

New soft porous frameworks based on lambda-zirconium phosphate and aliphatic dicarboxylates: Synthesis and structural characterization



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ABSTRACT

New dicarboxylate-functionalized pillared materials with a general formula of λ -ZrPO₄(OH)_{1-x}(OOC(CH₂)_nCOO)_{x/2}(dmsO) ($n=6, 8$ and 10) have been prepared by post-synthesis modification of the inorganic layers of λ -zirconium phosphate (λ -ZrP), where the superficial Chloride monovalent anionic ligands of λ -layer are partially exchanged with the divalent anionic ligands of a series of long-chain aliphatic dicarboxylic acids, namely octanedioic acid, decanedioic acid and dodecanedioic acid. The synthesized materials are characterized by X-ray diffractometry, FT-IR spectroscopy, elemental and thermogravimetric analyses. The X-ray diffraction patterns show that the obtained solid phases are pure. Furthermore, the interlayer distance of λ -ZrP systematically increases from 1.02 to 1.59 nm as a result of the incorporation of the mentioned acids inside the interlayer gallery.

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1. Introduction

Over past decades, the chemistry of zirconium phosphate (ZrP) compounds has been studied intensively. In particular, compounds with organic radicals covalently attached to the inorganic layers of ZrP. These organic-inorganic frameworks are prepared by two main synthetic approaches: (1) thermal decomposition of zirconium fluoro-complex in the presence of phosphonic acids (α -type derivatives) [1–5], (2) post-synthetic modification of the inorganic surface of γ - or λ -ZrP by means of topotactic ligand exchange reactions with phosphonic acids [2–8] or carboxylic acids [9–12], respectively.

Since the post-modification of the inorganic surface of ZrP is carried out without destruction of its framework structure, the rational design strategy of synthesis protocols can be easily applied when ZrP is used as a chemical-engineering tool to build organic-inorganic frameworks at solid state. The aforementioned strategy provides the opportunity to effectively adjust both the position and the molecular geometry of the organic radicals inside the solid matrix. Therefore, the global properties of the final materials are selected with high precision [1–12].

Layered zirconium phosphates (ZrP) are obtained in three main

structures: α -Zr(HPO₄)₂·nH₂O, γ -ZrPO₄(HPO₄)·nH₂O and λ -ZrPO₄Cl(dmsO) (Fig. 1) [13–15].

The lambda structure is based on a layer of phosphates sustaining the zirconium metals whose apical bonds are bonded to negative and neutral basic species that point to the interlayer space. In the typical starting lambda structure, each zirconium is bonded to chloride anions and neutral dimethylsulfoxide [15–17] that can respectively be replaced by carboxylates and amines in a topotactic manner [9–12]. The chemical properties of the ensuing composite can be tailored by carefully selecting the chemical function of the organic moieties that will be modified by their confinement between the inorganic layers.

From the practical perspective, pillared λ -ZrP is obtained when the topotactic Cl/carboxylate exchange reactions occur at the same time on the facing surfaces of two adjacent layers by a molecule with two carboxylic groups (dicarboxylic acid) [9–12]. Consequently, cross-linked hybrid layered materials with flexible or rigid pillars can be prepared. Moreover, the porosity of these materials are expected to be significantly affected with the length and rigidity of the dicarboxylate bridging ligands.

The introduction of flexible organic pillars between the layers of λ -ZrP results in construction of soft frameworks with dynamic porosity which can be adjusted by simple chemical means [18–20]. Concerning multilevel control of porosity, it cannot be obtained using rigid porous materials. It would have an effect towards enhancing the host-guest interactions as well as their structural

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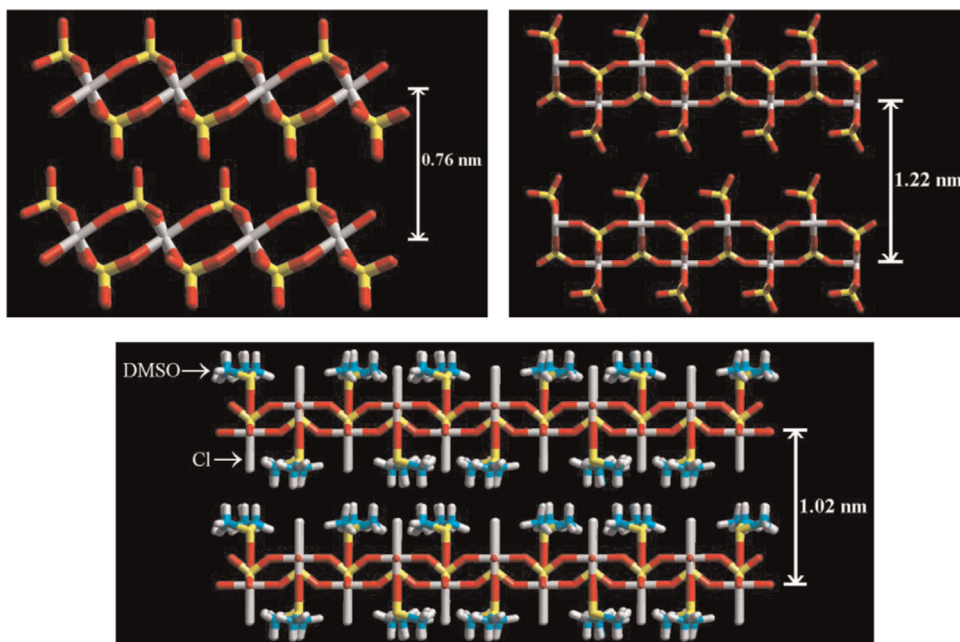


Fig. 1. Tubes models (Zr, gray; P, yellow; O, red; H, white) of two consecutive layers of α -ZrP (top left), γ -ZrP (top right) and λ -ZrP (bottom). The experimental interlayer distances are shown.

complementary. Thus, dynamic structural transformation based on flexible frameworks is among the most interesting phenomena and it can be considered as an excellent chemical engineering tool for obtaining comfortable space for specific guests [21–24].

It is noteworthy that organic derivatives of α -ZrP and γ -ZrP and their applications are well documented [1–8]. However, to date, little attention has been paid to the synthesis of porous organic-inorganic materials based on λ -ZrP [9–12]. In the most recent research in our laboratory (i.e. Al-Azhar University-Gaza), λ -ZrP has been functionalized with ethylenediaminetetraacetic acid (EDTA) [9] and hexanedioic acid (adipic acid) [10]. Regarding λ -ZrP/EDTA material, it was found that it exhibited significant potential for use in the field of hard water treatment.

The principle interest of this paper is to post-synthesize and characterize layered 3D soft frameworks based on λ -ZrP and a series of aliphatic dicarboxylic acids of different chain length, namely octanedioic acid, decanedioic acid and dodecanedioic acid)HOOC(CH₂)_nCOOH; $n=6, 8, 10$).

Theoretically, the orientation and conformation of the alkyl chains inside the solid matrix of λ -ZrP will be discussed using tentative structural models (Hyperchem).

2. Experimental

All chemicals and reagents used were of analytical grade. All of them were purchased from Aldrich Co., and used as supplied. λ -Zirconium phosphates was prepared using a literature described procedure (interlayer distance 1.02 nm) [17].

2.1. General procedure for topotactic exchange of octanedioic acid and decanedioic acid with λ -ZrP

A 0.25 g of ZrPO₄Cl(dmsO) was suspended in 17 mL of a 0.025 M dicarboxylic acid and 0.025 M sodium dicarboxylate solution using a 50% v/v dmsO/water mixture as solvent. The mixture was heated at 75 °C for 3 days. The resulting white solid was separated by centrifugation and washed with a 1:1 v/v dmsO/water mixture (2 × 25 mL). Finally it was dried at 80 °C for 24 h and stored over

P₂O₅.

2.2. Topotactic exchange of dodecanedioic acid with λ -ZrP

A 0.25 g of ZrPO₄Cl(dmsO) was suspended in 33 mL of a 0.025 M sodium dodecanedioate solution using a 29% v/v dmsO/water mixture as solvent. The mixture was heated at 75 °C for 3 days. The resulting white solid was separated by centrifugation and washed with a 29% v/v dmsO/water mixture (2 × 25 mL). Finally it was dried at 80 °C for 24 h and stored over P₂O₅.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were recorded at room temperature on Siemens D-5000 diffractometers with Cu K α radiation ($\lambda=0.154$ nm) and Ni filter at 40 kV, 30 mA, a scanning rate of 5°min⁻¹, and a 2 θ angle ranging from 3° to 70°. Infrared spectra were recorded on a FTIR-8201 PC spectrometer using KBr disk in the range 4000 to 400 cm⁻¹. Elemental analyses were performed on a Perkin Elmer II 2400 CHN analyzer. Thermogravimetric analyses was performed on a Mettler-Toledo TGA/STDA 851e apparatus and recorded at 5 °C/min. Structure modeling was carried out on PC computers using the Hyperchem release 7 and the molecular mechanics method MM+.

3. Results and discussion

The post-synthetic modification strategy is employed in this paper for the preparation of the dicarboxylate-functionalized λ -ZrP where dicarboxylic acids of different chain length (octanedioic acid, decanedioic acid and dodecanedioic acid) are embedded into the interlayer gallery of the native λ -ZrP through Cl/dicarboxylate anion exchange reaction.

Practically, three new layered pillared λ -type materials are prepared by contacting the native λ -ZrP with the dicarboxylic acid solutions of octanedioic acid (OCT), decanedioic acid (DEC) and dodecanedioic acid (DOD) using dmsO/water mixture as solvent (see “Experimental” section). The resulting materials denoted as λ -

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