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Red 33 dye co-encapsulated with cetyltrimethylammonium in mesoporous silica materials

Raphaël Bongur [a, 1], Didier Le Nouen [b], Fabrice Gaslain [a, 2], Claire Marichal [a, *], Bénédicte Lebeau [a, **], Philippe Guarilloff [c]

[a] Equipe Matériaux à Porosité Contrôlée (MPC), Institut de Science des Matériaux de Mulhouse (IS2M), UMR CNRS 7361, Université de Haute-Alsace, ENSCMu, 3bis, rue Alfred Werner, 68093 Mulhouse Cedex, France
[b] COB, Université de Haute-Alsace, ENSCMu, 3bis, rue Alfred Werner, 68093 Mulhouse Cedex, France
[c] Chanel PB Laboratory, 876 Centannial Avenue, Piscataway, NJ 08855, USA

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ABSTRACT

A water soluble dye, the Red 33, used in cosmetic industry was immobilized into mesoporous silica by a one-step method which consists in the introduction of the dye molecules in the precursor medium of the mesoporous silica i.e. containing surfactant and silica source.

A high loading rate of 25 wt% was achieved. The resulting Red 33-silica pigment is stable in water and oil media. The characterizations carried out on this material have shown that the encapsulation is effective and that the presence of Red 33 has an effect on the structure and texture of the material. The material exhibits an excellent stability in water due to the interactions between the Red 33 molecules, the silicate species and the surfactant molecules. It has been shown that the dye molecules interact with both the silica host matrix through the NH_2 and phenyl groups, as well as with the surfactant molecules, via electrostatic interactions between the polar head of the surfactant and the sulfonate group of Red 33 which undergoes no steric hindrance.

1. Introduction

In the cosmetic industry, the coloring of the formulations is currently provided by the use of pigments, which are insoluble in aqueous media. Most of these pigments are lake composed of organic dyes adsorbed on a substrate such as alumina. However, the fact that these organic molecules are simply adsorbed on the surface of the support involves potential release of the dye in the presence of a solvent. As a consequence the free dyes may color the application surface (nail, skin …), which is highly undesirable. Moreover, the pigment photostability could be reduced. Indeed the free dye is more UV sensitive, can oxidize which will change its color. In order to avoid these problems, the encapsulation of dyes inside the pores of mesoporous silica can prevent their release in a solvent medium. Indeed, the silicic matrix can form a permanent protective barrier. A successful permanent encapsulation of Parsol HS UV filter within mesoporous silica via a direct synthesis method has been developed in our group yielding materials with interesting properties [1]. Note that this direct synthesis method lead to a permanent encapsulation in solvents used for cosmetic formulations based on water and oil media. The direct synthesis method consists in the introduction of the active organic molecules in the precursor medium of the mesoporous silica. This one-step encapsulation (OSE) method was chosen due to both its simplicity and its rapidity which makes it a process easy for industrialization. Indeed the encapsulation was performed at ambient temperature in water an ecofriendly solvent; there was no need to remove the surfactant used as template by calcination, which is time and energy consuming. The direct or *in-situ* synthesis method have been reported in the literature for the encapsulation of enzyme [2], dyes [3,4], active organic molecule for cosmetics and pharmaceutics [5,6] in porous silica (surfactant templated or not) and Metal Organic Frameworks. Compared to the most conventional multiple-step method (MSE) consisting in post-synthesis encapsulation with

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* Corresponding author.
** Corresponding author.
E-mail addresses: claire.marichal@uha.fr (C. Marichal), benedicte.lebeau@uha.fr (B. Lebeau).
[1] Present address: Kermel S.A.S., 20 rue Ampère, 68027 Colmar Cedex, France.
[2] Present address: Centre des Matériaux, MINES Paristech, CNRS UMR 7633, 10 rue Henri Desbruères, BP 87, F-91003 Evry Cedex, France.

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at least 2 steps; synthesis of the host matrix and encapsulation, the OSE method have the advantages to be faster, more simple, to reach high loading rates [7] and to favor strong interactions between the guest molecules and the framework and/or the surfactant template molecules [4]. Note that in the MSE method, an additional step consisting in the activation of the host matrix before encapsulation is sometime necessary [7]. In the OSE method realized with templated silica, the presence of surfactant molecules favor the pore regularity in terms of size and spatial organization (depending on both the guest nature and concentration), and enlarge the pore size [2]. Moreover, for some applications it helps to highly disperse the guest molecules such as dye to limit dimerization [3]. Another method to entrap guest molecules consists in chimisorption which involves a covalent link between guest and host moieties, and most of the time the matrix has to be functionalized before the immobilization [8,9]. The main disadvantage of this method is that the fixation through a covalent bond may cause some changes to the guest molecule that, in our case, make it as a new ingredient and leading to the necessity to obtain an agreement for its use for cosmetic applications. Consequently, the OSE appeared the best encapsulation method because it allows to reach high loading rates [4], the stability of the encapsulation should be assured by the specific interaction between surfactant molecules and/or the inorganic framework [1,5] and it is easier to scale up a single step process. Moreover, the presence of the surfactant is expecting to assure a role of hydrophobic barrier to avoid any release of the hydrophilic dye molecules in aqueous medium. It is noteworthy that the OSE method is not adapted when synthesis conditions are not adapted to the guest molecules (solubility, chemical stability).

The aim of the present study was to generalize the direct encapsulation method to hydrophilic organic molecules such as water soluble dyes to form stable pigments in water and oil media. The disodium salt of 5-amino-4-hydroxy-3-(phenolazo)-2,7-naphthalenedisulfonic acid (Red 33), a water-soluble azo dye commonly used in the cosmetic industry was chosen for this study. Characterization of the obtained materials is presented in this work. The dye content of the material, the stability of the dye encapsulation in various solvents is determined. The structural and textural properties of these samples are compared with those of materials synthesized without dye according to the same protocol in order to determine the influence of the presence of dye on these properties. Finally, multinuclear solid state NMR study informs about the dominant tautomer form of the dye, the interaction between the components (dye, surfactant, silica) of the material suggesting an organization of the organic–inorganic interface.

2. Materials and methods

2.1. Materials synthesis

The synthesis of CTA^+-Red 33 co-encapsulated silica material was adapted from the one developed for the co-encapsulation of a hydrophilic UV filter in a mesoporous silica [1]. The protocol based on the synthesis method of MCM-41 materials described by *Voegtlin* et al., [10] with the use of cetyltrimethylammonium chloride (CTAC, 25% in distilled water, Fluka) as a templating agent, sodium silicate (SiNa, 10% NaOH, 27% SiO_2, Riedel-de-Haën) as silica source, NaOH (98–100%, Carlo-Erba) and Red 33, purchased from LCW.

0.38 g of NaOH was dissolved in 45.2 mL of distilled water. 5.2 g of SiNa were added to the previous solution and 1 g of Red 33 were then dissolved in the mixture. After complete dissolution, 6.6 mL of CTAC solution were added. The starting molar ratio was 1 SiO_2; 0.09 Red 33; 0.215 CTAC; 119 H_2O; 4.4 NaOH. The mixture was stirred for 2 h at room temperature and 48.4 mL of HCl 1 M were added drop by drop, in order to adjust pH to 8.5. The mixture is aged at 293 K for 2 h. After reaction, the solid was recovered by centrifugation at 15,557 G during 20 min with an Eppendorf 5804-R centrifuge, washed two times with distilled water, and dried overnight at 343 K.

For comparison purposes, a reference material was also synthesized by using the same procedure, without introduction of Red 33. The starting molar ratio was 1 SiO_2; 0.215 CTAC; 119 H_2O; 4.4 NaOH. In the reference and co-encapsulated samples, surfactants molecules are present inside the pores in cationic form (CTA^+), since a very low amount of chlorine was detected by elemental analysis.

2.2. Characterizations of the materials

The structural order of synthesized materials was evaluated by powder X-ray diffraction (XRD). Diffraction patterns were recorded at room temperature on a powder PANanalytical X'PERT PRO diffractometer, equipped with a Cu anode ($\lambda K_\alpha = 1.5418$ Å, $0.5 < 2\theta < 10°$, 0.02°/s).

After being calcined at 813 K for 6 h and outgassed (1 h at 363 K followed by one night at 573 K), the samples were studied by nitrogen adsorption/desorption measurements using a Micromeritics Tristar 3000 analyzer at 77 K. As-synthesized samples were analyzed too after degassing at 363 K for 24 h. Calculation of the specific surface area was performed by the Brunauer–Emmett–-Teller method [11]. Pore diameters and mesoporous volumes were evaluated by the Barett–Joyner–Halenda method [12] from the desorption branch of the isotherm using the Broekhoff-de-Boer model [13,14].

The organic content of the mesoporous silica samples was determined by thermogravimetry using a Setaram TG/ATD LABSYS thermal analyzer. Dry solid samples were placed in an aluminium oxide crucible and heated from 298 K to 1073 K at a heating rate of 5 K min^{-1} in air (Figure S1).

Elemental analysis of the CTA^+-Red 33 encapsulated material was performed by wavelength-dispersive X-ray fluorescence spectroscopy using a PHILIPS MagiX apparatus. 200 mg pellets were prepared under 8 ton pressures.

Stability of the encapsulation of Red 33 was studied under static condition by dispersing 40 mg of the co-encapsulated material in 30 g of an aqueous buffer solution at pH 7, mineral oil (Marcol) or ethanol. After 30 min in ethanol and 24 h at 318 K in aqueous buffer and marcol, visual inspection was performed. Quantification of the dye content in water or ethanol supernatants was possible thanks to UV–visible spectroscopy performed on a Lambda 35 Perkin Elmer spectrometer.

The ^1H decoupled ^{29}Si MAS NMR spectra were recorded on a Bruker Avance II 300 WB spectrometer operating at 59.59 MHz ($B_0 = 7.1$ T), with a pulse duration of 2 μs corresponding to a flip angle of $\pi/6$ and a recycle delay of 60 s. Experiments were performed on a standard double bearing 7-mm Bruker probehead with a spinning frequency of 4 kHz. ^1H–^{29}Si FSLG HETCOR experiments were performed with a 4-mm probe at a spinning frequency of 12 kHz, with a 4-ms contact time.

^1H–^{13}C Cross Polarization Magic Angle Spinning (CPMAS) NMR spectra have been recorded on a Bruker Avance II 400 WB spectrometer ($B_0 = 9.4$ T) operating at 100.2 MHz. Samples were packed in a 4-mm diameter cylindrical zirconia rotor and spun at a spinning frequency of 10 kHz. ^1H–^{13}C CPMAS NMR experiments were performed with a proton $\pi/2$-pulse duration of 3.2 μs, a contact time of 1 ms, and a recycle delay of 4 s. The dipolar dephasing ^1H–^{13}C CPMAS NMR spectra were recorded with a rotor synchronized dephasing delay of 70 μs between cross polarization and decoupling as suggested in the literature for organic solids [15].