Synthesis and characterization of zeolite-encapsulated porphyrins

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Abstract

porphyrins were prepared inside the large pores of the zeolite NaY by a process of sequential introduction of components followed by assembly inside the void space of the zeolite. The appropriate process chosen for the porphyrin synthesis was using the propionic acid solvent for reaction between pyrrole and benzaldehyde and this solvent was not destructive for zeolite. The resulting materials were purified by Soxhlet extractor. The zeolite-included porphyrins were identified for studies using UV-Vis and FTIR Spectroscopy and SEM techniques.

Keywords : Porphyrin; Zeolite; Immobilization; Encapsulation

1. Introduction

The study of the catalytic activity of the synthetic metalloporphyrins in solution has been reported by several groups who found that these substances provided very efficient systems for alkene epoxidation and alkane hydroxylation [1–3]. The combination of electron withdrawing substituted metalloporphyrins with immobilization on inorganic supports has resulted in efficient and selective catalysts to oxidation of hydrocarbons because the matrix support can impose a shape selectivity and promote a special environment to approach the substrate to the active species [4–6]. In addition, the immobilization may prevent molecular aggregation or bimolecular self-destruction reactions, which lead to deactivation of catalytic metalloporphyrin active species. Furthermore, the development of heterogeneous catalysts with metalloporphyrins appears to provide an easy way to recover and recycle them from the reaction media. Clays [7], silica gel [8,9], modified silica [10] and alumina have been used showing that this approach is possible. In the case of inorganic matrices, zeolites are an interesting choice because the pore diameters and geometry can introduce shape selectivity in the catalytic reaction [11–17].

In this work, we present the study of porphyrin synthesis TCPP-5,10,15,20-tetrakis(para-carboxy phenyl) porphyrin in the NaY zeolite by a ship-in-a-bottle approach. in a synthetic study, we synthesised porphyrin into the zeolite, this was carried out in order to define the best way to obtain the zeolite encapsulated porphyrin [26]. new material was called TCCPY and spectroscopic characterization (UV-Vis and FTIR) and SEM analysis of the new material obtained have provided evidence for the zeolite encapsulated porphyrins.

2. Results and discussion

The approach for preparation of zeolite NaY with entrapped porphyrins that has been used in this work is in-situ ligand condensation into the zeolite, template synthesis, yielding porphyrins with dimensions that prevent their removal from the cage of the zeolite (template ship-in-a-bottle methods). This approach requires four pyrrole molecules and four appropriated aldehyde molecules to diffuse into the zeolite matrix where the porphyrin can be synthesised into the zeolite to produce the encapsulated porphyrin.

2.1. Solid UV-VIS Spectroscopy analysis

Solid UV-Vis spectra of TCCPY was obtained (fig1). This material showed four Q bands at 668nm, 631nm, 601nm and 564 nm and had soret band at 427nm and these peaks have confirmed the formation of TCCP in the zeolite. Also, for more comparison, UV-Vis spectra of zeolite was obtained. As shown in figure 2, zeolite showed no peaks in the visible region and the shape of their spectra was completely different. UV-Vis spectra of TCCP in methanol showed Q bands at 634nm, 578nm, 554nm and 517nm and soret band at 414nm. This red shift can be expected because the porphyrins are inside the zeolite cage and subject to a high constrains from this support cavity.

2.2. FT-IR Spectroscopy analysis

Figure 3 shows FT-IR spectra of TCPPY. In comparison with FT-IR spectra of TCPP (fig4), sharp peaks with strong absorptions were observed at 500 cm^{-1}-1500 cm^{-1} region and these peaks are very similar to the FT-IR spectra of TCPP and these similar absorptions confirmed the formation of TCPP in the zeolite matrix. Broad band of zeolite at 500 cm^{-1}-1500 cm^{-1} region covered some peaks of TCPP, where the main bands associated with vibrational transitions of porphyrins can be observed, However, it is possible to see some of them present at 1250 cm^{-1} –1550 cm^{-1} attributed to C-C and C-N stretch vibrations of the phenyl from the porphyrin rings. Some peaks related to vibrations in porphyrin ring were summarized in fig 3 that shows formation of TCCP in the zeolite matrix.

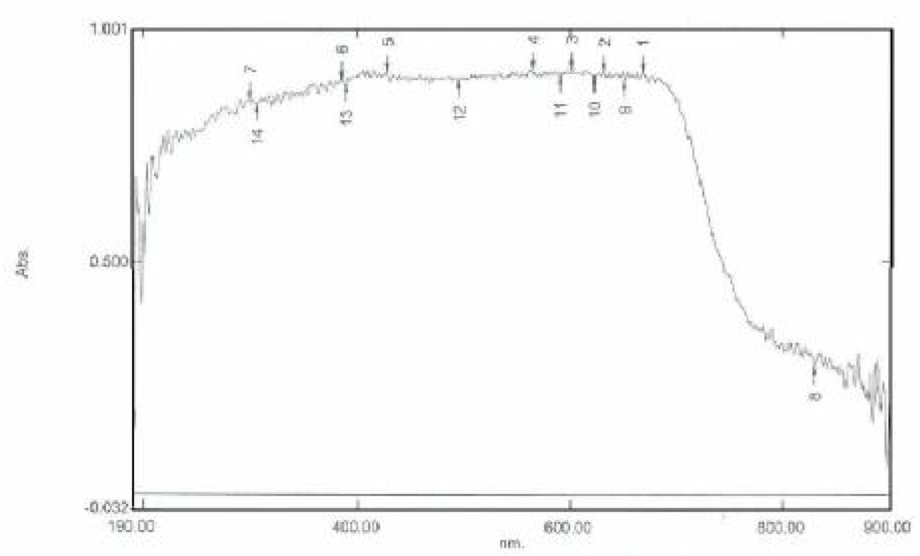

Fig 1. UV-visible spectra of TCPPY

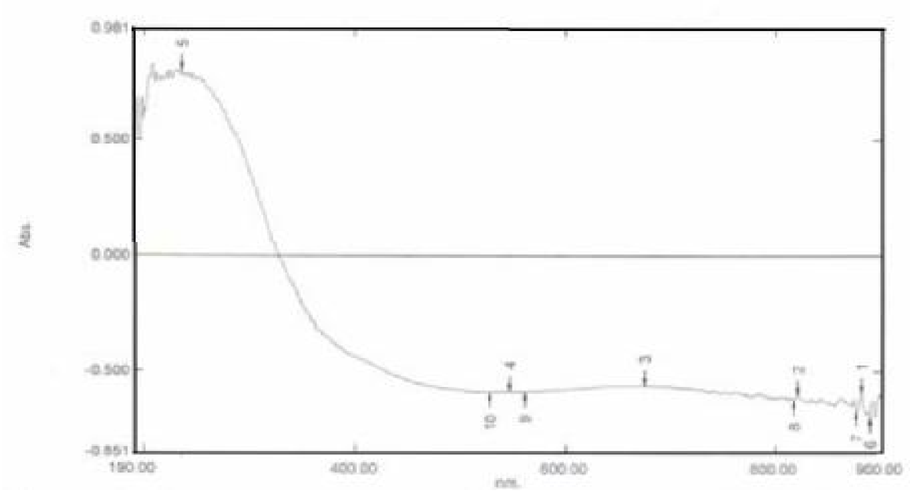

Fig 2. UV-visible spectra of zeolite

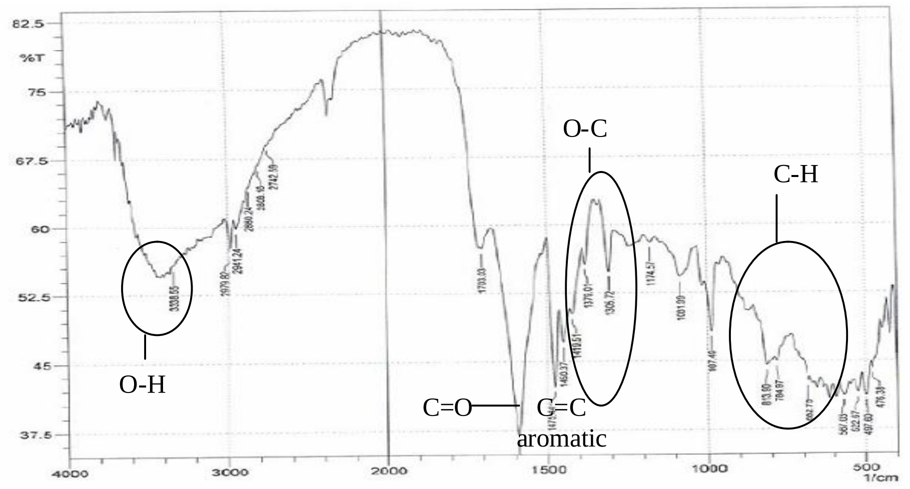

Fig 3. FT-IR spectra of TCPPY

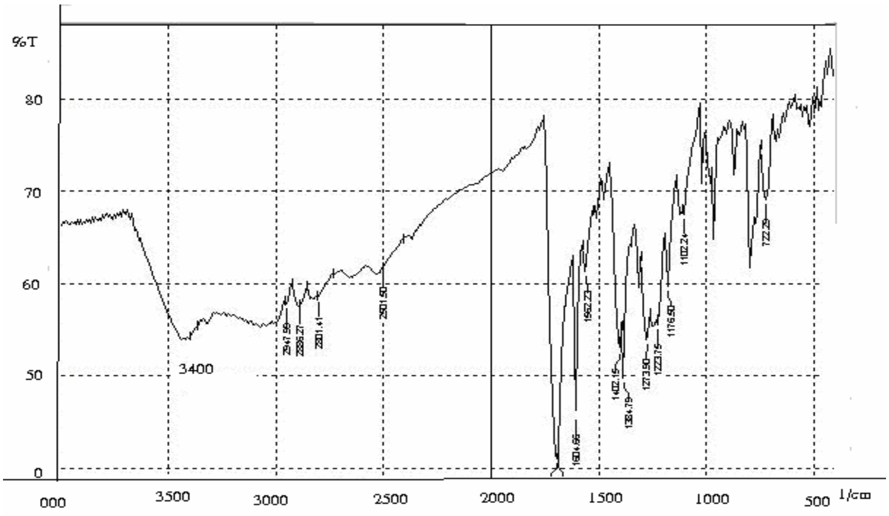

Fig 4. FT-IR spectra of TCPP

2.3. Scanning electron microscopy (SEM) analysis

The solid obtained in the porphyrin synthesis, after purification by extraction in Soxhlet, were analyzed by SEM. SEM images of TCPPY are shown in figure 5. In comparison with SEM images of zeolite (fig 6), the encapsulation of TCPP in the zeolite matrix was clear

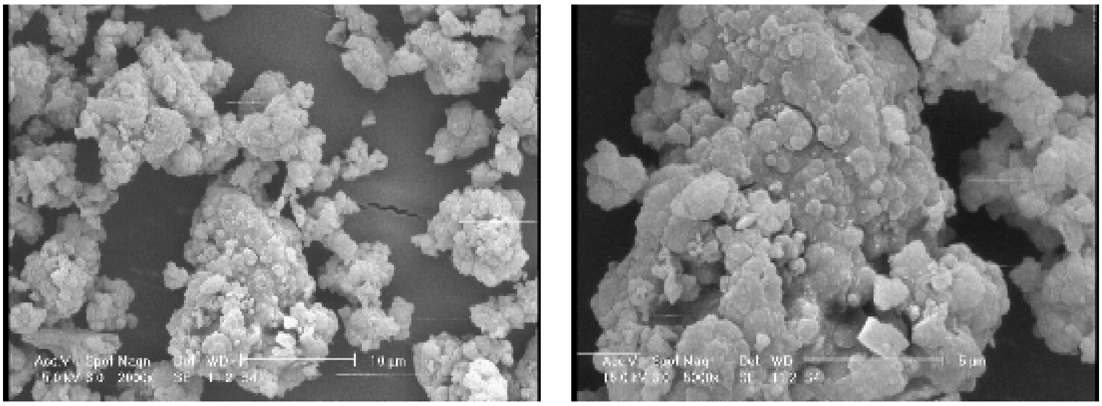

Fig 5a

Fig 5b

Fig 5. SEM image of TCPPY

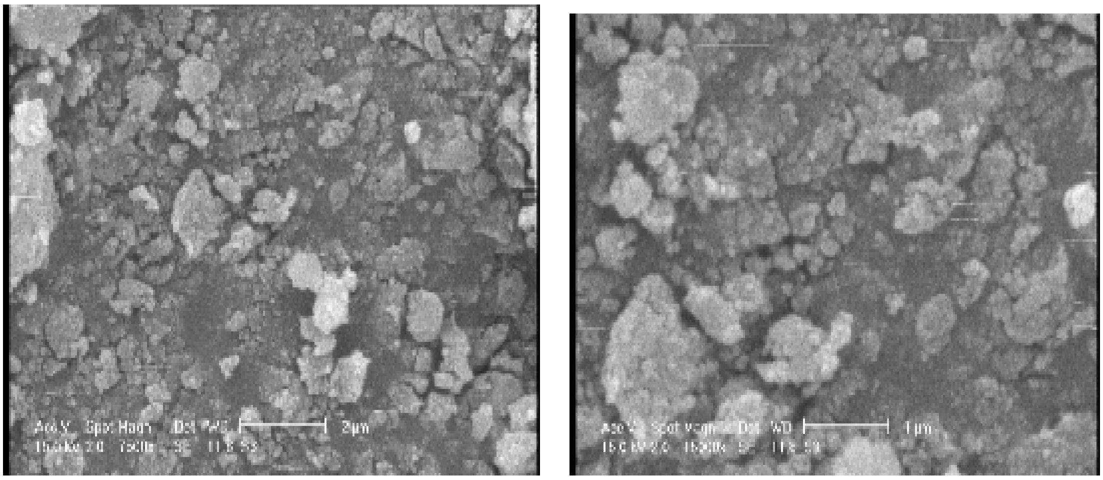

Fig 6a

Fig 6b

Fig 6. SEM image of zeolite

3. general experimental procedure

In a three neck round-bottomed flask, a mixture was prepared with 2.0 g of NaY, 100 ml of propionic acid, 450 ml of freshly distilled pyrrole and 660 ml of benzaldehyde. The suspension was stirred under reflux conditions for 18 h using an oil bath at 140°C. It was possible to observe the darkness of the suspension within a few minutes of the reaction beginning (13–15 min). After that time, the dark solid obtained was washed many times with dichloromethane and centrifuged (3000 rpm) to remove the adsorbed complex stuck to the zeolite surface. The solid was washed by Soxhlet extraction with dichloromethane for 50 h or until the obtained extract did not reveal the presence of porphyrin as indicated by an UV-Vis analysis. The solid was named TPPY.

4. References

[1] J.T. Groves, T.E. Nemo, R.S. Meyers, J. Am. Chem. Soc. 101 (1979) 7613.

[2] B. Meunier, Bull. Soc. Chim. Fr. 4 (1986) 578.

[3] D. Mansuy, Pure Appl. Chem. 62 (1990) 741.

[4] F. Bedioui, Coord. Chem. Rev. 144 (1994) 39.

[5] F. Bedioui, J. Devynck, C. Bied-Charreton, Acc. Chem. Res. 28 (1995) 30.

[6] L. Barloy, J.P. Lallier, P. Battioni, D. Mansuy, Y. Pitfard, M. Tournoux, J.B. Valim, W. Jones, N. J. Chem. 16 (1992) 71.

[7] P. Battioni, J.P. Lallier, L. Barloy, D. Mansuy, J. Chem. Soc. Chem. Commun., (1989) 1149.

[8] C. Gilmartin, J.R. Lindsay-Smith, J. Chem. Soc. Perkin Trans. 2 (1995) 243.

[9] Y. Iamamoto, Y.M. Idemori, S. Nakagaki, J. Molec. Catal. 99 (1995) 187.

[10] T. Tatsumi, M. Nakamura, H. Tominaga, Catal. Today 6 (1989) 163.

[11] P.P. Knops-Gerrits, D. De Vos, F. Thibault-Starzyk, P.A. Jacobs, Nature 369 (1994) 543.

[12] R.F. Parton, I.F.J. Vankelecom, M.J.A. Casselman, C.P. Bezoukhanova, J.B. Uytterhoeven, P.A. Jacobs, Nature 370 (1994) 541.

[13] I.W.C.E. Arends, R.A. Sheldon, M. Wallau, U. Schuchardt, Angew. Chem. Int. Ed. Engl. 36 (1997) 1144.

[14] N. Herron, G.D. Stucky, C.A. Tolman, J. Chem. Soc. Chem. Commun., (1986) 1521.

[15] N. Herron, G.D. Stucky, C.A. Tolman, Inorg. Chim. Acta 100 (1985) 135.

[16] G. Meyer, D. Wohrle, M. Mohl, G. Schulz-Ekloff, Zeolites 4 (1984) 30.

[17] N. Herron, J. Coord. Chem. 19 (1988) 25.