



# Multimodal porous zirconium silicate macrospheres: Synthesis, characterization and application as catalyst in the ring opening reaction of epichlorohydrin with acrylic acid

Emil Ioan Muresan<sup>a,\*</sup>, Doina Lutic<sup>b</sup>, Mioara Dobrota<sup>c</sup>, Adina Coroaba<sup>c</sup>, Florica Doroftei<sup>c</sup>, Mariana Pinteala<sup>c</sup>

<sup>a</sup> Department of Food, Organic and Biochemical Engineering, Faculty of Chemical Engineering and Environmental Protection, Gheorghe Asachi Technical University from Iasi, No. 73 D. Mangeron Avenue, 700050, Iasi, Romania

<sup>b</sup> Department of Chemistry, Faculty of Chemistry, Alexandru Ioan Cuza University from Iasi, No. 11, Carol I Avenue, 700506, Iasi, Romania

<sup>c</sup> Petru Poni Institute of Macromolecular Chemistry from Iasi, No. 41A, Grigore Ghica-Voda Alley, 700487, Iasi, Romania

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## ABSTRACT

Hierarchical zirconium silicate macrospheres with diameters in the range  $1.7 \div 1.8$  mm were synthesized by spray gelling technique using a multi-templating method. Inexpensive, environmentally benign and easily accessible natural resources (yeast, gelatin, agar and chitosan) were used as templating agents. These materials were characterized by different complementary techniques: XRD, XPS, EDAX/SEM, FTIR and  $N_2$  porosimetry. Infrared spectra of the adsorbed pyridine were used to investigate the type of the acid sites existing in the samples. Spherical zirconium silicate beads were tested as catalysts in the addition reaction of acrylic acid to epichlorohydrin. In order to evaluate the catalyst lifetime the zirconium silicate macrospheres were reused 10 times. No loss of the catalytic activity and no attrition of the macrospheres were noticed in these runs which prove that the zirconium silicate beads behave as an efficient and stable heterogeneous catalyst.

## 1. Introduction

The reactions of the unsaturated carboxylic acids with the epichlorohydrin are still extensively studied due to the practical significance of the reaction products. The chlorohydroxyalkyl esters of the acrylic and methacrylic acids are used as components of the coatings for leather, wood, metals and paper, as additives for the photosensitive materials and as copolymers for the obtaining of various materials employed in dentistry, at the manufacturing of the surgical dressings, for the immobilization of enzymes etc [1,2]. Various homogeneous and heterogeneous catalysts such as alkali metal carboxylates, amines, quaternary ammonium salts, heterocyclic organic compounds, chromium and cerium compounds, anion exchange resins, zeolites, clays were tested until now in the reactions of the oxiranes with the carboxylic acids [3–13].

The requirement for environmental and more efficient technologies amplified the interest for the synthesis and the use of different heterogeneous catalysts. Of these, an important class is that of the metallosilicate materials. Direct synthesis and post-synthesis methods are the two typical strategies used for the incorporation of the transitional

metals in the silica framework in order to obtain acid catalysts, efficient in various chemical reactions [14–33]. Metallosilicate materials with hierarchical porosity can be easily synthesized by combining the templating technique with the sol-gel method. For this purpose, a variety of hard or soft templates such as carbon particles [34], mesoporous carbon [35], resins [36], starch gel [37], polymers [38], biomolecules [39], surfactants [40] can be used to generate meso and/or macropores. The main limitation of the hierarchical metallosilicate materials synthesized via the techniques reported until now is that they are usually obtained in powder form and consequently they are difficult to be separated from the reaction mixture (high speed centrifugation or special filtration being often necessary). There are only few studies that report about the synthesis of the metallosilicates in the form of macrospheres which to exhibit mechanical, chemical and hydrothermal stability [41–44]. For industrial applications it is important to obtain porous metallosilicates with good catalytic activity and high stability that can be easily handled, recovered and reused.

This work is focused on the following main directions: (1) the synthesis of the multimodal porous zirconium silicate macrospheres of millimetric sizes by the “spray gelling technique” using a multi-

\* Corresponding author.

E-mail address: [eimuresan@yahoo.co.uk](mailto:eimuresan@yahoo.co.uk) (E.I. Muresan).

templating method; (2) testing of the obtained materials as catalysts in the esterification reaction of the acrylic acid (AA) with epichlorohydrin (ECH).

## 2. Experimental part

### 2.1. Materials

The reagents used  $ZrOCl_2 \cdot 8H_2O$ , ammonium solution (25%), tetraethylorthosilicate, HCl solution (37%), chitosan with high molecular weight, agar and gelatin were purchased from Aldrich. Yeast was delivered by Lesaffre Romania SRL. The chitosan solution was prepared by dissolving of 4g of chitosan in 96 mL acetic acid solution (92 mL distilled water and 4 mL acetic acid 98%).

### 2.2. Synthesis of the zirconium silicate microspheres

The synthesis of the zirconium silicate beads was performed as follows:

**Mixture A:** 0.72 g  $ZrOCl_2 \cdot 8H_2O$  were dissolved in a solution containing 12 mL of water and 0.45 mL HCl 37%. Subsequently 3 mL tetraethyl orthosilicate (TEOS) were poured into this solution and the mixture was magnetically stirred for 6 h at the room temperature.

**Mixture B:** 2.7 g of yeast were dispersed in 15 ml of distilled water and this suspension was heated under stirring at 80 °C for 1 h. Thereafter 0.36 g agar was added and the stirring continued for 0.5 h at 80 °C. 0.36 g of gelatin was then added in the flask and the stirring continued for 0.5 h at the same temperature. After the cooling of the mixture to the room temperature, 0.45 mL HCl 37% solution was added and the stirring continued for 10 min. Finally, 9 g of 4% chitosan solution was introduced and the resulting gel was mixed for 2 h.

**Mixture C:** 2.7 g of yeast were dispersed in 15 ml of distilled water and this suspension was heated under stirring at 80 °C for 1.5 h. 0.72 g of gelatin was then added in the flask and the stirring continued for 1 h at the same temperature. After the cooling of the mixture to the room temperature, 1.05 mL HCl 37% solution was added and the stirring continued for 10 min. Finally, 9 g of 4% chitosan solution was introduced and the resulting gel was mixed for 2 h.

The zirconium silicate microspheres denoted as the sample S1 and respectively as the sample S2 were obtained by putting together the mixture A with the mixture B (for the sample S1) and respectively the mixture A with the mixture C (for the sample S2). In both cases the resulted mixtures were homogenized by stirring for 2 h at the room temperature. The resulted gels designed for both samples were dropped with a syringe pump into an ammonia solution (25% v/v) and kept into the coagulating solution to harden for 30 min. The obtained microspheres were separated by filtration, dried first at 60 °C for 8 h, subsequently at 90 °C for 24 h and finally at 160 °C for 12 h. The dried zirconium silicate microspheres were calcined in air at 625 °C for 12 h in order to remove the template ( $1\text{ }^\circ\text{C min}^{-1}$ ).

### 2.3. Characterization techniques

The nitrogen adsorption isotherms were measured at the liquid nitrogen temperature (77 K) using a Nova 2200e system (Quantachrome). The samples were outgassed at 25 mmHg and room temperature for 12 h before the measurements.

SEM micrographs and EDX spectra were obtained with an FEI Quanta 200 Scanning Electron Microscope equipped with an EDAX Genesis 400 with Si(Li) detector, type Sapphire. The measurements were carried out at an accelerating voltage of 20 kV, with a Large Field Detector (LFD) in low Vacuum Mode.

The wide angle X-ray diffraction patterns of the calcined zirconium silicates were recorded on a Shimadzu LabX XRD-6000 diffractometer in the  $2\theta$  range of  $10^\circ$ – $70^\circ$ , at a scanning speed of  $1^\circ/\text{min}$ , using a nickel-filtered  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ).

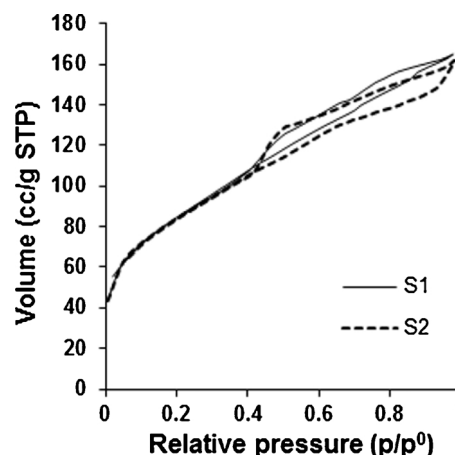


Fig. 1. Nitrogen adsorption–desorption isotherms.

X-ray photoelectron spectra were collected on a Kratos Analytical Axis NOVA instrument using monochromatic Al  $K\alpha$  X-rays source ( $h\nu = 1486 \text{ eV}$ ), 20 mA current and 15 kV voltage (300 W), and base pressure of  $10^{-8}$ – $10^{-9}$  Torr in the sample chamber. The incident monochromatic X-ray beam was focused on a  $0.7 \times 0.3 \text{ mm}^2$  area of the surface. The XPS survey spectra were collected in the range of  $-10 \div 1200 \text{ eV}$  with a resolution of 1 eV and a pass energy of 160 eV. The high resolution spectra for all the elements identified from the survey spectra were collected using a pass energy of 20 eV and a step size of 0.1 eV. The binding energy value was calibrated by the C1s peak (284.8 eV). Recorded spectra were always fitted using Gauss–Lorentz curves in order to determine more accurately the binding energy of the different element core levels. The curves deconvolution of the obtained XPS spectra were analyzed using the ESCAPE software.

The mid infrared spectra were recorded on a Bruker Vertex 70 FTIR spectrometer, in the wavenumber range  $4000$ – $400 \text{ cm}^{-1}$ , using the conventional KBr-disk technique.

The pyridine adsorption was performed at the room temperature until saturation. After the removal of the physisorbed pyridine, by drying of the adsorbents at 150 °C for 2 h, the samples were cooled down to room temperature and the spectra were recorded.

The catalytic activity of the zirconium containing microspheres was tested in the addition reaction of the acrylic acid to epichlorohydrin. Acrylic acid and epichlorohydrin were put into a two necked round-bottom flask equipped with a reflux condenser and heated in a glycerin bath using a magnetic stirrer with heating provided with a digital temperature controller. The required amount of catalyst was added after the attaining of the desired temperature. This moment was counted as the reaction startup time. All the experiments were run at a constant stirring speed of 600 rpm, to prevent the effect of the external mass transfer resistance.

The composition of the final reaction mixtures was determined using a Hewlett Packard 5890 gas chromatograph equipped with a SPB-1 column (30 m length, 0.32 mm diameter, 0.25  $\mu\text{m}$  film thickness) coupled with a QMD-1000 mass spectrometer. The conditions of GC analysis were: injector temperature 250 °C, oven temperature program 40(2)-10-250(1), amount of sample injected 0.1  $\mu\text{L}$ , carrier gas helium at a flow rate of  $1 \text{ mL min}^{-1}$ , splitting ratio 1:100 and detector temperature 250 °C. Propan-2-ol was used as internal standard.

The progress of the reaction was monitored by titration of the unreacted acrylic acid, from the samples withdrawn at established time values, with a 0,1 M NaOH solution.

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