

Preparation and characterization of mesoporous zirconium phosphates from alkyl phosphates

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Abstract

Zirconium alkyl phosphates (ZrAP) were prepared by the reaction of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ with a mixture of aqueous phosphoric acid solution and monoalkyl phosphates (alkyl = decyl, stearyl) synthesized in the laboratory. All of the ZrAP samples showed X-ray diffraction peaks at diffraction angles below $2\theta = 8^\circ$. The calcined powders were mesoporous containing POH groups which were stable at high temperatures, and were crystallized into ZrP_2O_7 by heating them at temperatures over 960°C . The pores could be classified into wedge-shaped pores and spaces between parallel plates using small angle X-ray scattering and high-resolution transmission electron microscopy, and the specific surface area was found to be $130\text{--}308\text{ m}^2/\text{g}$ by N_2 sorption measurements. A comparison of the materials synthesized under different conditions revealed that the ZrP layers supported by the neighboring particles maintained their layer structure during the calcination procedure performed to remove the alkyl chains.

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1. Introduction

Zirconium phosphate (ZrP) has various crystal structures such as α , γ , τ -ZrP and zirconium pyrophosphates depending on the water content and the synthesis method [1]. Layer structured α -ZrP has been investigated intensively, due to its interesting properties and possible applications as an inorganic ion exchanger [2–6], proton or cation conductor [7–9], and acidic solid for catalysts [10]. The α -ZrP monolayers consist of Zr^{4+} octahedra linked by six oxygens of the HPO_4^{2-} groups. In this structure, the Zr^{4+} ions are bonded to three different HPO_4^{2-} groups per side of the layer, while the HPO_4^{2-} groups are bonded to three different Zr^{4+} ions, and the protons of the HPO_4^{2-} groups are located on both sides of the monolayer [1,10]. Because the POH groups of α -ZrP are stable at high temperatures ($700\text{--}800^\circ\text{C}$) [11], and can be exchanged rapidly and

reversibly by monovalent cations such as Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Ag^+ , NH_4^+ and divalent cations such as Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Fe^{2+} , Co^{2+} and Ni^{2+} , α -ZrP is a promising material for use as an ion exchanger under extreme conditions in which organic resins fail to work. Moreover, α -ZrP has the potential to be used as a hydrogen sensor [12], an organic–inorganic composite [13] which can make up for the weak points of polymer membranes and a catalyst for hydrogen production [14], since it has the required features, such as proton conductivity and solid acidity at high temperature.

For the efficient utilization of its surface properties in the above applications, mesoporous ZrP has been synthesized using the surfactant-assisted templating sol–gel method [8,14–16], or obtained by calcination of zirconium phosphates or phosphonates intercalated by organic groups, which are formulated as $\text{Zr}(\text{ROPO}_3)_2$ or $\text{Zr}(\text{RPO}_3)_2$ (where R = alkyl, aryl, benzyl, acid radicals, etc.) [10,11,17,18].

In this study, lamella structured zirconium alkyl phosphates were prepared by a wet method using monostearyl

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and monodecyl phosphates synthesized in the laboratory, and the alkyl chains were removed by calcination to obtain mesoporous ZrP with a similar structure to that of α -ZrP. This study focused on the characterizations of the obtained materials to find the synthetic conditions in which the mesopores are developed, and the mechanism of pore formation.

2. Experimental

2.1. Synthesis procedure

Monodecyl and monostearyl phosphates were synthesized by the esterification reaction of decyl and stearyl alcohol with phosphorus pentoxide, as previously reported [19]. The product was identified using FT-IR and used without further purification. Zirconium alkyl phosphates (ZrAP) were prepared by the sol-gel method with the synthesized monodecyl and monostearyl phosphates. The monoalkyl phosphate (40–80 mmol) was diluted with 100 ml of ethanol and, separately, phosphorus pentoxide (40–80 mmol) was dissolved in 100 ml of distilled water. With the addition of the aqueous phosphoric acid solution to the monoalkyl phosphate solution at 65 °C, an emulsion started to form, in which the total amount of phosphate was 120 mmol. As the ratio of the stearyl phosphate to phosphoric acid increased, thicker micellar particles were formed, however micelle formation was not observed in the mixtures of the decyl phosphates. One hundred millilitres of the aqueous solution containing 60 mmol of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was then added, and the resulting suspension was rigorously stirred for 1 h, filtered off, and washed with distilled water and acetone. The solid product was dried at 110 °C for 24 h, heated to the calcination temperature (400–600 °C) at a rate of 2 °C/min and calcined for 12 h in air to remove the organic moieties. The chemical formula of the materials obtained using the mixture of phosphoric acid and alkyl phosphates is $\text{Zr}(\text{HPO}_4)_x \cdot (\text{RPO}_4)_{2-x} \cdot y\text{H}_2\text{O}$ (where $0 \leq x \leq 2$, y = the water content, and R = the stearyl or decyl group denoted by St or De). The terms $\text{ZrH}_x\text{R}_{2-x}\text{P}$ and $\text{ZrH}_x\text{R}_{2-x}\text{P}_n$ (n = calcination temperature) are used to represent the dried only samples and the samples calcined at n °C for 12 h, respectively.

2.2. Characterization

The IR absorbances of alcohol, the alkyl phosphates, ZrAP and the calcined powders were obtained with an FT-IR spectrophotometer (Nicolet Magna 550 series II, Midac) using a KBr method. The carbon content was measured by means of a CHN elemental analyzer (EA1110, CE Instrument). To obtain the carbon and hydrogen content, the samples were decomposed by heating to 1014 °C, oxidized to CO_2 and H_2O , and the gas was separated using gas chromatography. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed with a thermoanalyzer (SETA-

RAM, SETSYS 16/18) and the results were compared with those of the elemental analysis. In the case of ZrAP, the temperature range of the TG analysis was from room temperature to 1000 °C at a rate of 2 °C/min without drying, whereas the calcined samples were measured from 120 °C to 1000 °C at a heating rate of 5 °C/min after drying at 120 °C for 1 h. Small-angle X-ray scattering (SAXS, Bruker) with $\text{CuK}\alpha$ radiation was performed in the range of 0–9°. The pore shape was observed with high resolution transmission electron microscopy (HRTEM, JEOL JEM-3000F). N_2 sorption measurements (Micrometrics ASAP 2010) of the calcined powders were performed at the temperature of liquid nitrogen. Prior to these measurements, the samples were degassed at 200 °C until the pressure became lower than 5 Pa. The specific surface area was determined from the linear part of the Brunauer–Emmett–Teller (BET) equation in the range of relative pressure, $0.1 < p/p_0 < 0.3$, and the mesopore size distribution was calculated from the desorption branch using the Barrett–Joyner–Halender (BJH) pore distribution formula modified by Innes [20].

3. Results and discussion

3.1. IR spectroscopy

Fig. 1 shows the infrared absorbance spectra of stearyl alcohol, the synthesized monostearyl phosphates, $\text{ZrH}_1\text{St}_1\text{P}$ as dried at 110 °C for 24 h and the powders calcined at 400 °C and 600 °C for 12 h. Stearyl alcohol, the monostearyl phosphates and $\text{ZrH}_1\text{St}_1\text{P}$ which contain alkyl chains have absorption bands due to the CH_3 and CH_2 stretching vibrations at 2958, 2919 and 2850 cm^{-1} [21], methylene bending at 1471–1464 cm^{-1} , and the methylene rocking vibration at 723 cm^{-1} [22]. Only stearyl alcohol shows the bands of the C–O stretching vibration mode at 1062 cm^{-1} and the H-bonded O–H stretching vibration mode in the range of 3326–3234 cm^{-1} . However, in the spectrum of the stearyl phosphates, the H-bonded O–H

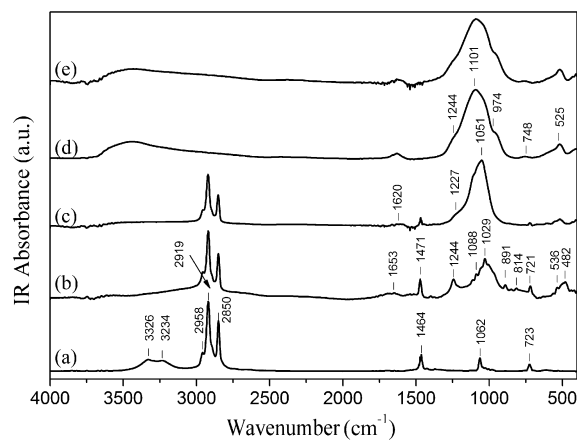


Fig. 1. FT-IR spectra of (a) stearyl alcohol, (b) monostearyl phosphates, (c) $\text{ZrH}_1\text{St}_1\text{P}$, (d) $\text{ZrH}_1\text{St}_1\text{P}_{400}$ and (e) $\text{ZrH}_1\text{St}_1\text{P}_{600}$.

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