formed in the interior of the channels, together with the micelles, it was anticipated that they would interact with the surfactant, impeding the exit of the latter when the molecular sieve was in contact with a liquid medium. Use of polymerization in microemulsion for encapsulation of polymers in the interior of the channels of CTA-MCM-41 has not been previously reported in the literature as a method for modification of the synthesis.

Microemulsions are transparent and thermodynamically stable, and are formed spontaneously by mixing water, emulsifier, and monomer, without any need for vigorous agitation [13–16]. The polymerization proceeds with the aid of an initiator (soluble in water or organic solvent) whose radicals are formed by application of heat or ultraviolet radiation [17]. When an initiator soluble in organic solvent is used, the polymerization only occurs within the micelles [18], where the three fundamental stages of a radical-based polymerization occur: initiation, propagation, and termination [19]. Polymerization in microemulsion is characterized by the formation of a turbid dispersion of emulsified polymers [20]. It has been reported that the polymerization occurs in the liquid phase within the micelles, which are maintained stable by the presence of the surfactant [21].

The objective of this work was to synthesize the mesoporous silica CTA-MCM-41, with the channels filled with polymers. To this end, polymerization in microemulsion was employed, with the step of formation of an emulsified polymeric phase being followed by the steps used in the conventional synthesis of MCM-41, as described in the literature, using the addition of a base for hydrolysis

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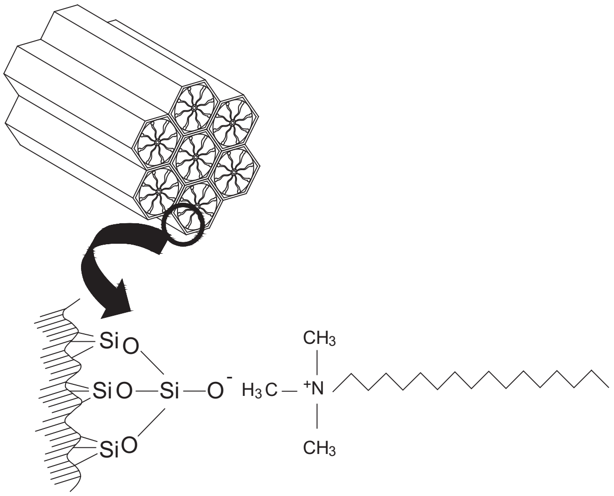

Fig. 1. Structure of CTA-MCM-41, with the siloxy anion (≡SiO⁻) in the entrance of the pore [9].

of the source of the silica and ageing. Details of the synthesis are provided in the Experimental section.

2. Experimental

2.1. Material preparation

The synthesis of the mesoporous silicas was based on two the synthesis of the mesoporous silicas was based on two previous studies: Schumacher et al. [22] and Grün et al. [23]. The procedure was followed as described, however alcohol was not added in the synthesis. This was because the monomers employed are soluble in ethanol, which would have resulted in their removal from the interior of the micelles. After adaptation of the procedure, the new compositions of the reaction mixtures were SiO_2: $12.5NH_3$: 0.4CTABr: $174H_2O$: 4EtOH and SiO_2:$11NH_3$:0.3CTABr:$144H_2O$:4EtOH. The four molecules of ethanol in the composition refer to the product of hydrolysis of the silica source (tetraethyl orthosilicate – TEOS). The highlight in this work was the polymerization in microemulsion step, which was added to the steps of the conventional procedure. These steps are shown schematically in Fig. 2.

Preparation of the emulsions employed monomer/surfactant molar ratios that varied in the ranges 0.2–1.8 (butyl acrylate), 0.2–1.4 (butyl methacrylate), and 0.2–3.0 (styrene). The surfactant concentration was maintained constant in all syntheses. The ratios 1.4, 1.8, and 3.0 were obtained from tests to determine the solubility of the monomers in an aqueous solution of the surfactant (cetyltrimethylammonium bromide – CTABr) used in the synthesis. In these tests, CTABr was mixed with distilled water, and the monomer was slowly added, under agitation, with formation of a clear solution, without any visible droplets of the monomer, until saturation was reached.

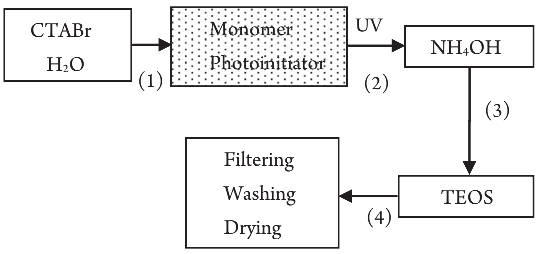

Fig. 2. Schematic diagram of the synthesis of CTA-MCM-41, with the polymerization in microemulsion step indicated (shaded block).

The steps involved in synthesis of the silicas are shown in the block diagram of Fig. 2. In step (1), the monomer and the solvent-soluble photoinitiator (benzoin, Aldrich) were added to an aqueous solution of the surfactant (CTABr, Aldrich). After formation of a clear solution, without any droplets of the monomer, the mixture was submitted to ultraviolet radiation for 5 h. The UV source consisted of a set of three 15 W mercury lamps. The exposure time was determined using polymerization kinetics experiments employing the emulsions prepared in the presence of the monomer. In step (2), ammonium hydroxide was added, followed by (step 3) the source of silica (TEOS, Acros), and the mixture was left under agitation for 2 h. Finally (step 4), the product was filtered and washed with distilled water to a pH of ~7.0, and the resulting white powder was dried at 80 °C for 24 h in a drying oven.

Fig. 3 presents the sequence for forming the CTA-MCM-41 polymer encapsulated. In an initial step (A) the formation of micelles CTA^+ occurs, then (B) monomers absorption takes place within micelles and subsequent polymerization promoted by ultraviolet radiation. At the end, (C) after addition of other reagents, the formation of CTA-MCM-41 followed with polymer encapsulation.

Table 1 presents the terminology adopted for the silicas prepared in this work. The letters A, M, and S indicate that the used was butyl acrylate, butyl methacrylate, and styrene, respectively. The parameter R is the monomer/surfactant ratio. $R = \infty$ signifies pure polymer, and the letter *I* represents this condition.

2.2. Material characterization

SAXS curves were obtained using the SAXS line at the Brazilian National Synchrotron Light Laboratory (LNLS). The radiation wavelength and the detector-sample distance were $\lambda = 0.1549$ nm and 562.5 nm, respectively. SAXS was used to characterize the emulsions prepared in the presence of the monomer and the silicas synthesized in the presence of the polymer. From the equation describing the scattering (q) Eq. (1) and the Bragg equation Eq. (2) it was possible to determine the intermicellar distance Eq. (3). 2θ is the scattering angle relative to the direction of the incident radiation, and λ is the radiation wavelength employed:

$$q = \frac{4\pi \sin\theta}{\lambda} \tag{1}$$

$$d = \frac{\lambda}{2\sin\theta} \tag{2}$$

$$d_{\text{intermicellar}} = \frac{2\pi}{q} \tag{3}$$

Turbidimetric analysis was performed using a photoelectric colorimeter (model B340, Micronal), operated at a wavelength (λ) of 520 nm. This technique was employed to determine the UV radiation exposure time required for the emulsions prepared in the presence of the monomer. The absorbance of the radiated samples was followed as a function of time, and the period required was determined as that at which the polymerization ceased, when the absorbance stabilized and remained constant. These times were 3 h for butyl acrylate, 2 h for butyl methacrylate, and 1 h for styrene. The standardized radiation time for all syntheses was therefore above the minimum necessary to ensure polymerization of all the monomers.

Turbidimetry was also used to determine the absorbance of the dispersion formed after the submission to ultraviolet radiation (step 2). In this procedure, the concentration of the monomer (butyl methacrylate) was varied, and at each level, the sample