

SUPERCRITICAL CO₂ IMPREGNATION OF ZEOLITES WITH ORGANIC BUILDING BLOCKS- THE “SHIP-IN-A-BOTTLE” TECHNIQUE

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In this paper we have investigated on the use of supercritical CO₂ (SCCO₂) as processing media for encapsulation of triphenylpyryl (TP) and triphenyltrityl (T) organic guests in the inner supercage of a HY faujasite (Si/Al 2.5) to form TP@Y and T@Y organic-inorganic hybrids. A ship-in-a-bottle technique was used because the size of these organic guests is larger than the faujasite channels (7 Å) that are connected to the supercage (12 Å).

INTRODUCTION

Faujasites are aluminosilicates that belong to the family of zeolites, whose porous structure allows the incorporation of guest molecules or ions in their open framework [1]. The resulting hybrid possess a wide range of new applications, mainly in the areas of sensor devices, catalyst design or optical data storage [2,3]. Frequently, a deep homogeneous impregnation of microporous materials is difficult to achieve. For instance, the organic compound/zeolite composites can be prepared by adding the guest component to the reaction mixture for the hydrothermal synthesis of the molecular sieve [4], although the pH and temperature values required in the process may result in the decomposition of the organic material. An alternative procedure involves impregnation of the organic compound in the previously synthesised zeolite by diffusion of the guest compound from a liquid solution or a gas phase [5].

In recent years, supercritical carbon dioxide (SCCO₂) has received considerable attention as a viable alternative to conventional liquid solvents for diffusion in microporous systems. The use of SCCO₂ for the infusion of organic molecules in zeolites appears to be advantageous in respect to conventional liquid solvents since it has very low viscosity, and null surface tension [6]. Another advantage of using SCCO₂ as a solvent is the lack of competition between the solvent and the organic material for the adsorption sites of the zeolites, thereby producing higher loadings and avoiding by-products formation. Previous experiments on the impregnation of organic compounds in zeolites using supercritical CO₂ were successfully achieved [7].

In this work, the organic compounds used for entrapment inside the faujasite cages were triphenylpyryl and the triphenyltrityl cation. Both cations are electron-transfer photosensitizers [8,9]. However, their use is sometimes only possible when the cation is trapped inside of a zeolite cage, since the free cation hydrolyzes in water [10]. Zeolites are transparent to UV-Vis radiation.

Regardless of all of the advantages that these composites offer, their synthesis is not straightforward, since their sizes (for both triphenylpyryl and triphenyltrityl cation) are larger than the zeolite channels that are connected to the supercage. Thus, the synthetic methodology is inspired in the building of ships inside of a bottle, where small molecules are introduced inside the zeolite channels and they react between them in the supercage to produce the larger size cation. The encapsulation of these cations in Y-zeolites have been carried out using conventional solvents using very extreme reaction conditions in terms of reaction times and temperatures [3]. Thus, the use of supercritical SCCO₂ is proposed here as a good alternative to ease and improve the synthesis and performance of these type of organic/zeolite composites.

I. MATERIALS AND METHODS

Used zeolite was ammonium Y-Faujasite (NH₄Y) (Strem). The zeolite was activated to HY-zeolite by removing ammonium cations from the cavities, after calcination at 520 °C for 48 h under N₂ atmosphere. The 1,3,5-triphenyl-2-pentene-1,5-dione (diketone) was the precursor of the triphenylpyryl cation. Benzaldehyde, anisole, diphenylmethanol and benzene were used for the synthesis of the encapsulated triphenylterityl cations. Reagents were purchased from Aldrich.

Experiments were performed in the batch mode in a high pressure equipment described elsewhere [11]. In short, cooled SCCO₂ was pressurized and added to a 100 mL reactor until the working pressure was reached. The reactor was then heated at the chosen temperature. The system was stirred at 400 rpm. In a typical experiment, the reactor vessel was charged with freshly calcined zeolite (light ivory colour) together with the diketone for the synthesis of the triphenylpyryl cation or the necessary building blocks for the synthesis of the triphenyltrityl cations. In all of the experiments the system was pressurized to 150 bars at 60 °C, and the conditions were maintained during 24 h, then, the temperature was increased to 150 °C and the pressure to 175 bars, and kept for 48 more hours. After this time, the system was depressurized and let it cool to room temperature. The reaction product was obtained as coloured powder that was washed either using a continuous flow of SCCO₂ (200 bar, 80 °C for 3 hours) or dichloromethane (DCM) in a Soxhlet apparatus (24 h and) and dry under vacuum (60 °C for 24 h).

Loaded zeolite samples were analysed by thermogravimetric analysis (TGA) with a thermogravimetric analyser Perkin Elmer. Solid Ultraviolet-visible spectrometry was carried out using a Perkin Elmer Lambda 19 UV/VIS/NIR spectrophotometer furnished with a 60mm integrating sphere was used for diffuse reflectance and transmittance measurements on solid samples. Principal component analysis (PCA) was used for classifying and characterising the impregnated zeolite materials under different experimental conditions. The algorithm was available from the “PLS_Toolbox”, version 3.5 [12] which was implemented for use with MATLAB for Windows (Version 6.5). A more detailed description is given elsewhere [13].

II. RESULTS

II.i Preparation of triphenylpyryl cation inside HY (TP@Y):

The sample was recovered as a bright orange powder. In this case, the schematic synthesis is depicted in Fig. 1. The synthesis of the triphenylpyryl cation was carried out using as starting material the diketone, whose size fits inside the channels of the zeolites. The reaction proceeds in two main steps, first by diffusion of the diketone into the internal cavity of the zeolites followed by a thermal dehydration to give the triphenylpyryl cation, with a size larger than the zeolite channels, thus impeding its departure.

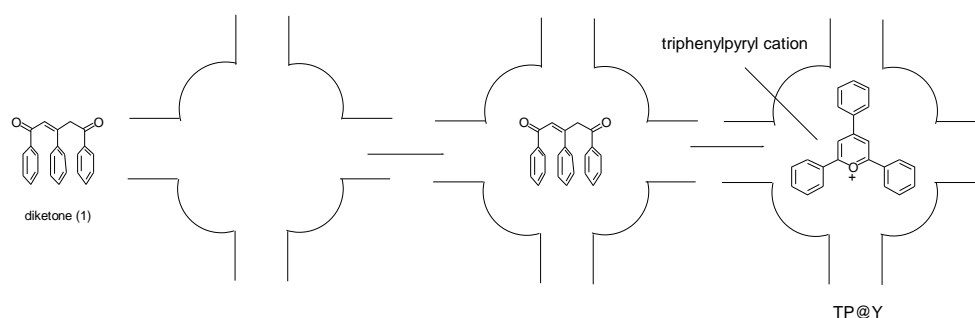


Figure 1: Schematic representation of the formation of triphenylpyryl cation.

The diffuse reflectance UV-Vis spectrum of the loaded zeolite (TP@Y) was compared to the spectra of the raw diketone, the isolated raw cation (TPT) and with the calcined zeolite (Fig. 2a). It can be observed that the spectrum of the treated and washed zeolite match the spectra of the TPT, evidencing the presence of the cation in the zeolite supercages. When comparing the UV-Vis spectra

of the zeolite cleaned by Soxhlet and by SCCO_2 extraction procedures, it can be observed that both spectra present the same pattern. However, it should be pointed out that the SCCO_2 cleaning process is less time-consuming and is more effective since the recovered sample does not need any further drying to eliminate the organic solvent. TGA analysis (Fig 2b) indicated that the amount of loaded sample was about a 9 wt%.

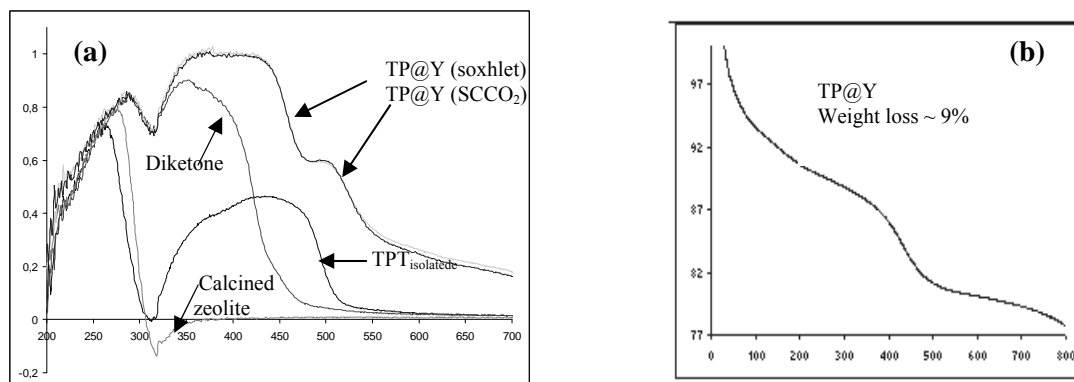


Figure 2: (a) Collection of UV-Vis spectra of TP@Y and starting materials; and (b) TGA of the TP@Y.

II.ii Preparation of triphenyltrityl cation inside HY (T@Y):

The synthesis of the triphenyltrityl cation, which involves the formation of C-C bonds, proceeds via different pathways depending on the starting materials used for the condensation reaction. In this case, the building blocks used are mainly of aromatic aldehyde or aromatic hydroxyl nature. Our target was to synthesise, using SCCO_2 as solvent, three different triphenyltrityl cations schematized in Fig. 3. The reaction approach is the same as for the formation of the triphenylpyryl cation, that is, first diffusion of the organic building blocks through the zeolite channels until they reach the internal supercage, then the condensation of these materials to form the triphenyltrityl compound takes place followed by the hydride transfer to form the cation.

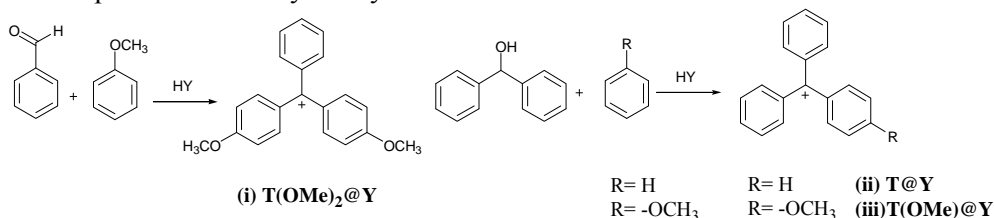
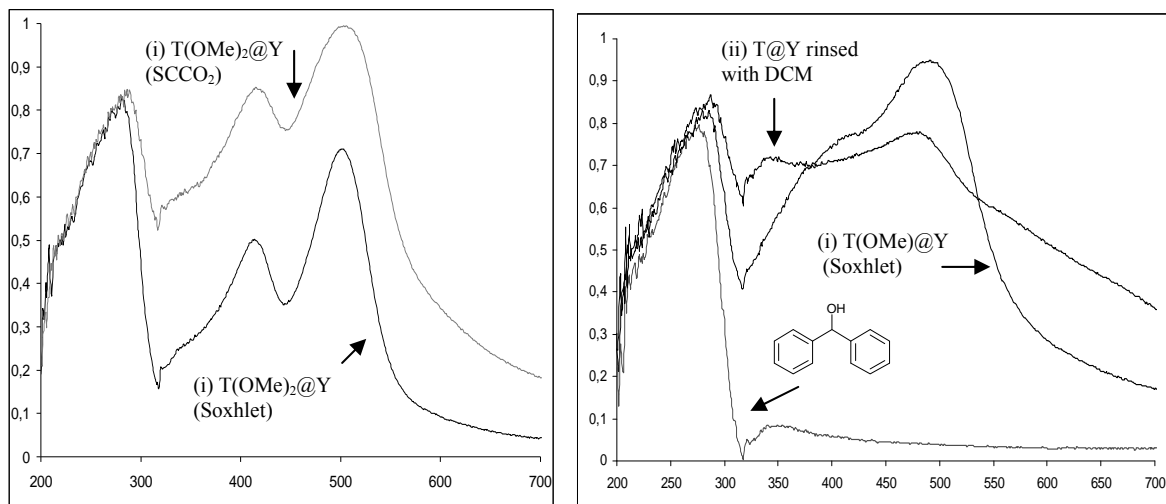


Figure 3: Target triphenyltrityl cations

The triphenyltrityl cation loaded zeolites were obtained as different coloured powders: (i) $\text{T(OMe)}_2@Y$ was obtained as brick red; (ii) T@Y as brown; and (iii) T(OMe)@Y as orange powder. As in the preparation of TP@Y, after depressurization of the system, the recovered samples were cleaned using Soxhlet extraction or continuous SCCO_2 flow. The UV-Vis diffuse reflectance of the zeolite encapsulated cations was carried out and compared with the starting materials. The λ_{max} of the pure triphenyltrityl cation (not shown) and the obtained products agree, indicating the formation of the different encapsulated triphenyltrityl cations. It should be taken into account that since there are different pendant groups in the aromatic rings of the prepared triphenyltrityl cation, it could be expected that the λ_{max} is not going to be exactly the same as for the isolated raw triphenyltrityl cation.



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Figure 4: UV-Vis spectra of representative samples

II.iii Chemometric analysis

A significant drawback of the previous studies deals with the lack of direct evidences supporting the synthesis and entrapment of the desired cation products in the supercage structure. Due to the complexity of measuring the products inside de zeolite, progressing on the sample characterization results in a difficult analytical challenge to be solved. In order to investigate more deeply the features of the modified zeolites, solid UV-Vis-NIR spectroscopy was used. Complementary information gained from the NIR range may help to extract additional conclusions on the properties of the samples. Chemometric techniques such as principal component analysis (PCA) have been applied to facilitate the recovery of relevant information from the spectroscopic data.

The raw data set consisted of spectra from 200 to 2500 nm recorded for some starting reagents (diketone (1) and diphenyl carbinol (2)), calcined zeolite (3), pure TPT cation (4), and loaded triphenylpyryl-zeolites (5-8) and triphenyltrityl-zeolites (9-14) obtained at different experimental conditions. Spectral ranges displaying high background absorption (200 – 320 nm) and high level of noise (2300 – 2500 nm) were removed prior to data analysis. The most important spectral features for describing the samples were in the UV-Vis interval from 320 to 540 nm and various NIR bands associated to residual water and cations such as 1600-1770 and 2090-2230 nm, respectively.

The study of UV-Vis data sub-set revealed that 2 principal components (PCs) were sufficient to extract all relevant information from the data (cumulative explained variance was 99%). The map of scores showed the distribution of samples on the space of PCs which provided information on analogies and differences among samples Fig 5. According to PC1, the brightest coloured compounds were to the right while poor coloured specimens (e.g., raw zeolite) appeared to the left side. Apart from colour intensity, PC2 contributed to distribute the samples as a function of the structure of the entrapped cation as triphenyltrityl and triphenylpyryl specimens were observed at the top and bottom, respectively. Note that starting reagents and pure TPT were closer to the respective zeolite samples. Regarding the cleaning procedure (Soxhlet or supercritical extraction), samples appeared in close position which confirmed that both processes had similar performance.

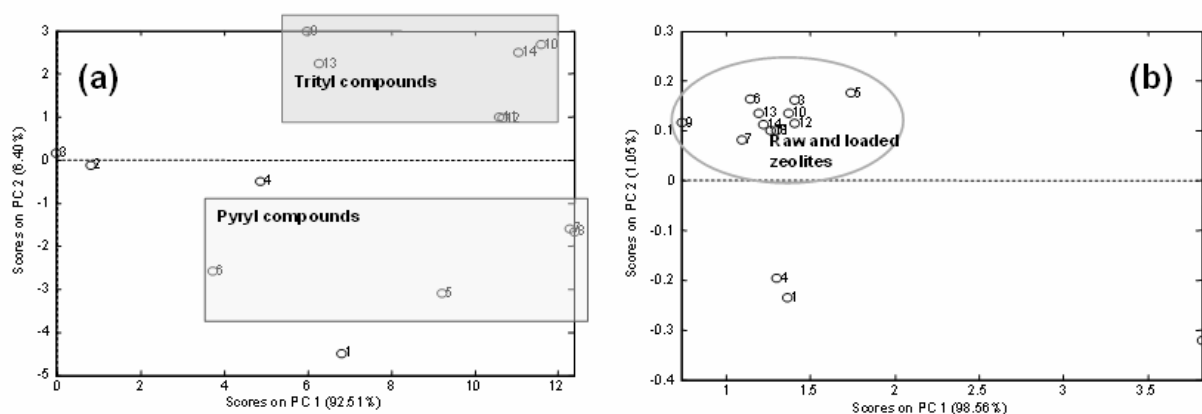


Figure 5: PCA results. Scores of samples. (a) Spectral working range: 320 – 540 nm; (b) Spectral working range: 2090 – 2230 nm.

Analogous studies were carried out using other spectral ranges. In the case of the NIR region from 2090 to 2230 nm, zeolites (raw and loaded) were clustered in a quite compact group (top and left part). This finding suggested that the presence or absence of zeolite was the main feature in this characterization.

From, this chemometric analysis, we can reasonably conclude that zeolites have successfully been loaded with significant amounts of cations. Furthermore, the amount triphenyltrityl or triphenylpyryl species entrapped in the zeolite supercages could be deduced from the position of samples on the graph of PCs.

CONCLUSIONS

The results obtained shown that the encapsulation of triphenylpyryl and triphenyltrityl cations in HY-faujasites can be successfully achieved using SCCO_2 as a solvent. The SCCO_2 technique for the preparation of these systems offers mayor advantages in comparison to conventional liquid methods, since the reaction times are shorter. The cleaning of the samples, that is, the elimination of the excess of the starting materials, is more effective using a SCCO_2 continuous flow equipment than using soxhlet extraction, where the recovered samples were obtained solvent free and drying under vacuum was not needed. In addition, the results obtained by TGA analysis show that the amount of triphenylpyryl cation loaded inside the zeolite was ~ 9 wt%, whereas the literature show maxima of 5wt% by using conventional methods.

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