Microporous and Mesoporous Materials 236 (2016) 228–234

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Fly ash as raw material for the synthesis of zeolite-encapsulated porphyrazine and metallo porphyrazine tetrapyrrolic macrocycles

Sandra Belviso [a], [**], Francesco Cavalcante [b], Antonio Lettino [b], Pietro Ragone [b], Claudia Belviso [b], [*]

[a] Università della Basilicata, Dipartimento di Scienze and LASCAMM, CR-INSTM, Unità della Basilicata, Potenza, 85100, Italy
[b] Istituto di Metodologie per l'Analisi Ambientale – CNR, Tito Scalo, PZ, 85050, Italy

ARTICLE INFO

Article history:
Received 18 July 2016
Received in revised form
22 August 2016
Accepted 31 August 2016
Available online 4 September 2016

Keywords:
Fly ash
Zeolite-encapsulated tetrapyrroles
Free-base thioalkyl-porphyrazines
Metallo-thioalkyl-porphyrazines

ABSTRACT

In this work, free-base thioethyl-porphyrazine and its copper (II) complex were encapsulated into zeolites during their synthesis by hydrothermal method at low incubation temperature (45 °C and 60 °C) using fly ash as raw material. The zeolite-included tetrapyrroles, H_2(OESPz)-Zeo and Cu(OESPz)-Zeo, were characterized by XRD, SEM, TG/DTA and UV–Vis. X-ray diffraction patterns show that large amount of zeolite A and sodalite formed in H_2(OESPz)-Zeo and Cu(OESPz)-Zeo, respectively whereas thermal analysis as well as UV–Vis spectroscopic investigation reveal the presence of tetrapyrroles inside newly-formed zeolitic solid matrix. The mechanism of zeolite synthesis around organic compounds to form "ship in a bottle" complexes is displayed by SEM analysis.

1. Introduction

Zeolites are tectosilicates characterized by a three-dimensional network of tetrahedral units that form a system of interconnected pores. The substitution of silicon with aluminium produces a net negative charge which is balanced by the presence of an extra cation in the framework. Due to their structure and their excellent ion exchange and sorption properties, zeolites are notably useful in a number of applications ranging from environment [1–7] to enzymatic model and catalysis [8–11]. Zeolites can be synthesised from different materials and among these, in the last few years, much research has been focused on the use of coal fly ash [12–18], a by-product of thermal power plants also used in concrete and cement manufacturing. More than half of this waste material is disposed in landfills and its huge production is extremely worrying because of this kind of disposal. Therefore, several investigations have been carried out to recycle this waste in the production of new materials. In this framework, the fly ash conversion into zeolites is a particularly interesting process, allowing to convert this waste into a multifunctional material. Expanding the scope and applications of fly ash synthesised zeolites we focused on the process of encapsulation of tetrapyrrole macrocycles. In fact, tetrapyrroles can be adsorbed or incorporated within mineral materials [19] thus changing their physicochemical properties and often giving rise to heterogeneous catalytic systems. Several examples are reported about the adsorption of porphyrins and metallo-porphyrins on minerals [20,21], while porphyrazines adsorption has been less investigated [22–24]. Zeolites-encapsulated porphyrins have been also extensively studied [19], while a few examples report phthalocyanines entrapped within zeolite supercages [25]. The macrocycle encapsulation is carried out either inserting or building the macrocycle inside the zeolite or synthesizing the zeolite around a tetrapyrrole template, the latter process offering several advantages, including mild preparation conditions and well-defined intrazeolite metal complexes [19]. The latter zeolite encapsulation mode has been reported for the zeolite synthesis around cationic porphyrins and metalloporphyrins [26–33] but, to the best of our knowledge, no studies have been performed to directly form zeolite-encapsulated porphyrazines and even more using fly ash as raw material for the synthesis of the mesoporous mineral. We then decided to investigate the direct zeolite-encapsulation of thioalkyl-porphyrazines from fly ash with the aim to develop a novel encapsulation procedure and to prepare novel composite materials from unprecedently employed tetrapyrroles. In fact, porphyrazines, which can be considered as structural hybrids of the more studied

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[*] Corresponding author.
[**] Corresponding author.
E-mail address: claudia.belviso@imaa.cnr.it (C. Belviso).

http://dx.doi.org/10.1016/j.micromeso.2016.08.044

porphyrins and phthalocyanines, represent an important class of tetrapyrroles containing meso nitrogen atoms and being characterized by β-pyrrole positions open for substitution [34]. They are also widely used for different application such as sensors, phototherapeutics, catalysts, and photosensitizers [35,36] due to their photo-physical and electrochemical properties [37,38]. Among the different types of porphyrazine-like macrocycles, the thioalkyl-porphyrazines, a family of compounds where thioether-groups are attached at the β-positions of the azaporphyrin ring, present attractive characteristics in terms of their electrochemical and optical properties as well as versatility and architectural flexibility. The latter allowing the tailoring of the physico-chemical parameters and redox properties [36,39–48]. The encapsulation of thioalkyl-porphyrazines in zeolites, never described before, could allow the obtainment of versatile composite materials endowed with easily tunable electrochemical, photophysical, and catalytical properties.

In this study, the synthesis of zeolite around both ‘free-base’ (H_2(OESPz)) and Cu(II) complex of 2,3,7,8,12,13,17,18-octakis(ethylthio)-5,10,15,20-porphyrazine (Cu(OESPz)) (see Fig. 1) using fly ash as raw material is described as well as a full characterization of the composite materials.

2. Experimental section

2.1. Material

A sample of fly ash (FA), resulting from coal combustion and coming from the Italian ENEL thermoelectric power plant in Cerano (Brindisi, Italy) was used as raw material for zeolite synthesis.

All chemicals and solvents (Aldrich Chemicals Ltd.) were of reagent grade. Solvents were dried and distilled before use by standard methods. Solvents used in physical measurements were of spectroscopic grade. Silica gel used for chromatography was Merck Kieselgel 60 (70–230 mesh).

2.2. Synthesis of porphyrazines

H_2(OESPz): 2,3,7,8,12,13,17,18-octakis(ethylthio)-5,10,15,20–21H,23H-porfirazine. The ‘free-base’ porphyrazine was prepared according to a literature method [43,44]. This method involved the synthesis of *cis*-1,2-dicyano-1,2-bis(methylthio)-ethylene by reaction of disodium *cis*-1,2-dicyano-1,2-ethylenedithiolate with bromoethane in MeOH at room temperature, followed by template condensation in a refluxed suspension of magnesium propoxide to form the 2,3,7,8,12,13,17,18-octakis(ethylthio)-5,10,15,20-porphyrazinate magnesium (II) complex Mg(OESPz). This Mg(II) derivative was dissolved in a small amount of concentrated CF_3COOH and carefully transferred on iced water. The solution was then washed with a NH_3 solution (30%) until the washing water was fully neutralized. The dark product was collected with $CHCl_3$ using a separating funnel, dried over sodium sulfate, and filtered. After removal of the solvent, the crude product was carefully purified by column chromatography on silica gel (first band) using (1:1) (v/v) CH_2Cl_2/*n*-hexane as eluant. The ‘free-base’ porphyrazine was obtained in a yield of ca. 65% with respect to Mg(II) complex. UV–Vis ($CHCl_3$), λ_{max}/nm (log ε): 360 (4.64); 500 (4.26), 641 (4.42), 711 (4.58). ^{1}HNMR ($CDCl_3$, 500 MHz), δ/ppm: −1.12 (s, 2H, $N_{pyrrolic}H$), 1.56 (t, 24 H, CH_3), 4.10 (q, 16 H, $S{-}CH_2$). Other characterization data matched those reported in the literature [44].

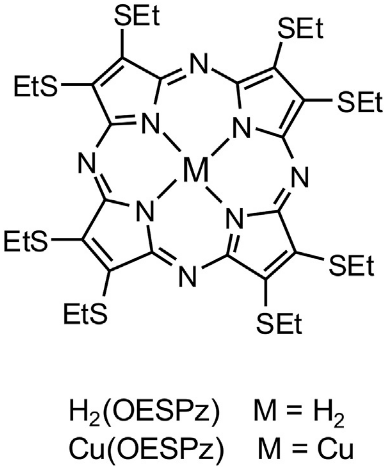

Fig. 1. Molecular structure of the ‘free-base’ thioethyl-porphyrazine H_2(OESPz) and the corresponding Cu(II) metal complex Cu(OESPz).

Cu(OESPz): [2,3,7,8,12,13,17,18-octakis(ethylthio)-5,10,15,20-porphyrazinate] copper(II). The complex was prepared according to a literature method [43,44]. 0.10 g (0.13 mmol) of H_2(OESPz) were dissolved in $ClCH_2CH_2OH$ (10.0 mL). A warm solution of 0.028 g (0.16 mmol, an excess of 20% respect to a 1:1 molar ratio) of $(CH_3CO_2)_2Cu\cdot H_2O$ in EtOH (3.0 mL) was added and the mixture was refluxed at 110 °C for 1 h under magnetic stirring. The progressive formation of the metal complex was monitored through UV–Vis spectroscopy. After cooling, a precipitate was obtained by addition of MeOH (5.0 mL) to the reaction mixture and freezing at 0 °C for 12 h. The precipitate was collected under vacuum filtration, washed with MeOH and then purified by column chromatography on silica gel using (1:1) (v/v) CH_2Cl_2/*n*-hexane as eluant (first band). Removal of the solvent and recrystallization from CH_3OH/CH_2Cl_2 (9: 1) at ca. 0 °C gave the pure blue product Cu(OESPz) with a yield of ca. 57%. UV–Vis ($CHCl_3$), λ_{max}/nm (log ε) 356 (4.70) Soret, 493(4.29), 620 sh(4.44), 670 (4.84) Q bands. Other characterization data matched those reported in the literature [44].

2.3. Synthesis of zeolite

Fly ash pre-fused with NaOH (1:1.2 wt ratio) was stirred for some hours at room temperature with a solution of H_2(OESPz) or Cu(OESPz) in chloroform (separate experiments). The crystallization occurred in separate experiments at 45 °C and 60 °C for 4 days. The temperature of synthesis was chosen based on previous studies [14,16]. After the heating, the solids and solutions were separated by centrifugation. The solids were washed with distilled water and dried in an oven at 80 °C.

2.4. Characterization

Chemical analysis of the major elements of fly ash was performed using X-ray fluorescence (XRF) (Philips PW 1480). The mineralogical composition of raw material and synthetic products was determined by powder X-ray diffraction (XRD) using Rigaku Rint Miniflex powder diffractometer with Cu-Kα radiation; sample spinner and 30 kV × 15 mA. The data collections were performed in the 2θ range 2–54° with step size of 0.02°. The morphological features were observed using a field emission scanning electron microscope (SEM, Zeiss Supra 40). The samples were carbon-sputtered (10 nm thick) in order to avoid charging of the surface. Elemental analyses were performed with an energy-dispersive X-ray spectrometer (EDS, Oxford Inca Energy 350) equipped with a Si(Li) detector.

Comparative thermogravimetric analyses were performed on zeolite free of organic compound as well as on ‘free-base’