

Feature Article

Catalytic transesterification using a silica hybrid containing encapsulated polyacrylates



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ABSTRACT

The CTA-MCM-41 silica hybrid contains basic sites due to the presence of siloxy anions ($\equiv\text{SiO}^-$) associated with CTA cations. A problem is that this material progressively loses its catalytic activity during successive reuse in transesterification reactions. The challenge of the present work was therefore to stabilize the catalytic activity of this silica hybrid by means of the encapsulation of polymers, using an initial emulsification step in the synthesis. Samples of monomers and polymers emulsified in colloidal solution were characterized using small angle X-ray scattering (SAXS), which confirmed their presence in the interior of the micelles. The solids were analyzed by X-ray diffraction, elemental analysis (CHN), infrared absorption spectroscopy, and thermogravimetry. The findings confirmed the presence of monomers and polymers in the channels of the CTA-MCM-41, and the polymers acted to increase the stability of these new materials during catalytic transesterification.

1. Introduction

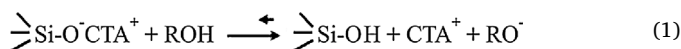
Zeolites are microporous materials that are widely used as catalysts in the petroleum industry. However, the extraction of petroleum at greater depths means that the average molecular mass of this primary material is increasing. Consequently, the processing of these larger molecules will require catalysts with pore diameters in the mesopore range. Researchers at Mobil were first to announce the discovery of mesoporous silicas of the type MCM-41 [1]. These silicas, when calcined, present hexagonally organized cylindrical pores, with diameters among 1.5–2.0 nm and very high surface area (700–1.500 m²/g) [3].

Since then, research efforts have been directed towards modification of the structure of the channels of these silicas, for example by inducing expansion [2] or producing hybrid composites [4]. The synthesis of hybrid materials with combined organic and inorganic composition has been widely reported in the literature, and has opened up a broad field of research [5,6], notably concerning the insertion of monomers into the channels of the calcined inorganic matrix, followed by subsequent polymerization [7]. The objective is to use the inserted polymeric phase to prepare polymer fibers molded in the form of the porous structure of the host solid [8].

The structure of MCM-41 silica containing the cetyltrimethylammonium surfactant in the interior of the channels (CTA-MCM-41) is represented in Fig. 1. This material exhibits pronounced basic catalytic properties due to the association of siloxy anions ($\equiv\text{SiO}^-$) with the CTA cations [9,10].

The characteristics and possible applications of this silica remained unexplored until the identification of its basicity by Kubota et al. [9]. Subsequent research provided more systematic evaluation of the material, using reactions that require the presence of basic sites in order to proceed [10–14]. This research opened up new perspectives for the application of these highly basic low-cost silicas.

The industrial reactions in which these hybrid solids can be utilized include the Knoevenagel condensation [10–12] and the transesterification of vegetable oils using heterogeneous catalysts in order to produce biodiesel [13]. In the case of the latter, CTA-MCM-41 silica was evaluated as a catalyst in the transesterification of canola oil with ethanol, achieving 65% conversion under conditions similar to those used in the industrial process that employs homogeneous catalysis. One of the advantages of the heterogeneous catalyst is that, in contrast to the homogeneous process, it can be used repeatedly, and only needs to be filtered from the liquid reaction medium. A disadvantage is that the catalytic activity decreases after successive reuse, due to leaching of the CTA cations and protonation of the siloxy anion (Eq. (1)), hence diminishing the number of catalytic sites [14,15].



The focus in this work was therefore on the need to stabilize the activity of this catalyst. A new hybrid material of the type CTA-MCM-41 is presented, which in addition to the surfactant also contains a polymer in the interior of the channels. Previous work [16] showed that the polymer serves to physically block the exit of the CTA cations, hence

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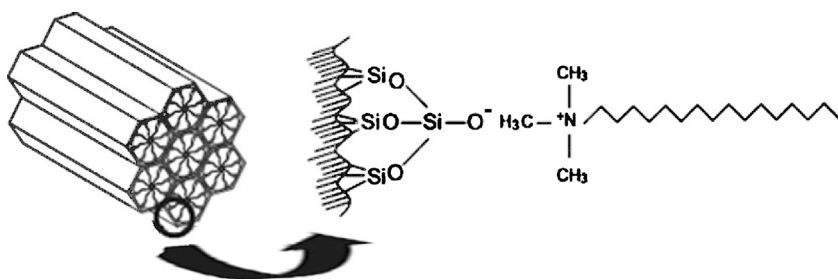


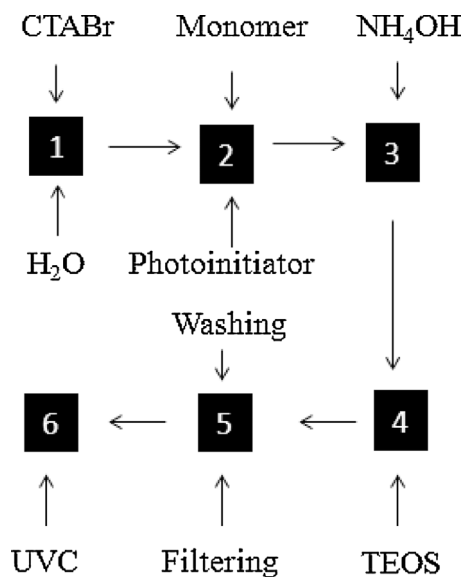
Fig. 1. Structure of CTA-MCM-41, with the siloxy anions ($\equiv\text{SiO}^-$) in the mouth of the pore [10].

restricting the leaching of the latter.

2. Experimental

Synthesis of the mesoporous silicas was based on the work of Schumacher et al. [17] but with the addition of acrylates in the synthesis reaction mixture. The procedure followed was as described in the earlier work, without addition of ethanol to the reaction mixture in order to avoid solubilization of the acrylate monomers in the aqueous phase, which would have prejudiced their incorporation into the micelles. This modification was also necessary then, in the presence of ethanol, it forms MCM-48 [17] and not MCM-41 as desired. The new composition of the reaction mixture used in the syntheses was: $\text{SiO}_2:12.5\text{NH}_3:0.4\text{CTABr}:174\text{H}_2\text{O}:4\text{EtOH}:R\text{Ac}$, where $R \leq 0.5$ is the molar fraction of acrylate used. The 4 mol of ethanol present in this composition are derived from the hydrolysis of tetraethyl orthosilicate (TEOS), which was used as the silica source. In the syntheses in which the acrylates were used, the MCM-41 was subjected to ultraviolet irradiation to induce their polymerization. A schematic of these steps is provided in Scheme 1. The procedure was as follows: (1) The surfactant (cetyltrimethylammonium bromide – CTABr, Aldrich) was dissolved in the quantity of water indicated above in the reaction mixture composition; (2) the acrylate monomer (2-ethylhexyl acrylate, Aldrich) was added together with the solubilized photoinitiator (benzoin, Aldrich); (3) ammonium hydroxide was added, followed by (4) the source of silica (TEOS, Acros), and leaving under agitation for 2 h; (5) the precipitate formed was filtered and washed with distilled water to pH ~ 7.0 ; (6) the precipitate was submitted to UVC irradiation for 5 h, resulting in the formation of a white powder.

In the reaction mixtures containing the monomers (butyl or 2-



Scheme 1. Schematic of the synthesis of CTA-MCM-41 with encapsulated monomers, employing UVC irradiation.

ethylhexyl acrylate), monomer/surfactant molar ratios (R) of 0.2 and 0.5 were employed. Ratios lower than 0.2 were not used, due to the difficulty in handling smaller quantities of monomer, as well as its loss by volatilization during the synthesis. In this concentration range, the monomers were totally dispersed in the aqueous phase containing the surfactant, without the formation of two liquid phases. The preparation of these reaction mixtures first involved dissolution of the photoinitiator (benzoin, Aldrich) in the acrylate. This solution was then slowly added prior to step (2), with agitation until formation of a transparent dispersion without any drops of monomer. The solid obtained in step (4) was submitted to ultraviolet irradiation for 5 h. Drying of the powder was performed at the same time as the polymerization process.

Ultraviolet radiation in the UVC range (280–100 nm) was provided from a set of three 15 W mercury lamps. The duration of exposure to UVC was determined from assays of the polymerization kinetics of aqueous emulsions of the monomers.

Table 1 presents the terminology adopted for the hybrid silicas prepared in this work. The symbols H and B signify the use of 2-ethylhexyl acrylate and butyl acrylate, respectively. Since the concentrations were varied, the value of the monomer/surfactant molar ratio (R) was added to the symbol. A value of R equal to infinity signifies that the polymer was pure, without surfactant, and this condition is represented by the symbols HI and BI.

2.1. Characterization

The aqueous emulsions of CTABr and the synthesized silicas, with or without acrylates, were characterized by small angle X-ray scattering (SAXS). The scattering curves were obtained using the SAXS2 beamline of the Brazilian National Synchrotron Light Laboratory (LNLS). The radiation wavelength (λ) was 0.1549 nm, and the distance between the sample and detector was 562.5 nm.

From the equation describing the scattering (q) (Eq. (2)) and Bragg's Law (Eq. (3)), it was possible to determine the intermicellar distance (Eq. (4)). In these equations, 2θ is the scattering angle relative to the direction of the incident radiation, and λ is the radiation wavelength.

$$q = \frac{4 \cdot \pi \cdot \sin \theta}{\lambda} \quad (2)$$

Table 1
Terminology employed for the synthesized samples.

Monomer	Monomer/surfactant ratio (R)			
	0.0	0.2	0.5	∞
H ^a	–	H02	H05	HI
B ^b	–	B02	B05	BI
S ^c	S00	–	–	–

^a H = 2-ethylhexyl acrylate.

^b B = butyl acrylate.

^c S represents the silica hybrid without the presence of the monomer.

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