

Development of New Sorbents: I. Ordered Porous Phase of Titanium Phosphate

M.J. Hudson^a, S. Waqif Husain^{b,*} and M. Anbia^b

^a *Department of Chemistry, University of Reading, Whiteknights, Box 224, Reading, Berkshire RG6 6AD, U.K.*

^b *Department of Applied Chemistry, Chemistry Faculty, University of Tarbiat Moallem, 49-Mofatteh Avenue, Tehran-15614, IRAN.*

(Received 5 September 2003, Accepted 23 January 2005)

A new phase of titanium phosphate with a highly organized porous framework has been synthesized by a non-thermal digestion method. FTIR, TGA-DTA, XRD and SEM have been employed to study the primary product, calcined and digested materials. Pore diameters in the range of 22-90 Å have been obtained for the digested material as determined by nitrogen absorption measurements. Quantitative removal of copper(II) phthalocyanine and its derivative from aqueous medium have been achieved.

Keywords: Mesopore, Ordered titanium phosphate, Copper(II) phthalocyanine removal

INTRODUCTION

Since the appearance of a group of new porous materials [1], there has been an increasing interest in the development of new porous solids owing to their wide applications in separation, purification and catalytic processes [2,3]. However, only a few preparative approaches have been reported for the synthesis of mesoporous transition metal phosphates including iron phosphate [4], tin phosphate [5], nickel phosphate [6], zirconium phosphate [7] and titanium phosphates [8-11]. Although most of the mesoporous titanium phosphates have good potential to be used as catalysts for liquid phase oxidation reactions and photo-reactions, almost no attention has been paid to study their effectiveness as new sorbents. Input of bigger molecules such as organometals and their derivatives from different industrial plants as pollutant into aquatic environment [12-13] demands the synthesis of new sorbents with ordered porous framework [14] and larger

pore size, which can be used in their removal. The blue pigment copper(II) phthalocyanine (CuPc) and its derivative copper(II) phthalocyanine-3,4',4'',4'''-tetrasulfonic acid tetrasodium salt [Cu(tsPc)⁴⁻] are used widely in different industries such as enamels, plastics, printing inks, linoleum and rubber goods [15,16]. Entrance of such big molecules as pollutant in aquatic environment, has drew attention to study their behavior in aqueous systems [16] and demands new sorbents for their removal. Employing a modified method [17] at ambient temperature, we have synthesized a highly ordered porous phase of titanium phosphate with larger pore size range and have used it as an effective sorbent for the removal of CuPc and Cu(tsPc)⁴⁻ from aqueous medium.

EXPERIMENTAL

Chemicals

All the chemicals used were of analytical grade from Merck (Germany) except hexadecyltrimethyl ammonium bromide and titanium isopropoxide, which were supplied by

* Corresponding author. Email: syedwhusain@yahoo.com

Aldrich (U.K.). Ammonia solution (35 wt%) from Fischer (U.K.) was used. Copper(II) phthalocyanine and copper(II) phthalocyanine-3,4',4'',4'''-tetrasulfonic acid tetrasodium salt, were also purchased from Aldrich (U.K.) and were used without further purification.

Synthesis

Hexadecyltrimethyl ammonium bromide template (2.4 g, 6.6 mmol) was dissolved in deionized water (50 ml) and technical grade ethanol (50 ml). Aqueous ammonia (12 ml, 32 wt%, 0.20 mol) was added to the surfactant solution. The solution was stirred for 10 min and then 4.6 g of titanium isopropoxide $\{\text{Ti}(\text{OPr}^i)_4\}$, was added. The stirring was continued for further two hours at ambient temperature. The resulting solid was filtered and washed thoroughly with deionized water and dried in air at room temperature. This primary (precursor) product was digested in 1 M phosphoric acid solution for 48 h with intermittent slow shaking. It was vacuum filtered, washed three times with deionized water and dried in air at ambient temperature. The primary (precursor) product was also calcined at 823 K for 6 h.

Apparatus

The X-ray powder diffractograms of the samples were recorded using a Siemens D5000 diffractometer with Cu-K α radiation. FTIR Spectra were recorded on Perkin Elmer FT-IR Spectrometer Model Paragon-1000, using KBr disc technique. The nitrogen sorption measurements were made on an ASAP 2010 Micromeritics. Scanning electron micrographs were obtained from a JEOL-JSM-5300 scanning electron microscope. Samples were deposited on a sample holder with an adhesive carbon foil and sputtered with gold. Thermogravimetry-differential thermal analysis (TGA-DTA) was carried out with a Stanton-Redcroft STA 1000 instrument with lidless platinum pans, using recalced alumina as the DTA reference.

Sorption Studies

Copper phthalocyanine was dissolved in 98% sulphuric acid [18] to make a 1×10^{-4} M solution and when diluted with deionized water insoluble floating flocculates appeared. Copper phthalocyanine-3,4',4'',4'''-tetrasulfonic acid tetra sodium salt was easily dissolved in deionized water to make a

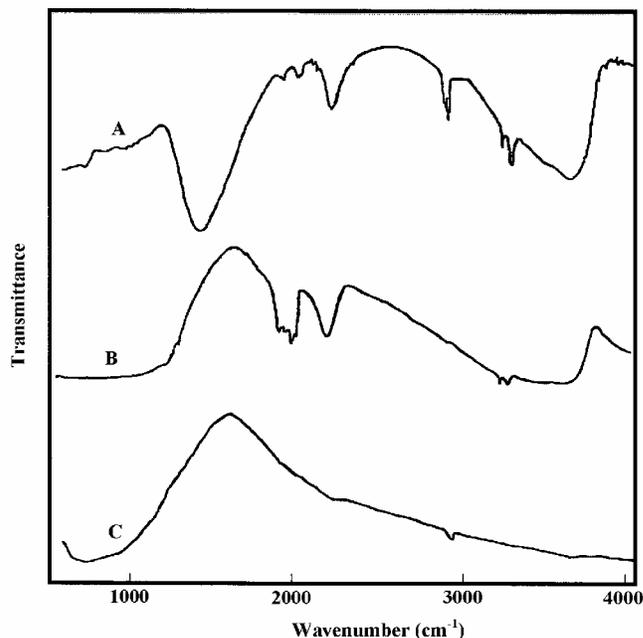


Fig. 1. FTIR spectra of surfactant-titanium phosphate product (A), primary (precursor) product (B) and calcined propoxide precursor (C).

1×10^{-4} M solution. In 150 ml conical flasks containing 10 and 20 ml of the above solutions, 300 mg white powder of highly ordered porous titanium phosphate was added. Intermittent shaking was done for about thirty five minutes. After that the sorbent was removed by filtration and the filtrates were analysed.

RESULTS AND DISCUSSION

The FTIR spectrum of the surfactant-titanium phosphate product (Fig. 1A) shows stretching bands corresponding to C-H bonds, in the zone between 2850 and 2960 cm^{-1} [19] and bending modes between 1460-1490 cm^{-1} [19]. The spectrum of the primary precursor product (Fig. 1B) revealed some typical peaks related to the surfactant [20]. When the titanium propoxide precursor is calcined at 823 K for six hours, complete elimination of the surfactant is observed as all the IR peaks disappear after calcinations [8], as shown in Fig. 1C. After the primary (precursor) product is digested in 1 M phosphoric acid for 48 h, the phosphate groups are heavily

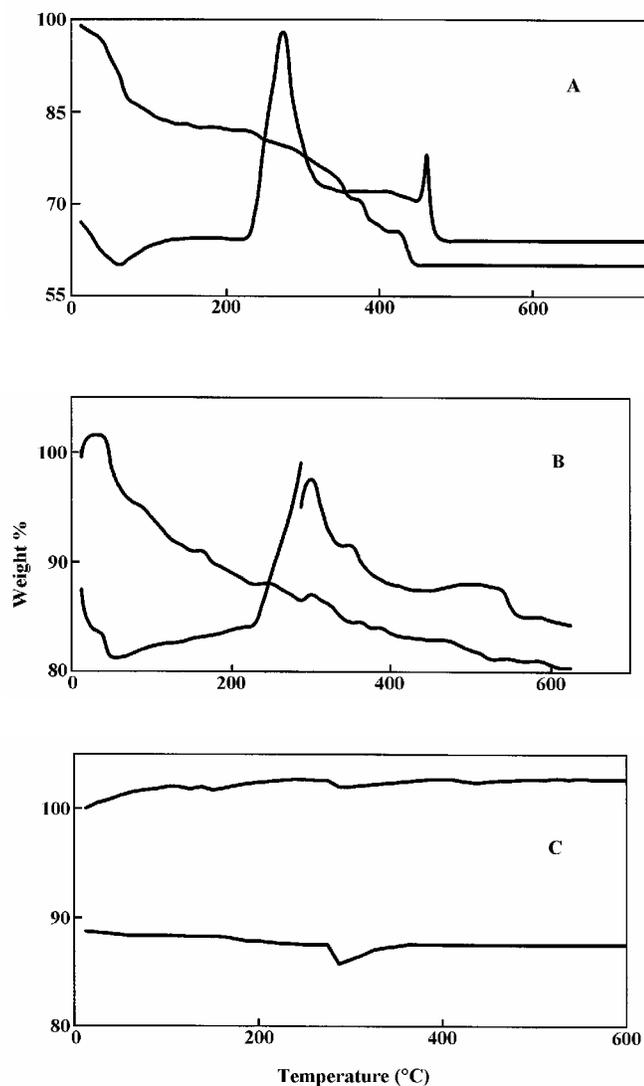


Fig. 2. TGA-DTA curves of primary (precursor) product (A), digested (surfactant-titanium phosphate) material (B) and calcined precursor material (C).

embedded, resulting in a highly ordered mesoporous structure [8]. A strong band related to phosphate ion has appeared at $1000\text{--}1080\text{ cm}^{-1}$ [10], as shown in Fig. 1A. Stretching bands corresponding to $\text{P}=\text{O}$ are also observed in the zone of $1200\text{--}1500\text{ cm}^{-1}$ [21].

Differential thermal analysis and thermogravimetric analysis curves of the samples are recorded in Fig. 2.

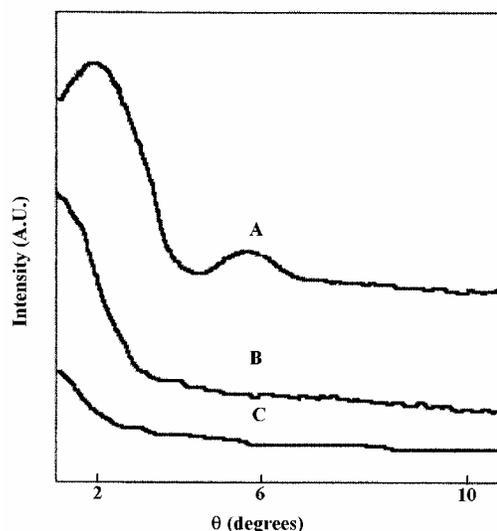


Fig. 3. XRD patterns of surfactant-titanium phosphate product (A), primary (precursor) product (B) and calcined precursor material (C).

Figure 2A shows that the slow calcination of the primary (precursor) product, effected in a dry air atmosphere, results in the decomposition of the surfactant according to a three stage sequence, most possibly corresponding to the primary amine decomposition ($240\text{--}340\text{ }^{\circ}\text{C}$), breaking of the hydrocarbon chains ($345\text{--}400\text{ }^{\circ}\text{C}$) and combustion of the surfactant fragments ($480\text{--}630\text{ }^{\circ}\text{C}$) [22]. While, the digested material seems to be more stable than the primary (precursor) product, so that it possesses a different pattern of the slow surfactant elimination (Fig. 2B). However, after calcination of the primary (precursor) product at a higher temperature ($550\text{ }^{\circ}\text{C}$) for six hours, it is converted to titania, the corresponding DTA-TGA curve of which shows very little change with increasing temperature (Fig. 2C).

The XRD patterns of the primary (precursor) product, calcined material and digested material are shown in Fig. 3. The primary (precursor) material shows a low-angle thin peak (Fig. 3B). The digested material (Fig. 3A) revealed a pronounced single low-angle diffraction peak and there were no noticeable high angle reflections as in the XRD pattern of the mesostructured titanium phosphate [11]. The calcined material shows a crystalline pattern of titania (Fig. 3C). It is rather difficult to distinguish clearly between the XRD

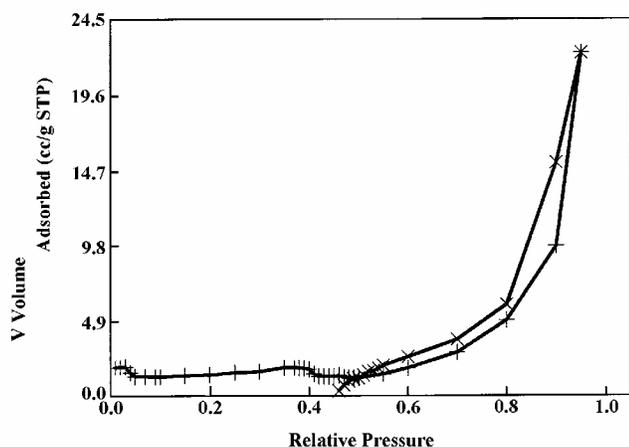


Fig. 4. Nitrogen sorption isotherm plot of digested material at 77 K.

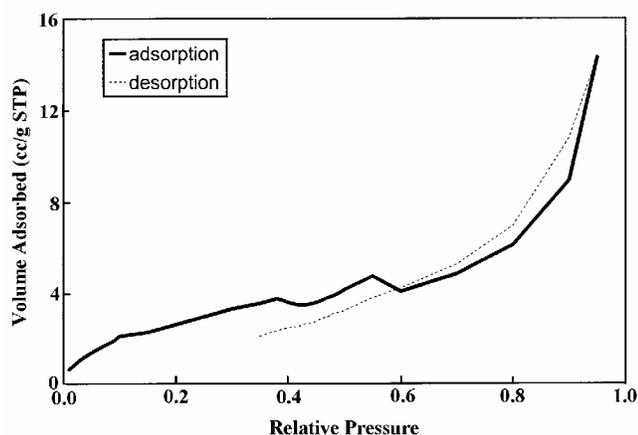


Fig. 5. Adsorption-desorption isotherm plot of digested material.

patterns of the primary (precursor) material and the digested material, since this technique is known to be unable to distinguish between some materials with porous structure [23].

Owing to their suitable pore size, the porous materials can be used as important adsorbents. Nitrogen adsorption is a standard and most commonly used method to assess pore size distribution [24]. Therefore, the nitrogen adsorption-desorption isotherm plots for the digested sample have been measured at low pressure and at 77 K. The resulting plots are recorded in Figs. 4 and 5. As is obvious, the plots show a

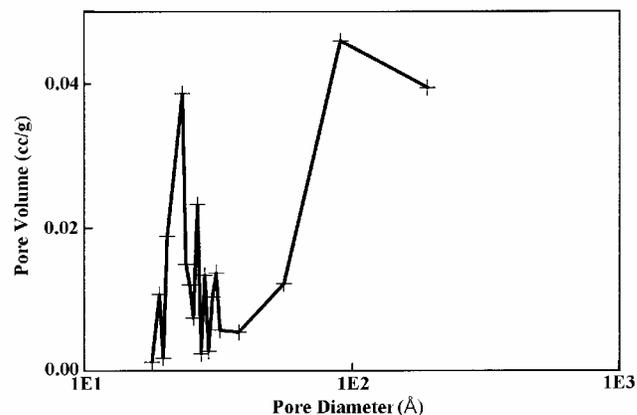


Fig. 6. BJH pore size distribution plot for the digested material calculated from desorption branch of the isotherm plot.

sharp and steeply inclined hysteresis loop which suggests the presence of a wide range of pores [25]. The pore size distributions were calculated from the desorption branch by the Barret-Joyner-Halenda (BJH) Method [26]. Ahn *et al.* [27] have made a comparative study of fifteen titanium containing *meso*-structure molecular sieves with surface areas ranging from 750 to 1350 m² g⁻¹ and have found that, with the increase in surface areas, BJH pore diameter of these samples decreased from 38 to 25 Å. Pan *et al.* [11] have recently reported the synthesis of a mesoporous phase of titanium phosphate using a long-chain alkylamine, and they have admitted that it has a disordered porous framework and shows a narrow pore size distribution with a maximum at 33 Å. However, the novel titanium phosphate, prepared by digestion method, shows a wide range of large pore size from 22 to 90 Å (Fig. 6). The magnified scanning electron micrograph of the digested material, depicted in Fig. 7, shows a highly ordered porous framework which makes it a new promising sorbent.

CuPc has a low solubility in water (< 0.001 g l⁻¹) and is usually present as a floating flocculate. However, the substitution of CuPc with hydrophilic sulfonic groups (Cu(tsPc)⁴⁻) makes this derivative easily soluble in aqueous solutions [28]. When the white powder of the digested material (*i.e.*, ordered porous titanium phosphate) was added to a solution containing CuPc, the resulting flocculates were sorbed on the surface of the sorbent, turning it to deep blue

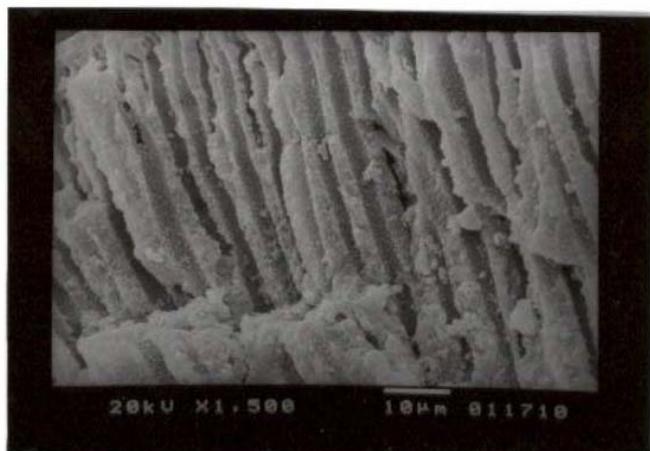


Fig. 7. Scanning electron micrograph of the digested material (Ordered-Porous titanium phosphate).

Table. 1. Quantitative Sorption of CuPc and Cu(tsPc)⁴⁺ on the Ordered Titanium Phosphate, (Concentration in mg)

	CuPc		Cu(tsPc) ⁴⁺	
Before treatment	0.57	1.15	0.98	1.96
After treatment with sorbent.	T.A.	T.A.	T.A.	T.A.

T.A.= Total adsorption.

CuPc = Copper(II) Phthalocyanine.

Cu(tsPc)⁴⁺ = Copper(II) Phthalocyanine-3,4',4'',4'''-tetrasulfonic acid, tetra sodium.

and leaving behind a colorless solution. When a solution of Cu(tsPc)⁴⁺ was treated with the sorbent, the Cu(tsPc)⁴⁺ anions were easily trapped inside the pores of sorbent, and the sorbent color turned light blue while turning the aqueous solution from blue to colorless (Table 1). The obtained results clearly indicated that this material can be used as a potential sorbent for the removal of bigger pollutant molecules from aquatic media.

CONCLUSIONS

A new phase of surfactant-titanium phosphate with highly ordered porous framework and larger pore size range has been

developed as a novel sorbent employing the digestion method at ambient temperature. It has been successfully applied to the removal of bigger molecules such as copper phthalocyanine and its derivative copper phthalocyanine-3,4',4'',4'''-tetrasulfonic acid tetrasodium salt from aqueous medium.

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