Boosting sunscreen stability: New hybrid materials from UV filters encapsulation

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\textbf{ABSTRACT}

Unprotected exposure to solar UV is the main recognized cause of the spreading of skin cancer that has occurred in the last decades. Organic and inorganic UV filters are the main defense against UV exposure and have become ubiquitous in personal-care products, packaging, plastics, dyes, and many other sectors. UV filters still have some stability and efficacy issues making it important to find stable and broad-spectrum UV absorbers, safer for human health and the environment.

In this work UV filters octinoxate and avobenzone were encapsulated into zeolites with different chemistry and topology leading to the production of hybrid zeolites/organic filter sunscreens. The obtained materials were deeply characterized and their filtering capacity evaluated.

The encapsulation of UV filters in cationic zeolites resulted in an enhanced UV filtering capacity, whereas that in acid zeolites seem less effective in absorbing UV radiation, with emerging visible coloring.

The enhancement of UV filtering power is of paramount importance for the future development and exploitation of ZEOfilters, possibly being the key to reduce the quantity of actives, stabilizers, and co-formulants employed, with benefits for humankind and the environment.

\section{1. Introduction}

The solar UV radiation reaching the Earth’s surface is increasing since the 1970s at middle-high latitude, even if, after the Montreal Protocol (1989), the trend significantly slowed down due to the recovery of the ozone layer \cite{1}. While the UV irradiance is also affected by local factors \cite{2}, its rise leads to an increased UV exposure for human beings, and specifically for open-air workers, with growing health concerns, particularly, UV exposure is considered the main cause of skin carcinogenesis \cite{3,4}.

The number of annually diagnosed skin cancers, including both malignant melanoma (MM) and non-melanoma skin cancer (NMSC), is growing year after year. The American Cancer Society estimates 106,110 new diagnosed melanomas in the United States for 2021, with over 7000 deaths \cite{5}. European countries have also shown an overall increase in melanoma incidence rate in the last decades \cite{6}.

These alarming numbers explain why sunscreen products are becoming of utmost importance in recent times. Organic and inorganic UV filters (hereafter UVfs) are the main means of UV protection and are components of many personal-care products. Moreover, due to the detrimental effect of UV radiation on many goods, UVfs have also become ubiquitous in packaging, plastics, dyes, and many other sectors where UV radiation can promote product degradation (e.g. Refs. \cite{7–10}).

Despite the massive use of organic UVfs, some issues linked to their stability and efficacy are still unresolved. It is well known that organic UVfs undergo photodegradation under UV exposure, losing protection efficacy and decaying in by-products of unknown toxicity \cite{11}. The combination of different UVfs, to reach a broad-spectrum UV protection, may foster the photodegradation process. As an example, a sunscreen lotion thin film containing both octinoxate and avobenzone (two of the most used organic UVfs) loses completely its UV blocking property under 4 h of light exposure \cite{12}.

Various strategies were explored to stabilize UVfs and obtain more efficient and safer sunscreens. Among them, co-formulants are often added as stabilizers (e.g. Refs. \cite{13,14}), although they may increase the
system complexity fostering allergic reactions [15,16], and photochemically incompatible ingredients must be avoided.

Recently, encapsulation has also been investigated as an alternative approach to the stabilization of organic and inorganic UVs. Inorganic UVs (e.g. TiO$_2$ and ZnO) are commonly encapsulated to reduce their photocatalytic activity [13]. Indeed, uncovered oxide particles cause the formation of reactive oxygen species (ROS) and enhance the photodegradation of organic UVs [17]. As for organic UVs, different studies explored the stabilizing effect of their encapsulation into organic and inorganic materials (for a review see Ref. [18]). The use of inorganic matrices - such as hydrotalcites [19], amorphous silica [20–22], and MOF [23] - has been proposed to increase sunscreen stability and to prevent their absorption across the skin. In most cases, the encapsulation systems demonstrated to be effective under the usage timescale (few hours) but showed generally high filter leaching on longer timescales, such as those of storing and end-of-life disposal.

Zeolites have been only marginally investigated [24–26] as a scaffold for the encapsulation of UVFs: among them, only zeolite Y was studied as a host for Oxybenzone (OXY) and Para-Aminobenzoic Acid (PABA), the latter being no longer added to cosmetic sunscreens due to health issues (U.S. Food and Drug Administration, FDA, Federal Register 84FR6204, 2019–03019).

Reducing UVFs interaction with the skin and their transdermal permeation was the focus of most of the studies on encapsulated UVFs (e. g. Ref. [27]), but a deeper investigation of encapsulation properties and filter stability is needed before these materials could be employed in commercial formulations.

In this study, we report the synthesis and characterization of hybrid materials (hereafter ZEOfilters) obtained by the encapsulation of UVFs into zeolites. Among all, two of the most commonly employed organic UVFs were selected: the UV-A filter avobenzone (AVO) and the UV-B filter octinoxate (OMC) (Fig. 1). As for the zeolites, we chose framework types suitable for hosting small molecules, particularly MOR, LTL, FAU, and MFI as reported in Fig. 2 [28].

This research is part of a broader project aimed at the manufacture of stable UV filters effective in blocking radiation damage, but also safe for human health as well as for the environment. The ZEOfilters are expected to overcome the issues linked to both the use of the bare UVFs and the matrices other than zeolites. Eventually, this investigation proves the efficacy of zeolites in encapsulating UVFs and the capacity of the hybrid materials to absorb UV radiation, with interesting perspectives for new-generations sunscreens.

2. Experimental section

2.1. Materials

2.1.1. UV filters

Octinoxate (C$_{18}$H$_{26}$O$_3$, liquid, molar weight (MW) 290.40 g/mol, specific gravity (SG) 1.01 g/ml, purity >96.0%) and avobenzone (C$_{26}$H$_{32}$O$_5$, powder, MW 310.39 g/mol, SG 1.08 g/ml, purity >98.0%) were purchased from TCI (Tokyo Chemical Industry Co., Ltd.).

2.1.2. Zeolites

All the synthetic zeolites used in this work (High Silica Mordenite (hereafter HS-MOR), Zeolite L (hereafter LTL), High Silica Faujasite (hereafter HS-FAU), Sodium Faujasite (hereafter 13X-FAU), High Silica ZSM-5 (hereafter ZSM5-398), low silica ZSM-5 (hereafter ZSM5-30)) were purchased from commercial suppliers as detailed below.

Table 1 summarizes the main characteristics of the employed zeolites.

All zeolites appear as white powders in their pristine form.

Mordenite (framework type MOR [28], Fig. 2a) was purchased from Tosoh Corporation (Japan, code HSZ-690HOA) in its protonated high-silica (dealuminated) form (HS-MOR; Si/Al = 110). The mordenite framework presents a 1D channel system with two parallel channels running along the c axis: a large 12-membered ring channel (12 MR, maximum diameter of a sphere that can diffuse along it: 6.45 Å), and a strongly elliptical 8 MR channel. HS-MOR was thoroughly investigated by our group and was demonstrated to be a suitable host for organic molecules under different conditions [30–33]. We have previously shown that the HS-MOR sample is strongly defective as a consequence of the dealumination process and shows some degree of acidity [33].

Zeolite L (framework type LTL [28], Fig. 2b) was purchased from Tosoh (code HSZ-500KOAI, Si/Al = 2.9) and used by our group in other studies (e.g. Refs. [34–37]). The LTL framework has a 1D channel system constituted by a circular 12 MR channel (maximum diameter of a sphere that can diffuse along it: 7.5 Å) and a smaller elliptical 8 MR one, both running along the c axis. The extra-framework K cations are sited into three distinct crystallographic sites as fully described by Ref. [35].

Faujasite zeolite (framework type FAU [28], Fig. 2c) was used in both high- and low-silica forms [38,39]. High silica faujasite (HS-FAU, Si/Al = 280) was purchased from Tosoh Corporation (Japan, code HSZ-390HUA), while low-silica faujasite (13X-FAU, Si/Al = 1.2) from BDH Chemicals, (Product 54017, out of stock). The FAU structure is characterized by a tridimensional 12 MR channel system (maximum diameter of a sphere that can diffuse along them: 7.35 Å). While HS-FAU has almost no extraframework cations, 13X-FAU has Na cations spread over different crystallographic sites, accounting for about 100 Na per unit cell (p.u.c.).

ZSM5 zeolites (framework type MFI [28], Fig. 2d) were purchased from China Catalyst (China) in both high- and low-silica protonated forms (ZSM5-398, code CCG05Z4001, Si/Al = 237 [40], and ZSM5-30, code CCG05Z301, Si/Al = 14 respectively). The MFI topology consists of straight 10 MR channels running along b direction intersecting a sinusoidal 10 MR channel running along a axis (maximum diameter of a sphere that can diffuse along them: 4.46 Å and 4.7 Å respectively).

Fig. 1. Structures and molecular models of a) octinoxate (OMC) and b) avobenzone (AVO); ticks on the molecular axis are in Å, 1 tick = 1 Å.
2.1.3. ZEOfilters synthesis

The zeolite loading procedure, aimed at the preparation of hybrid ZEOfilters, can be summarized in 4 phases: 1) Zeolite activation; 2) UVF loading; 3) ZEOfilter washing; 4) ZEOfilter drying, according to the following procedure.

All zeolites were dehydrated at 450 °C for 3 h before UVFs loading to remove all the H₂O molecules.

Dehydrated zeolites were then mixed, at room temperature, with the organic UV filter (AVO or OMC, separately) into glass tubes. The mixtures were stirred and homogenized for a few minutes and then sealed with Teflon stoppers. All tubes, covered with aluminum foil to prevent light exposure, were heated at 100 °C for 48 h. The samples were frequently checked and homogenized. Since at 100 °C both OMC and AVO are liquid, the loading is actually performed by soaking the zeolites with the neat UV filters.

The samples were then washed to remove the unloaded UV filter present on the external surface of the zeolite grains. Two different washing techniques were tested and compared in terms of efficacy and efficiency: Soxhlet extraction (SE) and ultrasound-assisted extraction (UAE). The Soxhlet extraction was carried out using a 70 ml Soxhlet extractor with acetone as solvent. Ethanol was tested too, but it was discharged since less effective (see results). A small amount of hybrid was sampled at regular intervals during the washing procedure and analyzed by elemental analysis (EA) to follow the evolution of the system over washing. An overall liquid-over-solid ratio (l/s) parameter was used to evaluate the washing degree from the chemical data since the amount of hybrid powder prepared and then washed varied. The l/s parameter is defined by the following equation:

\[
l/s = \frac{\text{Liquid Volume}}{\text{Solid Mass}}
\]

All samples were loaded at 100 °C for 48 h.

Table 1
Summary table of the selected hybrid samples reporting synthesis conditions and results from elemental (EA) and TG analyses (* = optimized washing, i.e. Total UVf wt.% = encapsulated UVf wt.%). TGA was not performed on the HS-FAU/AVO system due to the low UV-filter content. All samples were loaded at 100 °C for 48 h.

| Label          | Synthesis conditions | l/s [ml/mg] | EA  | TG  | UVf molecules p.u.c. |
|----------------|----------------------|-------------|-----|-----|----------------------|
|                | UVF/Zeolite [mol/mol]|             | C wt.% | UVf [wt.%] | Total UVf [wt.%] | Encapsulated UVf [wt.%] |
| 13X-FAU/OMC    | 55.91                | 0.10        | 13.53 | 18.19         | 16.0 | 9.9 | 6.9 |
| 13X-FAU/AVO    | 13.20                | 0.00        | 17.29 | 22.34         | 20.7 | 16.1 | 11.2 |
| HS-FAU/OMC     | 87.46                | 0.60*       | 10.29 | 13.83         | 13.2 | 13.2 | 6.1 |
| HS-MOR/OMC     | 19.96                | 0.15        | 8.21  | 11.03         | 8.5  | 8.5  | 0.9 |
| HS-MOR/AVO     | 1.30                 | 0.19*       | 4.60  | 5.94          | 5.6  | 5.6  | 0.6 |
| LTL/OMC        | 17.31                | 0.84        | 4.17  | 5.60          | 5.88 | 5.3  | 0.5 |
| LTL/AVO        | 0.57                 | 0.22*       | 4.42  | 5.71          | 5.3  | 5.3  | 0.5 |
| ZSM5-30/OMC    | 40.31                | 1.71*       | 5.87  | 7.89          | 7.6  | 7.6  | 1.8 |
| ZSM5-30/AVO    | 5.44                 | 1.55*       | 3.15  | 4.07          | 4.6  | 4.6  | 1.0 |
| ZSM5-398/OMC   | 40.50                | 1.71*       | 1.88  | 2.53          | 2.6  | 2.6  | 0.5 |
| ZSM5-398/AVO   | 5.83                 | 0.81*       | 1.09  | 1.41          | 1.4  | 1.4  | 0.3 |

Fig. 2. The framework of a) MOR, b) LTL, c) FAU, d) MFI zeolites [29].
The samples washed with UAE were split into various portions and washed with acetone using a constant solid/liquid ratio of 0.03 ml/mg. The aliquots underwent a different number of cycles of 20 min ultrasonic bath followed by centrifugation (the solvent was refreshed at each cycle). Samples of the hybrids at different degrees of washing were analyzed by EA to monitor the washing process as done for the Soxhlet method. The same L/s parameter was employed for both SE and UAE. Before analysis, all samples were dried for 48 h at 60 °C for solvent removal after the washing process. The obtained dried material is referred to as ZEOfilter.

The loading/washing protocol was optimized to yield ZEOfilters with the maximum possible filter loading and without molecules on the zeolite grains surface, as detailed in the Result section. Then, hybrids were produced on a multi-gram scale to allow their complete physico-chemical characterization.

As mentioned, the maximum possible UV filter loading was not known in advance for the investigated zeolites. Thus, the first exploratory loading were made with large UV filter excess. Further syntheses of ZEOfilters were performed by significantly reducing the initial excess of UV filter.

2.2. Elemental analysis (EA)

Elemental analyses were performed using a Thermo-Fisher CHNS FLASH 2000 analyzer. The samples were brought at 1800 °C with a “FLASH” dynamic combustion. After the reduction, the elementary gases released by the decomposition were analyzed in a GC (gas-chromatograph) comprising a chromatographic column and a sensitive TCD detector. The amount of sample used for the analyses ranges from 0.7 mg to a few mg. The analyzed elements are C and H.

2.3. Thermogravimetric analysis (TGA)

TG analyses were carried out using a Seiko SSC/5200 thermal analyzer. TGA were performed on about 20 mg of ZEOfilters loaded into an open Pt crucible and heated under helium stream from room temperature to 1050 °C, at a heating rate of 10 °C/min.

Samples at different washing stages were analyzed by TG to determine their filter content and to determine weight losses due to filter molecules in the zeolite cavities and on the surface of the grains. TGA were also performed on pure octinoxate and avobenzone in the same conditions used for the hybrids, and on pristine zeolites in an air stream.

2.4. UV–Vis spectroscopy

UV–Vis measurements were performed with a UV–Vis V-570 Jasco spectrophotometer in transmission mode. UV–Vis spectra were collected in the 200–800 nm interval with 1 nm resolution, at 25 °C.

Solution spectra of octinoxate and avobenzone in ethanol and ethylacetate were collected employing a 1 cm quartz cell at different concentrations (1 ppm < c < 200 ppm).

UV–Vis spectra of pure filters in vaseline oil (v.o.), zeolites in v.o., and of hybrids in v.o. were collected using a quartz slide sandwich [41].

2.5. Infrared spectroscopy

FTIR spectra were collected on a Bruker IFS66 spectrophotometer equipped with a La-DTGS detector and a KBr beamsplitter. Each spectrum is the average between 128 scans in the 4000–400 cm⁻¹ range with a resolution of 4 cm⁻¹. The spectra of OMC were collected by the thin film method by putting a drop of liquid between two KBr windows, while the ZEOfilter spectra were obtained by making a self-supporting pellet of powder with an optical thickness of about 10 mg/cm² and by evacuating it (residual pressure 10⁻⁴ mbar) into a traditional infrared cell equipped with KBr windows.

3. Results and discussion

3.1. ZEOfilter loading

Zeolite loading represented a challenging aspect in the preparation of the hybrid ZEOfilters, particularly because the UVfs maximum loading was unknown and the washing procedure had to be effective in removing the surface excess of the UVfs without affecting the encapsulated molecules. These two achievements are crucial for the realization of safe and effective sunscreen hybrid materials. The selected samples of ZEOfilters are summarized in Table 1 along with their loading conditions and chemical data.

As already mentioned, all ZEOfilters were initially prepared by using a high UV filter excess. Once the maximum loading of each system was experimentally determined, subsequent samples were obtained with a smaller UV filter excess (+1–2 wt%). Whatever the reagent excess, all samples of the same zeolite/UV filter system displayed the same final composition and features. In Table 1 are reported samples with very variable initial UV filter/zeolite ratio (i.e. from a more than ten-fold excess in the case of 13X-FAU/OMC and HS-FAU/OMC, to an almost ad-hoc loading of LTL/AVO).

The carbon content (%) variation of the different hybrid materials was followed upon washing by EA. The different washing effect of ethanol and acetone on the LTL/OMC system is shown in Fig. 3a that exhibits the decrease of C wt.% under the effect of SE. Both solvents induce a significant decrease in UVf content in the first cycles, followed by a smoothing of the curve upon successive washing cycles, leading to a compositional final plateau. Conversely, the residual C% is different for the two solvents attaining the final value of about 4% and 1% for acetone and ethanol respectively. Taking into account the molecular weight of OMC, the plateau of the acetone-washed curve corresponds to about 0.5 OMC molecule p.u. of LTL (Table 1), which is given the size of the molecule and of the LTL channel could account for the maximum OMC loading. We can thus assume that at the plateau the unadsorbed UVf molecules on the surface are removed, leaving only the more strongly trapped ones in the cavities. The washing profiles indicate that ethanol is not suitable for this purpose, as it tends to remove the OMC molecules even from the zeolite channels. Instead, acetone is able to remove the physisorbed molecules on the surface of the grains without affecting those hosted in the cavities. Nevertheless, we have noticed that upon prolonged washing even with acetone the C% decreases constantly albeit slowly (data not shown); it is thus essential to stop the washing procedure once the plateau is reached. Based on these results, acetone was used as the solvent for all the other samples.

Soxhlet extraction (SE) and ultrasound-assisted extraction (UAE) were both evaluated as washing methods, and the results for LTL/OMC system are shown in Fig. 3b. Both SE and UAE led to similar final UVf concentrations in the hybrid material, even if at different L/s values. We deem the UAE more suitable for large-scale preparation since no heating source is required, a larger volume can be obtained faster and the procedure is more easily tunable, even if it is more labor-intensive. On the contrary, the SE fits better for small-scale operations. We then decided to choose the appropriate washing technique on a case-by-case basis, and hereafter no specification of the employed method will be given for each sample.

The optimum loading for each sample was estimated as the plateau of the washing curve, corresponding to the maximum encapsulated filter content (wt.%). These data are those reported in Table 1 together with the TG results (see below for discussion), showing the number of UVf molecules actually encapsulated p.u.c.

As different framework types have different pores volume, it is to be expected that FAU can host more molecules compared to the other investigated zeolites. Indeed, FAU accessible volume corresponds to
27.42% of the total cell volume (more than 14000 Å³), compared to 12.27 and 15.37% for MOR and LTL framework, respectively (cell volumes about 3000 Å³ and 2000 Å³, respectively). The two UVFs behave differently when encapsulated in different matrices: AVO seems to be more suitable to be hosted in cationic zeolites - particularly, 13X-FAU shows the highest loading - while in high silica zeolites it seems to be not loadable at all, probably for the absence of cationic sites to graft. Conversely, OMC can be loaded in all the investigated zeolite types, both cationic and high silica. Interestingly, zeolites LTL and 13X-FAU can host almost the same amounts of both filters. Both the UVFs have hydrophobic character, although AVO behaves as a weak acid due to the β-diketo group. The keto-enol tautomerism is hampered in the solid-state within the zeolite channels, but the proximity to zeolite acid sites may catalyze the interconversion of the keto-enolic form into the diketo one. On the other hand, the presence of metal ions in the zeolite cavities could account for a shifting of the tautomeric equilibrium toward the keto-enol due to its enhanced metal-binding ability \[42-44\]. The slight differences in loading between AVO and OMC can be attributed to their steric hindrance. OMC is bulkier and characterized by a hydrophobic and mobile aliphatic side chain, while AVO, particularly in the keto-enol form is an almost linear rigid structure, probably able to better fit into zeolite channels.

3.2. ZEOfilter characterisation

Elemental analysis performed during and after washing allowed a first, quick, estimation of UV filter content in each ZEOfilter. However, EA does not provide any information about the effectiveness of encapsulation. Thus, thermodgravimetric analyses were performed under inert atmosphere (He) on the selected hybrid samples before and after the washing process to investigate the differences in the desorption temperatures of physisorbed molecules on the grain surface and within the zeolite pores (Table 1). The pristine zeolites and pure UVfs OMC and AVO were used as reference systems. The results are reported in Table 1. The differences among the values obtained by EA and TGA may arise from various factors. First of all, even if samples were homogenized before analysis, some inhomogeneities can be present at the scale of sampling (1 mg for EA and 20 mg for TGA). Then, low-C measuring by EA is challenging in silicate matrices. Finally, the possible water content variability in zeolites can induce weight variation of the samples. Thus TGA was preferably used for the final UV f.u.c determination.

The pure UVfs (Fig. 4) decompose over a 100-degrees range below \(~300 ^\circ \text{C}\) (OMC) and \(~350 ^\circ \text{C}\) (AVO). These temperature ranges are lower than those reported in the literature for their boiling temperature (i.e. 382 ^\circ \text{C} and 400 ^\circ \text{C} for AVO, respectively \[45\]), as expected for a TGA in the open crucible setup \[46\].

The thermal profiles for the systems with the highest loading, i.e. FAU13X and LTL hybrids, are reported in Fig. 5 and Fig. 6, respectively, while the weight losses of the whole sample set are reported in Table 1. The pristine 13X-FAU (Fig. 5a and b, black line plot) displays a single broad weight loss below 400 ^\circ \text{C}, accounting for 23% weight loss, that can be correlated to the removal of H₂O molecules in the solvation sphere of cations in different sites, consistently with what reported in the literature \[47\]. The two 13X-FAU hybrids reported in Fig. 5a and b (13X-FAU/OMC, 13X-FAU/AVO) show a DTG peak at about 100 ^\circ \text{C} that can be attributed to H₂O molecules readsorbed during the preparation and/or storing of the ZEOfilters. The lower temperature at which these losses occur suggests that H₂O molecules are more loosely bonded in ZEOfilters than in the pristine zeolites. This hypothesis is supported by the insertion of mostly hydrophobic UVfs into the zeolite channels that prevent the access to H₂O molecules. The DTG curves of the optimized samples (l/s 0.16 and 0.06 for OMC and AVO hybrids, respectively) show a shoulder at slightly higher temperature (about 150 ^\circ \text{C}), which is not visible in the unoptimized ones in which an excess of UVfs is on the surface of zeolite particles (l/s 0.10 and 0 for OMC and AVO, respectively) as shown in Fig. 5. A possible explanation is that the physisorbed UVfs on the surface hamper the access of the H₂O molecules to the zeolite pores; upon washing the removal of UVfs excess from the grain makes the channels more accessible to water once again and allows the formation of some more stable H₂O-zeolite bonds, similarly to what observed in the pristine sample. At higher temperatures, the DTG curves of 13X-FAU ZEOfilters show two peaks of different breadth. Unoptimized 13X-FAU/AVO DTG (l/s = 0) displays a noticeable peak at 250 ^\circ \text{C} (Fig. 5b) that completely

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**Fig. 3.** Example of washing curves of ZEOfilters. a) Soxhlet extraction (SE) of hybrid LTL/OMC with ethanol (green curve) and acetone (orange curve); b) comparison of ultrasound-assisted extraction (UAE) and SE washing methods for LTL/OMC sample. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

**Fig. 4.** TGA of OMC (a) and AVO (b) in a helium atmosphere.
disappears in the optimized sample and can be attributed to UVFs loosely bound to the surface. Similarly, unoptimized 13X-FAU/OMC shows a DTG peak at 220 °C but, in this case, a small signal remains in the optimized sample (I/s = 0.16, Fig. 5a), indicating incomplete removal of the UVf molecules from the zeolite grains surface. The DTG broad bands registered in the range 270–550 °C can be attributed to the decomposition of the UVFs encapsulated into the zeolite porosities, which are calculated as 6.6% and 10.6% wt. for the 13X-FAU/OMC and the 13X-FAU/AVO systems, respectively. Since the TG losses corresponding to these peaks are higher for the unoptimized samples, we cannot exclude a contribution of molecules more strongly bonded on the zeolite grains surface. It is worth noting that the decomposition temperatures observed for the UVF molecules encapsulated into the zeolites are higher than those observed for the pure filters, as a clear consequence of the UVF-zeolite interactions. By comparing the total UVF loss with the weight of the anhydrous zeolite it can be calculated that 13X-FAU/OMC samples host 4.3 molecules of OMC per unit cell while the 13X-FAU/AVO hosts 6.6 molecules of AVO p.u.c. These data are in good agreement with those obtained from elemental analyses (Table 1).

All DTG signals -relative to the organic decomposition-of 13X-FAU/AVO are shifted toward higher temperatures compared to 13X-FAU/OMC. This shift can be ascribed in the first instance to the chelating properties of the 🍂 donor group of the β-keto-enol moiety of AVO that can form stronger interactions with the cations of the zeolite than the weak coordination bond of the carbonyl oxygen in the ester moiety of OCM as depicted in Fig. 7.

Pristine LTL zeolite loses all water molecules below 250 °C, with a total weight loss of 11.2% (Fig. 6). We observe a comparable weight loss of ~9 wt% below 220 °C for both LTL ZEO filters, possibly due to rehydration of the zeolite after loading. It is difficult to unequivocally assign this weight loss to structural water or rather to physisorbed surface H

H2O since LTL hosts a large number of weakly bonded H2O molecules that can be released below 150 °C [34]. Interestingly, the hybrids show a lower temperature for water release compared to the pristine zeolite, possibly due to the higher amount of physisorbed H2O molecules. For the sake of brevity, in the following discussion, we discuss the results only to the more interesting optimized hybrid LTL systems since the considerations made for the unoptimized FAU13X hybrids apply also to the unoptimized LTL hybrids.

The DTG curve of the LTL/OMC sample (Fig. 6a) shows three peaks at 280, 315, and 360 °C, accounting for a total weight loss of 5.9%. These peaks can be attributed to OMC molecules differently bonded to the zeolite. The data are in good agreement with the 5.60 wt% calculated by elemental analyses. LTL hybrids can hence host 0.5 OMC molecules p.u.c. and this corresponds nicely with the maximum loading predictable by structural considerations. In fact, the 12 MR channel can host, compatibly with its size, only one OMC molecule elongated along the c axis of LTL unit cell, which has a length of about half of the OMC molecule.

The LTL/AVO hybrid DTG curve shows a broad peak, with a shoulder, between 300 and 650 °C, accounting for a total weight loss of 5.3 wt %, in good agreement with the 5.71 wt% of AVO measured by EA. This value corresponds to 0.5 AVO molecules p.u.c. compatible with the LTL structure as above reported for OMC hybrid.

For LTL hybrids the temperature shift between OMC and AVO loss is more marked than that observed for 13X-FAU. This could be ascribed to
the stronger interactions between the UVIs and the extraneous cations in LTL, which presents more accessible cation sites compared to FAU. The broader DTG peak widths of the FAU ZEOfilters could be ascribed to the presence of many different Na sites in the large Y cage. In this case, UV molecules interact with cations at different crystallographic sites and with different bond strengths, thus the molecule release occurs in a wide range of temperatures broadening the DTG peaks.

Based on the EA and TGA results obtained for FAU- and LTL-based ZEOfilters, it can be concluded that the encapsulation process is effective.

### 3.3. ZEOfilters efficacy in UV-light absorption

The second important goal of this paper is the assessment of ZEOfilters UV filtering power, which will enable their future exploitation. The UV-filtrating power of ZEOfilters should be comparable or better than that of the pure UVIs (Fig. 1Sa,b). UV-Vis spectra of bare UVIs in ethanol (EtOH), ethyl acetate (EtOAc), and vaseline oil (v.o.) were collected to compare their absorption capacity in different media. The AVO and OMC filters show minor solvatochromic effects since insignificant differences in transmittance are observed when the solvent is changed. OMC and AVO filters display full transmittance in the visible light range (400–700 nm), together with a neat absorption peak in the UV-A (AVO) or UV-B (OMC) range. This feature is maintained also at a high UVI concentration (data not shown), with a consequent total absorption of UV light. In addition, UVIs maintain their transparency also at high concentration, a feature mostly desired for cosmetic formulations. The anomalous behavior of EtOAc solutions below 250 nm corresponds to the solvent UV-cutoff.

To evaluate the effect of the zeolite scaffold on the UV absorption, pristine zeolites dispersed at 25 wt% in v.o. were analyzed. As shown in Fig. 1Sc, the spectra do not show absorption bands in the visible nor the UV range. HS-MOR and ZSM5-398, however, show a very low transmittance in the whole region at 25 wt%, mainly linked to particle scattering. With increasing concentration of zeolite into v.o. (data not shown), the transmittance profile lowers steadily in the whole UV–Vis range, increasing the sample opacity.

The UV-Vis measurements on ZEOfilters were performed on a suspension of the hybrid material in v.o. The final concentration of the UVI in this mixture was equal to 1 wt%. This filter concentration was chosen firstly because it allowed the observation and comparison of the UV-Vis spectral features of the investigated hybrids and secondly in view of further cosmetic applications (Fig. 8).

ZEOfilters based on HS-MOR, HS-FAU, ZSM5-30, and ZSM5-398 seem less promising since exhibit limited UV filtering properties compared to hybrids of 13X-FAU and LTL, and bare UVIs (Fig. 8). Moreover, all ZEOfilters based on acid zeolites show selective visible light absorption as apparent from the final color of the hybrid powders (Fig. 9). The absorption color of hybrids tends to change from white to violet or yellow (for OMC and AVO ZEOfilters, respectively) while increasing the zeolite Si/Al ratio, even if for ZSM5-398/AVO and HSFAU/OMC colors are very pale. Preliminary Infrared Spectroscopy (IR) results revealed the protonation of the UVIs molecules interacting with the HS-MOR acid sites.

Fig. 10 shows the infrared spectra for OMC (a) compared to the HS-MOR/OMC ZEOfilter (b). It is noticeable that the interaction with the zeolite causes changes in the structure of the OMC. Indeed, the most characteristic signal responsible for the stretching of the carbonyl group \(\nu_C = \delta (C = C)\) is dampened in the ZEOfilter as well as the signal attributed to the \(\nu_C = C = C\) at 1635 cm\(^{-1}\). On the other hand, the signals attributed to the aromatic skeleton at 1604 cm\(^{-1}\), 1575 cm\(^{-1}\), 1512 cm\(^{-1}\), and 1422 cm\(^{-1}\) stand out in the ZEOfilter spectrum having a higher relative intensity, with respect to the OMC one. A less important modification occurs for the group of signals with maximum at 1465 cm\(^{-1}\) that contain the deformation of CH\(_2\) (\(\delta(CH_2)\)).

This behavior can be compatible with the protonation of the \(\alpha,\beta\)-unsaturated ester system due to the high definitiveness of the HS-MOR zeolite, which notably contains a high amount of acid sites. This protonation might explain the absorption bands in the visible light range (Fig. 8a), but a deeper IR investigation of the UVIs–zeolite interaction is needed for all ZEOfilters.

Using a mixture with 1% of UVI, ZSM5-398 hybrid samples are opaque, thus not measurable as a consequence of the high ZEOfilter amount to be used in the mixture due to the low UVI loading in this zeolite (2.53% OMC and 1.41% AVO, respectively, Table 1). The amount of UVIs for these samples was then decreased to 0.5 wt%. However, even at lower ZEOfilter content, these samples display a very low transmittance over the whole wavelength range, indicating a major contribution of zeolite particle scattering to the spectra.

Concerning the low silica ZEOfilters, 13X-FAU and LTL hybrids display an enhancement of UV filtering power even when compared to bare UVIs, and, in addition, they maintain perfect visible transparency. Conversely, ZSM5-30 hybrids display spectral features similar to HS-MOR, probably because both these zeolites are in protonic form. Both these hybrids display some absorption bands in the visible range leading to colored samples (Fig. 9) with very limited absorption in the UV region. It is worth noting that the UV absorption band of the ZSM5-30 hybrids, and, to a lesser extent, of the HS-MOR ones, is shifted towards higher wavelengths compared to the other ZEOfilters. This shift towards lower energy can be related to the acidic environment of ZSM5-30 and HS-MOR, favoring the keto-enol form for AVO, and the protonated ester form for OMC (as shown by FTIR data).

The enhancement of the UV filtering power of LTL and 13X-FAU ZEOfilters is very promising for their future development and industrial application. Indeed, the increased efficiency in UV filtering can be key to reduce the amount of UVIs employed in cosmetic formulations.

Another important point to pave the way for the use of these ZEOfilters in cosmetic formulations (and in other product categories) is to assess their photostability under protracted UV exposure. The preliminary exposure tests performed by a solar lamp (not reported here) show promising results, and high ZEOfilter stability. Indeed, the
confinement in zeolite scaffold probably prevents i) the molecules isomerization [11], and ii) the interactions among the different filters in the formulation [12].

4. Conclusions

We presented an efficient approach to the production of ZEOfilters, hybrid UV filtering materials constituted by the encapsulation of organic UV filters (avobenzone and octinoxate) into zeolites with different framework topologies (LTL, MOR, FAU, MFI) and chemistry. ZEOfilters displayed variable spectral features depending on the combination zeolite/UVf, with some of them being greatly effective in UV absorption. Overall, the encapsulation of UV filters resulted in an enhanced UV filtering power for cationic, not protonated, zeolites (i.e. LTL and 13X-FAU) hybrids, whereas high silica zeolites (i.e. HS-MOR and HS-FAU e ZSM398) yielded materials with reduced filtering power. The protonated ZSM5-30 hybrids display spectral features in between cationic and high silica ZEOfilters. The increased UV filtering power makes LTL and 13X-FAU ZEOfilters more effective than the bare UV filters, thus requiring a lower organic filter amount in the formulations.

Compared to traditional organic UV filters, ZEOfilters are expected (also thanks to some preliminary tests here not reported) to enhance the photo stability of the filters thanks to guest-host stabilization, a feature able to limit their detrimental effects on human health and the environment, particularly the direct contact of UVs with skin is avoided. Furthermore, a sensible reduction of stabilizers in the formulations is also expected since UVfs are encapsulated separately in the zeolites, and photochemically incompatible filters can be applied simultaneously as a mixture of different ZEOfilters, paving the way to more effective and safer formulations.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Patent application

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.micromeso.2021.111478.

References

[1] J.R. Herman, J. Geophys. Res. 115 (2010).
[2] I. Fountoulakis, H. Diemoz, A.M. Siani, G. Hulsen, J. Grobner, Earth Syst. Sci. Data 12 (2020) 2787–2810.
[3] U. Osterwalder, M. Sohn, B. Herzog, Photodermatol. Photoimmunol. Photomed. 30 (2014) 62–80.
[4] P. Gies, E. van Deventer, A.C. Green, C. Sinclair, R. Tinker, Health Phys. 114 (2018) 84–90.
[5] American Cancer Society, Facts & Figures 2021, American Cancer Society, Atlanta, Ga, 2021. https://www.cancer.org/cancer/melanoma-skin-cancer/about/key-statistics.html. (Accessed 30 June 2021).
[6] A.M. Forsea, Dermatol. Pract. Concept. 10 (2020).
[7] A. Wechsler, S. Hizirolg, Build. Environ. 42 (2007) 2637–2644.
[8] Y.Q. Li, Y. Yang, S.Y. Fu, Compos. Sci. Technol. 67 (2007) 3465–3471.
[9] L. Szente, E. Fenyesesi, Molecules 23 (2018).
[10] Q.H. Yang, L. Zhao, H. Yu, Q.H. Min, C.Z. Chen, D.C. Zhou, X. Yu, J.B. Qiu, B. Li, X. H. Xu, J. Alloys Compd. 784 (2019) 535–540.
[11] B. Herzog, M. Wehrle, E. Quans, Photochem. Photobiol. 85 (2009) 869–878.
[12] D.G. Beasley, T.A. Meyer, Am. J. Clin. Dermatol. 11 (2010) 413–421.
[13] J. Kockler, M. Oelgemoller, S. Robertson, B.D. Glass, J. Photochem. Photobiom. C Photochem. Rev. 13 (2012) 91–110.
[14] R. Jansen, S.Q. Wang, M. Burnett, U. Osterwalder, H.W. Lim, J. Am. Acad. Dermatol. 69 (2013).
[15] T. Wong, D. Orton, Clin. Dermatol. 29 (2011) 306–310.
[16] K.M. Hanson, S. Narayanan, V.M. Nichols, C.J. Bardeen, Photochem. Photobiol. Sci. 14 (2015) 1607–1616.
[17] D. Dondi, A. Albini, N. Serpone, Photochem. Photobiol. Sci. 5 (2006) 835–843.
[18] E. Damiani, C. Puglia, J. Pharmaceut. Sci. 108 (2019) 3769–3780.
[19] L. Perioli, V. Ambrogli, B. Bertini, M. Ricci, M. Nocchetti, L. Latterini, C. Rossi, Eur. J. Pharm. Biopharm. 62 (2006) 185–193.
[20] N. Lapidot, O. Gans, F. Biagini, L. Sosonkin, C. Rottman, J. Sol. Gel Sci. Technol. 26 (2003) 67–72.
[21] V. Ambrogli, L. Latterini, F. Marmottini, C. Pagano, M. Ricci, J. Pharmaceut. Sci. 102 (2013) 1468–1475.

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Fig. 9. ZEOfilter powders. Samples are organized as a function of the Si/Al ratio.

Fig. 10. FTIR spectra of OMC (a) and HS-MOR/OMC (b) subtracted for the HS-MOR spectrum.

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[22] A.L.M. Daneluti, F.M. Neto, M.V.R. Velasco, A.R. Baby, J.D. Matos, J. Therm. Anal. Calorim. 131 (2018) 789–798.

[23] L. Dan, X. Lixian, Nano Sunscreen Agent, Preparation Method, and Application Thereof. 2018. CN20181003, https://patentscope.wipo.int/search/en/detail.jsf?docId=CN223049992.

[24] M.N. Chretien, L. Migahed, J.C. Sciano, Photochem. Photobiol. 82 (2006) 1608–1611.

[25] M.N. Chretien, Pure Appl. Chem. 79 (2007) 1–20.

[26] M.N. Chretien, E. Heafey, J.C. Sciano, Photochem. Photobiol. 86 (2010) 153–161.

[27] Y. Deng, A. Ediriwickrema, F. Yang, J. Lewis, M. Girardi, W.M. Saltzman, Nat. Mater. 14 (2015) 1278–1285.

[28] C. Bauerlocher, L.B. McCusker, B. Olson, W.M. Meier, Atlas of zeolite framework types. Published on Behalf of the Structure Commission of the International Zeolite Association, Elsevier, Boston; Amsterdam, 2007.

[29] K. Momma, F. Izumi, J. Appl. Crystallogr. 44 (2011) 1272–1276.

[30] R. Arletti, A. Martucci, A. Alberti, L. Pasti, M. Nasi, R. Bagatini, J. Solid State Chem. 194 (2012) 135–142.

[31] A. Martucci, M.A. Gremontini, S. Blasioli, L. Gigli, G. Gatti, L. Marchese, I. Braschi, Microporous Mesoporous Mater. 170 (2013) 274–286.

[32] M. Fabbiani, G. Confalonieri, S. Morandi, R. Arletti, S. Quartieri, M. Santoro, F. Di Renzo, J. Haines, R. Fantini, G. Tabacchi, E. Fois, G. Vezzalini, G. Ricchiardi, G. Martra, Microporous Mesoporous Mater. 311 (2021).

[33] R. Fantini, R. Arletti, S. Quartieri, M. Fabbiani, S. Morandi, G. Martra, F. Di Renzo, G. Vezzalini, Microporous Mesoporous Mater. 294 (2020).

[34] L. Gigli, R. Arletti, S. Quartieri, F. Di Renzo, G. Vezzalini, Microporous Mesoporous Mater. 177 (2013) 8–16.

[35] L. Gigli, G. Vezzalini, S. Quartieri, R. Arletti, Microporous Mesoporous Mater. 276 (2019) 160–166.

[36] L. Gigli, R. Arletti, G. Tabacchi, E. Fois, J.G. Vitillo, G. Martra, G. Agostini, S. Quartieri, G. Vezzalini, J. Phys. Chem. C 118 (2014) 15732–15743.

[37] L. Gigli, R. Arletti, J.G. Vitillo, G. Alberto, G. Martra, A. Devaux, G. Vezzalini, J. Phys. Chem. C 119 (2015) 16156–16165.

[38] L. Braschi, S. Blasioli, L. Gigli, C.E. Gens, A. Alberti, A. Martucci, J. Hazard Mater. 178 (2010) 218–225.

[39] D.H. Olson, Zeolites 15 (1995) 439–443.

[40] A. Martucci, E. Rodeghero, L. Pasti, V. Boss, G. Cruciani, Microporous Mesoporous Mater. 215 (2015) 175–182.

[41] E.T. Kaye, J.A. Levin, I.H. Blank, K.A. Arndt, R.R. Anderson, Arch. Dermatol. 127 (1991) 351–355.

[42] E. Ferrari, B. Arezzini, M. Ferrali, S. Lazzari, F. Pignedoli, F. Spagnolo, M. Saladini, Biometals 22 (2009) 701–710.

[43] R. Benassi, E. Ferrari, R. Grandi, S. Lazzari, M. Saladini, J. Inorg. Biochem. 101 (2007) 203–213.

[44] V. Deneva, G. Dobrikov, A. Crochet, D. Nedeltcheva, K.M. Fromm, L. Antonov, Bielstein J. Org. Chem. 15 (2019) 1898–1906.

[45] European Chemicals Agency. https://echa.europa.eu/it/search-for-chemicals. (Accessed 30 June 2021) accessed.

[46] P. Gabbott, Principles and Applications of Thermal Analysis, Blackwell, Oxford, 2008.

[47] M. Polisi, J. Grand, R. Arletti, N. Barier, S. Komaty, M. Zaaour, S. Mintova, G. Vezzalini, J. Phys. Chem. C 123 (2019) 2361–2369.