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Theoretical and experimental study of isothiazolinone adsorption onto ordered mesoporous silica

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ABSTRACT

Mesoporous silica SBA-15 particles were synthesized in order to evaluate their effectiveness as encapsulating agents for a commercial biocide composed of a mixture of methylisothiazolinone and chloromethylisothiazolinone (MIT/CMIT). Three powdered samples of silica particles having different textural properties, sizes and morphologies were hydrothermally obtained and then characterized by SEM, TEM, SAXS, and nitrogen adsorption–desorption measurements. Adsorption of the biocide on the prepared materials was investigated, and the results showed that adsorption capacities increase as the particle size becomes smaller. Higher biocide amounts were also retained on particles having increased pore size and pore volume. Additionally, a most probable interaction mechanism between MIT/CMIT and SBA-15 is proposed on the basis of molecular modeling calculations. The theoretical approach indicates that two adsorption geometries with comparable minimum levels of strength can be adopted by the biocide: planar adsorption when the biocide molecule rings are adsorbed on the silica surface and vertical adsorption when the O atom of the MIT/CMIT interacts with the H atom of silanols.

1. Introduction

Coatings are usually susceptible to deterioration by a number of different microorganisms (bacteria, fungi or algae), so additives such as biocidal products are essential for the coating formulation. The results of microorganism colonization are the loss of several properties of the product that reduce its performance, generating a negative economic impact and potential health risks.

The presence of microorganisms on the coating surface is related to the degradation of the film (loss of mechanical and aesthetic properties), and also to the risk of transmission of certain diseases.

It is known that the addition of biocides to the coating film contributes to remedying the above-mentioned drawbacks; the substances most commonly used are objected from the point of view of current legislation on environmental matters because most products used in the coating industry are based on isothiazolinones or formaldehyde. Some of these biocides exhibit poor efficiency because of the decrease of their killing power by aging, pH sensitivity, low thermal and alkali stability, etc.

Developments in the field of coatings and modified surfaces include the incorporation of a polymer matrix containing biocides to provide controlled toxicant release. The process consists of a rather complex methodology in which active substances are introduced into a matrix, providing a further release of these active agents, depending on the specific requirements of the substrate on which the matrix is deposited [1–5].

Methylisothiazolinone/chloromethylisothiazolinone (MIT/CMIT) is the active ingredient in a family of commercial microbiocides and preservatives that has a broad spectrum of activity against fungi, yeasts and both gram-positive and gram-negative bacteria [6]. Owing to its high water solubility, MIT/CMIT is prone to leach under humid conditions, resulting in increased concentrations required during initial processing, but this may not be economically or environmentally acceptable. Microencapsulation can contribute to solving these drawbacks by increasing the protection of the active adsorbate from the surrounding environment, or by controlling its release rate into the medium, or by a combination of both.

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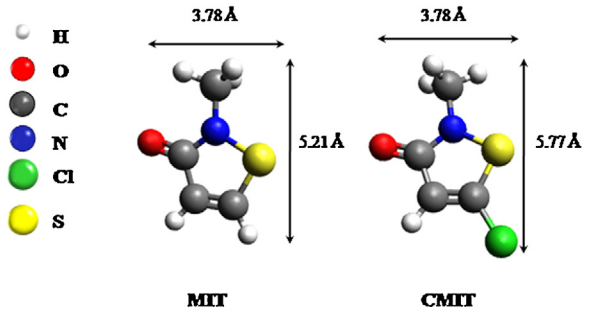

Fig. 1. 3D methylisothiazolinone and chloromethylisothiazolinone molecules.

Several studies are related to bioactive agent encapsulation by using different matrices: polymeric nanoparticles [7–9], microspheres [1,5], porous silica microparticles [10] and modified nanoclay [11]. Regarding the use of mesoporous silica materials for this purpose, the ordered members of the group have recently been proposed as hosts for stabilizing different active agents. Adsorption processes are favored because of an improved ability of these structures to participate as adsorbents, facilitated by their singular surface geometry [12–19]. In particular, in previous work we studied the adsorption of different gases [19–22] and medicinal compounds [23–29] onto these distinctive silica matrices. Additionally, the biocide cations Ag^{+1} and Zn^{+2} were encapsulated in the cavities of an ordered aluminosiliceous framework, and their effective antimicrobial activity after incorporation in different coating formulations was confirmed [30,31].

The main objective of the research presented here is to stabilize organic biocides into micrometer-sized silica particles with a surface that is compatible with coating components and also allow a high biocide loading. Having that in mind, SBA-15 matrices were used for the encapsulation and stabilization of MIT/CMIT, aiming to demonstrate the effective location of the biocide inside the silica pores and to verify that the biocide molecular structure remains unaltered after adsorption. To do this, the biocide location was determined by recording changes in the textural properties of the support during the adsorption process, and the molecular integrity of the adsorbed biocide was determined by FTIR. To go further in this research, the possible interactions of MIT/CMIT with SBA-15 were modeled using a theoretical approach.

2. Materials and methods

2.1. Chemicals

The chemicals used in this study include triblock copolymer poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (Pluronic P123, MW: 5800, Aldrich), tetraethyl orthosilicate (TEOS, 98%, Aldrich), hydrochloric acid (HCl, 37%, Anedra).

2.2. Synthesis of materials

SBA-15 materials were synthesized according to the procedure reported by Zhao et al. [32] by using tetraethyl orthosilicate (TEOS; Aldrich) as silica source and Pluronic 123 triblock copolymer (P123, EO20–PO70–EO20; Aldrich) as template. The molar composition used was 1TEOS:4.88HCl:0.0172Pluronic:158.33H_2O. The solution was heated up to 35 °C before adding the TEOS. The resultant solution was stirred at a selected rate (400 rpm) for 20 h at 35 °C, and then the mixture was aged at 80 °C for 24 h under static conditions. The solid product was recovered by filtration and air-dried at room temperature overnight. The template was removed from the as-synthesized material by calcination at 540 °C for 6 h (heating rate = 1 °C min^{-1}). The resultant solid was named SBA_{24}.

The pore size and thickness of the silica wall were adjusted by increasing the time under static conditions of SBA-15 in the reaction solution (48 h). The sample was called SBA_{48}.

Additionally, using the same procedure described for obtaining the sample SBA_{24}, a silica sample having a smaller particle size was obtained by decreasing the stirring rate from 400 to 120 rpm. This sample was named SBA_{120}.

2.3. Materials characterization

The catalysts were characterized by SEM, TEM, SAXS, adsorption–desorption of N_2, and FTIR.

A Philips 505 scanning electron microscope (SEM) was used to perform the morphological analyses of each sample. Transmission electron microscopy (TEM) was performed with a Leo EM-910 instrument operated at 120 kV.

The small angle X-ray scattering (SAXS) measurements were carried out on a model XEUSS 1.0 XENOCS (Grenoble) diffractometer using CuKα radiation (1.5419 A).

Nitrogen adsorption–desorption isotherms were measured at the temperature of liquid nitrogen (−196 °C) using a Micrometrics ASAP 2020 instrument. Before adsorption, samples were outgassed by heating at 100 °C in vacuum, with a pressure lower than 3×10^{-2} mm Hg for 12 h. The surface area was calculated according to the Brunauer–Emmett–Teller (BET) equation. The pore size was obtained by the Barrett-Joyner-Halenda (BJH) method. The pore volume was taken at the $P/P_0 = 0.989$ single point.

Shimadzu IR Affinity-1 equipment, pellets in KBr, and a measuring range of 400–4000 cm^{-1} were used to obtain the FTIR spectra. The samples were placed directly into the chamber, and 48 scans were used for each spectrum.

2.4. Biocide adsorption

In order to evaluate the amount of biocide loaded in the pores of the carrier, 1 g of adsorbent was added to 100 mL of an aqueous solution containing 200 g/L of MIT/CMIT with stirring. After a contact time of 6 h, the solid phases were separated from the liquids by filtration and dried at room temperature. The biocide content in the liquid phases was determined by UV–vis spectroscopy at 274 nm (UV-1800 Shimadzu, Japan).

2.5. Computational method

Calculations were performed with a DFT based code using a Linear Combination of Atomic Orbitals and considering pseudopotentials for the core electrons as implemented in the SIESTA code [33–36] and charge population analysis has been obtained following Bader methodology [37,38]. The interaction between the CMIT/MIT biocide and the silica surface was studied using a two dimensional slab of 168 atoms containing 56 Si, 104 O and 8H atoms, so as to better simulate the semi-infinite nature of the solid surface. A geometry optimization was performed applying relaxation calculations. During the calculations, the structures of both the biocide and the substrate were optimized at convergence in energy of 0.01 eV.

3. Results and discussion

A molecular modeling of methylisothiazolinone and chloromethylisothiazolinone was carried out by employing Avogadro 1.0.0, an advanced molecule editor, arriving at the lower energy configuration shown in Fig. 1.