

Preparation and Characterization TiO₂ Microspheres for the Liquid Chromatography Stationary Phase

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Abstract

TiO₂ microspheres with a uniform particle size distribution were synthesized by hydrothermal method. After being sintered, the titania microspheres that are obtained have an average diameter of 5 μm, a surface area of 383.5 m²/g, an average pore volume of 0.25 cm³/g, and an average pore diameter of 35.9 nm. Normal phase chromatography was separated the mixture of benzene, nitrobenzene and nitro-anisole, three substances were separated well on the titania column. The microspheres possess enough rigidity to withstand high packing pressure and are very useful as a new kind of chromatographic packing material for high performance liquid chromatography (HPLC).

Keywords: Hydrothermal treatment; TiO₂ microspheres; Liquid chromatography stationary phase

Introduction

TiO₂ has been extensively used in photocatalysis [1], lithium battery [2], sensor materials [3], dye degradation [4], cosmetics [5] and other technical fields [6]. In recent years titania materials for high performance liquid chromatography (HPLC) has attracted considerable attentions attributed to the good chemical stability, mechanical strength, enough rigidity and amphoteric ion-exchange properties [7-9]. By far silica is the most popular material for manufacturing chromatographic columns. While the chemical and thermal stability of silica has limited application in commercial use. The silica only can be used in a narrow pH range as the strong hydrolysis and the instable Si-O band when pH>8 or pH<2 that leads to the changes of peaks sharp and retention characteristics of the separations [10]. In addition, bare Si-OH of the silica surface affected the mesidino, chelate and hydrogen bond will generate irreversible effect that cause serious detail and reduce the efficiency of separation. Both these conditions reduce the lifetime of the HPLC column.

Titania has greater mechanical and pH stability (pH 1-14) that may compensate for the narrow pH range of silica and it is suitable for the separation of the alkaline substances especially the biological macromolecules [11]. Nowadays, the research about the TiO₂ used as the chromatographic packings instead of the silica column is less reported, not to mention the practical application. The main difficult is due to how to synthesize the uniform and controllable size TiO₂ microspheres. So the preparation of the TiO₂ microspheres that meet the conditions is the key.

Recently the methods about how to prepare the TiO₂ microspheres are broadly reported, including the sol-gel [12,13], hydro-thermal method [14], Polymerization-Induced Colloid Aggregation (PICA) [15], non-aqueous emulsions [16], co-precipitation [17] and so on. While the latter three methods cannot be applied in the extensive production as the ways are so verbose and thereagent are expensive. Thus in our paper, the TiO₂ microspheres are prepared by the hydro-thermal method. Through a large number of experiments, we have discovered the optimal experimental conditions of synthesizing the TiO₂ and the morphology and particle size of the microspheres are controlled. So TiO₂ can be made into the normal phase packing. In order to test the chromatographic performance, we plan to separate some basic materials.

Experimental Section

Apparatus

A scanning electron microscope, model JSM-5610LV (Electron Optics Corporation, Japan) was used to record the electron micrograph. An X-ray diffractometer model D/max-2500 VL/PC (Science Instruments, Japan) was used to determine the crystal shape of the titania. An oven, model DGF-30 (Experiment Instruments Corporation, Nanjing, China) was used to control the reaction temperature. An autoclave of a 50 mL polyfluortetraethylene cup was to be the reaction vessel. A Micromeric model ASAP-2010 surface analysis instrument (Micromeric Corporation, U.S.A) was used to collect nitrogen adsorption/desorption isotherms. A laser particle size analyzer, model Master Sizer2000 (Malvern Company, U.K) was used to determine pore size distribution (PSD). A HPLC/MS model 1290-6460 (Agilent Corporation, American) was used to separate the special substances.

Reagents

Titanium tetrachloride, ammonium sulphate, urea and other reagents were all analytical grade. n-hexane, ethanol, benzene, nitrobenzene, o-nitroanisole are HPLC grade. Water (H₂O) was distilled and deionized using a Millipore Milli-Q system (Bedford, MA, USA).

Synthesis of Porous Titania Microspheres

The synthesis of TiO₂ microspheres are prepared by the following steps: 0.72 g of ammonium sulphate, 8.5 g of urea, 8mL of water and 8mL of ethanol were added into the conical beaker. Under continuous stirring, 0.6 mL of titanium tetrachloride was added drop by drop. After stirring for 5h, the transparent solution was obtained and the pH was

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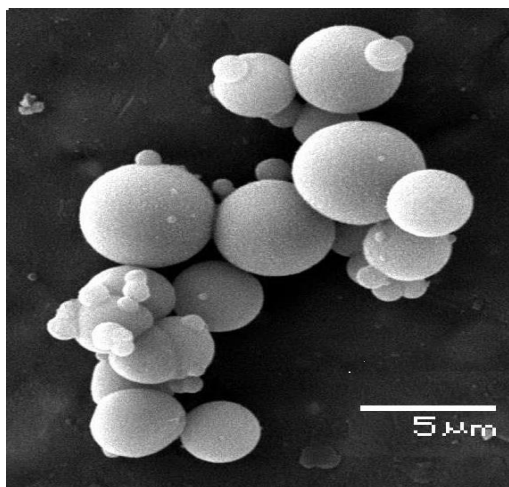


Figure 1: SEM image of TiO₂ microspheres.

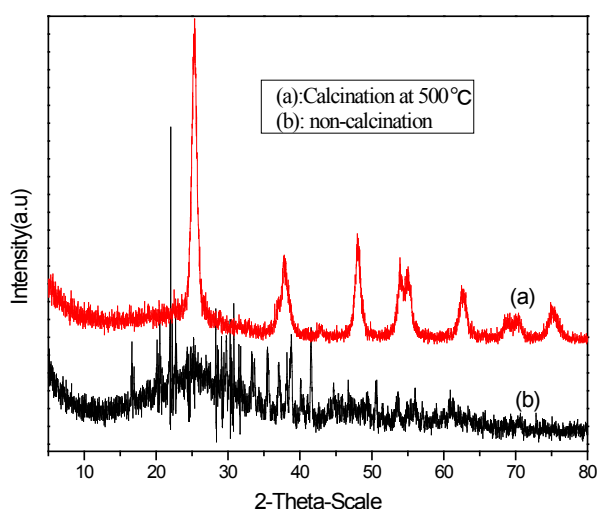


Figure 2: XRD patterns of TiO₂ microspheres.

about 2. Then the solution was transferred into an autoclave of a 50 mL polyfluortetraethylenecup. The autoclave was heated and maintained at 393 K for approximate 5h and then the autoclave was cooled to the room temperature. After the suspension was filtered, the precipitate was washed twice with deionized water and washed third with ethanol. The microspheres was dried at 353K and carbonized at 773K in a muffle furnace after grinded. Then, the TiO₂ microspheres sample can be obtained.

Column packing

The chromatographic column (250×4.6 mm i.d.) was filled with titanium oxide and a pressure of 450psi was applied by the use of a high-pressure pump, model DSTV-150 (HASKEL Technical Company, American). Isopropanol and methanol was used as propulsion solvent.

Results and Discussion

SEM images and X-ray diffraction of porous titania microspheres

TiO₂ synthesized by hydrothermal treatment are spherical and free

from clustering. The SEM micrograph is shown in Figure 1. It can be seen the TiO₂ microspheres are 6-10 μm in diameter.

Figure 2 shows the X-ray diffraction of the TiO₂. It is clearly seen from Figure 2, the X-ray diffraction intensity of the TiO₂ without the heat treatment is very lower and the crystal structure is amorphous. After being sintered, the diffraction intensity sharply increase and the diffraction peaks in 25.32°, 37.88°, 48.11°, 53.94°, 62.51° are the characteristic peaks of anatase TiO₂. It is proved that the crystal shape of titania microspheres is anatase-type.

The specific surface area of TiO₂ microspheres

The specific surface area of the stationary phase is one of the most important parameters in chromatogram [7] Chromatographic separation requires the packing be a larger surface area in order to facilitate the carrying load lots of more samples and provide sufficient separation efficiency. The specific surface area of titania that being sintered is 383.5 m²/g, whereas the microspheres without heat treatment is 276.0 m²/g, which was calculated using the standard Brunauer Emmett Teller (BET) method. This is because the water adsorbed in the TiO₂ microspheres will dissociate to Ti-OH bond formation owing to the heat treatment. With the temperature rising, the adjacent Ti-OH bond will concentrate to Ti-O-Ti bond. Though this agglomeration leads to decrease the specific surface areas, the TiO₂ microspheres synthesized by hydrothermal treatment still have large surface areas.

Pore Size Distribution (PSD) of porous TiO₂ microsphere

According to the theoretical analysis and practical application, Carr [12] has considered that the ideal packings should be in accordance with the suitable physical and chemical parameters. The diameter of the microspheres must be in the range of 2 to 50 nm and the pore diameter should show a narrow pore size distribution. Meanwhile it is necessary the appropriate pore size is supposed from 0.2 to 0.7 μm. Figure 3 shows nitrogen adsorption /desorption isotherms of porous TiO₂ microspheres after heat treatment. As is shown, it is intuitively seen that the adsorption branch is consistent with the IV isothermal map of the ideal chromatography. In accordance with the IUPAC classification, the most favorable stationary phases should have a type IV adsorption isotherm and a H type hysteresis loop [18]. According to the desorption isotherm the average pore volume of TiO₂ is 0.25 cm³/g and

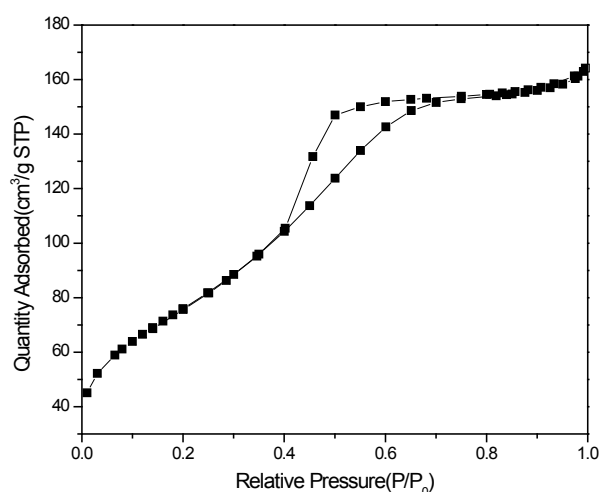
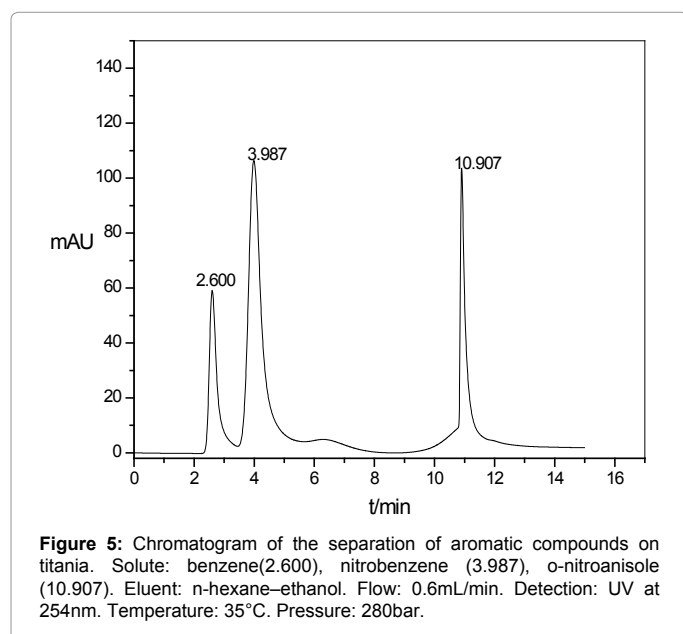
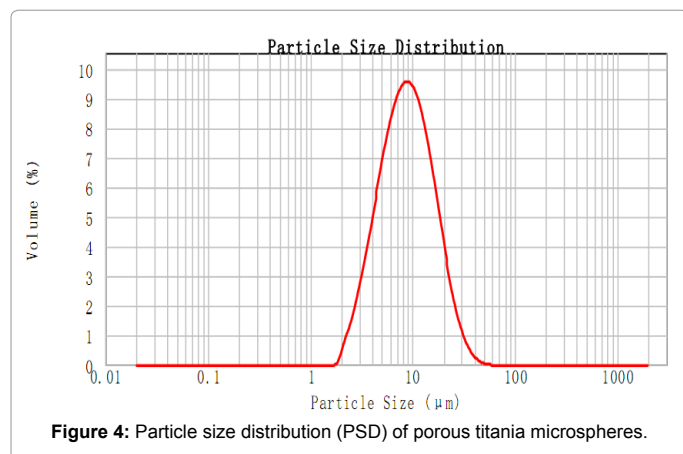


Figure 3: Nitrogen adsorption / desorption isotherms of porous titania microspheres.



the pore diameter is 35.9 nm based on the BJH models. The pore size distribution of TiO₂ microspheres is shown in Figure 4. It is seen that the PSD of TiO₂ is narrow and relatively uniformity. The average size of TiO₂ is 7 μm which is consistent with the results of scanning electron microscope.

Chromatographic condition

Normal-phase separation of aromatic compounds was performed on the titania column using n-hexane and ethanol as the mobile phase. The mixtures contained benzene (10 μg/mL), nitrobenzene (0.4 μg/mL) and o-nitroanisole (0.2 μg/mL). Injections of 5 μL of appropriate concentrations of these mixtures produced satisfactory chromatographic peaks with detection at 254 nm and the mobile phase was controlled at 0.6 mL/min. The mobile phase was gradient elution :0~7 min,100% n-hexane, 7~8 min,100%~90%n-hexane, 8~20 min, 90% n-hexane. The column temperature was controlled at 35% and the initial pressure of the column was about 280 bar. The separation results are shown in Figure 5. As can be seen the three substances were separated well on the titania column. Benzene and nitrobenzene were retained on the stationary phase as Lewis base of the π electron of the aromatic compounds was reacted with the Lewis acid of the TiO₂. o-nitroanisole was retained longer in the chromatographic column

due to the strong polarity. As can be seen, titania that is synthesized by hydro-thermal method is useful as a packing material for HPLC.

Conclusions

The traditional silica column will enhance solubility in basic mobile phases and at higher temperatures. Meanwhile the tailed peaks are appeared when the alkaline substances are separated on the column. Thus our work hammers at exploring a new liquid chromatography stationary phase. The TiO₂ microspheres synthesized by hydrothermal treatment was about 5 μm. The PSD of TiO₂ was relative narrow and uniform. The pore size of TiO₂ was 35.9 nm which is in the range of mesopore. Simultaneously specific surface area was 383.5 m²/g and pore volume was 0.25 cm³/g. Benzene, nitrobenzene and o-nitroanisole were separated well in the titania column. All these parameters are showed that TiO₂ is the excellent normal phase for the liquid chromatography.

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