Preparation of Cage Nanoporous Silica and Its Application in Chromatographic Fillers

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ABSTRACT

In this paper, the cage nanoporous silica is composed of ethyl orthosilicate as silicon source, triblock copolymer poly (ethylene oxide) -poly (propylene oxide) -polyethylene oxide (F127) as structure guide agent and additive, while the Fm3m cubic structure of cage type nanoporous silica was prepared by hydrothermal synthesis method. It is easy to control the self-assembly of the silica triblock copolymer intermediates thermally. In addition, the change in sample pore size and pore volume can be achieved by a hydrothermal reaction at a temperature of 100 °C to 150 °C. Small angle X-ray diffraction shows that these samples have ordered pores, while adsorption studies show that they have high porosity, uniform distribution of bimodal pores and large pore volume. Use separation of p-methylbenzene borate, iodobenzene and biphenyl by using three kinds of cage-type nanoporous silica materials as chromatographic fillers. The results showed that the material prepared at 130 °C under hydrothermal condition had the best effect on the separation of three organic compounds.

KEYWORDS: cage type nanoporous silica; chromatography;


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1. Introduction

According to the provisions of the International Union of Purely Applied Chemistry (IUPAC) [1], the porous materials can be divided into three types according to their pore size. Pore size range of 2nm below the solid material known as microporous materials, including siliconite, activated carbon, zeolite, etc., is a class of Si, Al and other based crystalline aluminosilicate; pore size range between 2-50nm called mesoporous or mesoporous materials, including some airgel, glass-ceramic etc; pore size greater than 50nm are macroporous materials, including porous ceramics, cement, airgel and so on. According to the distribution characteristics of the holes in the space, the mesoporous materials can be divided into two kinds which are ordered and disorder. The holes of the former are arranged in the space, and the holes of the latter are irregularly distributed. Ordinal mesoporous materials can be divided into 3 classes which are aligned columnar (channel) holes, parallel arrangement of layered holes and three-dimensional regular arrangement of polyhedral holes (three-dimensional interconnection). While the mesoscopic materials in the hole, the shape of complex, irregular and connected to each other, and the type of hole commonly used to describe the shape of the ink bottle and the neck is equivalent to the hole between the channels. According to the classification of chemical composition, mesoporous materials can generally be divided into silicon and non-silicon-based composition. Silicon-based mesoporous materials mainly include silicates and aluminosilicates; non-silicon-based mesoporous materials mainly include transition metal oxides, phosphates and sulfides.

Mesoporous molecular sieve material is a new kind of ordered mesoporous material [2,3] represented by M41S developed by Mobil in 1992. This discovery is a major breakthrough in the field of porous materials. This major discovery has opened up new prospects for the development and application of nanomaterials, as well as the further development of nanoscience and nanotechnology [4]. They have the following characteristics: (1) the synthesis process requires the participation of surfactants; (2) the mesoporous channels are arranged in periodic order, 'crystalline' mesoporous materials; (3) has a high specific surface area and high porosity; (4) the pore size distribution is very narrow, and the pore size can be controlled within a wide range; (5) good hydrothermal stability and regular morphology; (6) skeleton elements adjustable, so far ordered mesoporous; (7) is widely used, such materials have been used as a good catalyst or catalyst carrier application; the use of such materials as a good catalyst or catalyst carrier application in the...
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macromolecule catalytic reaction; can be used to separate biological macromolecules; have a good application prospects in microelectronics and optics field; and can also be a good material.

Cage nanoporous silica act as an important silicon-based mesoporous material with structural control and good thermal stability etc. In the catalytic, biological materials, sensors, adsorption materials, luminescent materials and other fields have great application value, so this research also get more attention by scientists [6-9]. OOn-PoM-EOn is one of the important templating materials for the synthesis of ordered mesoporous materials. It is inexpensive, nontoxic and biologically degradable and other characteristics, in the application to meet the economic and environmental requirements of both.

The experiment was carried out by hydrothermal reaction of CKT - T at 100 ℃, 130 ℃ and 150 ℃ using tetrahedral block F127 (EO106PO70EO106) as template, using tetraethoxysilane (TEOS) as the silicon source, where T is the thermal reaction temperature. The samples were removed by calcination at 550 ℃, after the samples were obtained, it was sieved with simulated powder X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM) and N2 adsorption-desorption characterization. In the cage nanoporous silica applications, the use of the three kinds of cage-type nanoporous silica and the other two kinds of silica gel column separation and separation of standard stock solution separation effect, resulting in cage nano separation effect of pore silica.

2. Experimental part

2.1. Experimental materials and instruments

2.1.1 Instruments

<table>
<thead>
<tr>
<th>Name</th>
<th>Model</th>
<th>Manufacture name</th>
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<tr>
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<td>DF-101S</td>
<td>Gongyi City to China Instrument Co., Ltd.</td>
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<tr>
<td>magnetic stirrer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Three with UV analyzer</td>
<td>WFH-203B</td>
<td>Shanghai Jingke Industry Co., Ltd.</td>
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<tr>
<td>Type electric heating oven</td>
<td>SZ202-0</td>
<td>Zhejiang Zhiu Electric Instrument Factory</td>
</tr>
<tr>
<td>Analysis of electronic balance</td>
<td>RH-200</td>
<td>Beijing Sartorius Instrument System Co., Ltd.</td>
</tr>
<tr>
<td>Circulating water type vacuum pump</td>
<td>SHZ-D(III)</td>
<td>Gongyi City to China Instrument Co., Ltd.</td>
</tr>
<tr>
<td>Buchner funnel</td>
<td></td>
<td>Qiyang County of Hunan Province Seiko Science and Education Equipment Co., Ltd</td>
</tr>
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</table>

2.1.2 Drugs

<table>
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<tr>
<th>Name</th>
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<th>Manufacture name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl orthosilicate</td>
<td>Analysis of  pure</td>
<td>Chengdu Kelon Chemical Reagent Factory</td>
</tr>
<tr>
<td>F127 (EO106PO70EO106)</td>
<td>Analysis of  pure</td>
<td>Anqiu Luxing Chemical Co., Ltd.</td>
</tr>
<tr>
<td>Concentrated hydrochloric acid</td>
<td>Analysis of  pure</td>
<td>Laiyang City Double Chemical Co., Ltd.</td>
</tr>
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<td>Acetone</td>
<td>Analysis of  pure</td>
<td>Chengdu Kelon Chemical Reagent Factory</td>
</tr>
<tr>
<td>Petroleum ether</td>
<td>Analysis of  pure</td>
<td>Tianjin Jindong Tianzheng Fine Chemical Reagent Factory</td>
</tr>
<tr>
<td>Thin layer chromatography on silica ge</td>
<td>Analysis of  pure</td>
<td>Qingdao Shenghai Chemical Co., Ltd</td>
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</tbody>
</table>

2.2. Preparation of cage nano-pore silica

Sulfonated nanoporous silica, named CKT, was prepared using the triblock copolymer F127 (EO106PO70EO106) as a structural template for the initiator, using orthosilicate as the predecessor of silica. It was dissolved in 360 g of distilled water with 7.5 g of F127 and 15.7 g of concentrated hydrochloric acid (35 wt% HCl). Fast addition of 36g TEOS was carried out at 45 °C for 24 hour to form a mesoporous product. Next, the reaction mixture was subjected to hydrothermal reaction at 100 °C for 24 hours, subjected to hydrothermal reaction, filtered and washed, and the solid was dried at 100 °C. The other two synthetic samples were prepared by varying the temperature of the hydrothermal reaction from 100 °C to 150 °C and 150 °C. The sample is labeled CKT- (T), T is the synthetic temperature. The mass
ratio of the heterozygote is 1 TEOS: 0.0035 F127: 0.88 HCl: 119 H2O. Finally, the sample was roasted at 550 °C to remove the template [10]. Finally, get the sample.

2.3. Experimental characterization

At present, the characterization of mesoporous materials is mainly divided into X-ray diffraction, energy spectrum, microscopy, adsorption-desorption and thermogravimetric analysis. The diffraction is mainly used for phase analysis, the crystal structure information and grain (including the type of elements, content, chemical valence and the formation of chemical bonds), the surface structure (including surface morphology, phase analysis which includes surface morphology, content, chemical composition and chemical bond formation), the surface structure (including surface morphology, phase analysis, the distribution of elements, surface atomic arrangement, etc.) and the surface electron state (electron cloud distribution, energy level structure), etc.; the microstructure of the material mainly through microscopic techniques such as transmission and scanning electron microscopy. Adsorption - desorption mainly gives the surface area, pore size or pore volume of the pores. The thermogravimetric analysis mainly gives the relevant component information. At present, the characterization of mesoporous silicon materials is mainly characterized by small angle XRD, pore size and distribution. The pore volume is observed by scanning electron microscopy (TEM). In terms of the mesoporous material itself, the specific surface data of the material is an important parameter of the surface properties because the various properties of the solid are closely related to the size of the surface.

2.3.1 SEM scanning electron microscopy to observe the appearance of the sample

Fig. 3 shows the SEM images of three kinds of CKT-X calcined at different temperatures. Sample A (CKT-100), it can be seen that the morphology of the surface of the bulk particles exhibits irregular lumps. Sample B (CKT-130), it can be seen that the surface morphology of the massive particles is agglomeration of spherical particles. Sample C (CKT-150), it can be seen that the morphology of the surface of the bulk particles is made up of numerous layers. The results show that the surface morphology of the material is different under the hydrothermal reaction conditions at different temperatures. This indicates that the temperature of the hydrothermal reaction has an effect on the surface morphology. It affects the massive particles and layered stacks.

2.3.2 Morphological Analysis of Cage Nanoporous Silica

Transmission electron microscopy showed that CKT had a cubic mesoporous structure. It should be noted that the photographs do not observe the presence of internal growth of the three-dimensional hexagonal phase, which is consistent with the recent reports of other cage materials (SBA-2, SBA-12, FDU-1) [11-13]. The material is a face-centered cubic Fm3m structure. The TEM photographs of the prepared materials presented in this paper are contrary to those reported by Fanetal et al. [13]. It has been found that the presence of (111) projections is not observed by TEM photographs. It is obvious that the desired dense packed Fm3m cage structure is obtained. The TEM photograph of this result also proves that it is clear that the Fourier diffraction composition is consistent with the strongest XRD peaks. (111) diffraction peak is a characteristic diffraction peak of the Fm3m lattice, but does not include (111) or (200) in the cage-type lattice diffraction peak reported in the literature Fanetal [14]. This shows that Fanetal had observed a different cage material. Figure 4 is the actual CKT TEM picture, it can be estimated from the photo scale that the size of each aperture is about 5nm, and physical adsorption obtained by the same diameter.

2.3.3 Adsorption - desorption analysis of cage nanoporous silica

Figure 5 shows the pore size distribution of the N2 adsorption-desorption curve and the desorption curve of CKT-T. It can be seen from the figure that the N2 adsorption-desorption isotherm of the prepared mesoporous material belongs to Langmuir IV type. The typical mesoporous material absorbs the curve and has three distinctly differentiated regions, namely the monolayer-multilayer adsorption region, the capillary concentration region and the outer surface multilayer adsorption region. There is an H1-type hysteresis loop in the medium-pressure section and near-saturated vapor pressure, whereby the adsorption and desorption branches are almost parallel, indicating that the synthesized product has a three-dimensional regular polyhedral pore structure. The relative pressure of the middle section determines the size of the sample pore size, and the steepness of the change of the adsorption line is also an important basis for measuring the homogeneity of the mesoporous distribution. The desorption branch occurs at a relative partial pressure of 0.40, indicating a regular three-dimensional pore structure. It can be seen from the pore size distribution of the pore size CKT - 100 diameter of 3.8nm, specific surface area of 722.7m2g-1 pore capacity of 0.62cm3g-1, CKT - 130 diameter 5.3nm, specific surface area 673.6m2g - 1, pore volume 0.43cm3g - 1 and CKT - 150 diameter 3.6nm, specific surface area 487.3781 m2g - 1, volume 0.33cm3g - 1.
3. Application of cage type nanoporous silica

3.1. Preparation of mixed standard solution

Before the application, I had chosen the p-methyl benzene boric acid, iodobenzene, biphenyl three organic mixtures as the mixed stock solution. I had separated the mixed stock solution into 5 spare parts.

Structure of three organic compounds

3.2. TLC method detection

Thin layer chromatography (Thin-Layer Chromatography) was used to detect the mixed standard stock solution. Thin layer of the plate cut into a 5cm high plate, 0.5cm away from the edge of the point with the fan blowing, the amount of about 10μL point, and point circle diameter of not more than 2mm. Then, the sheet was spread in a chromatographic cylinder saturated with the developing solvent, and the developing agent was v (acetone): v (petroleum ether) = 1: 3. After the start, dry at the UV wavelength of 254nm detection of mixed standard stock solution spots. There are three points on the thin layer as the picture shows.

3.3. Packed column

The experiment was carried out using a dry column. The prepared CKT - 100, CKT - 130, CKT - 150 and silica gel G, silica gel H were filled directly into the column, and then gently beat the sides of the column, until the silica interface is no longer so far, the stationary phase Of the height of about 30cm, and finally with the pump column packed real. As shown in Figure 7:

3.4. Separation

Separate the standard stock solution into the column and add the developing agent (acetone and petroleum ether 1: 3). The separation rate of the five columns is the fastest of the CKT-150 liquid flow rate, while the silica gel G is the slowest and even slower than the volatilization rate of the developing agent. The flow rate of the other three columns is almost as fast.

The liquid separated from the five columns of the sample bottle was used to detect the spots separated by the mixed standard stock solution by TLC while receiving the liquid. Each column has 5 bottles of liquid.

Silica G due to the slow flow rate is not the final separation effect.

Silica gel H separated six bottles of liquid by TLC method to detect each bottle has several substances. There is one substance in the first bottle; two substances in the second bottle and third bottle, while the fourth and fifth bottles are not detected. As shown in Figure 8:

CKT - 100 separates five bottles of liquid by TLC method to detect several substances in each bottle. There is one substance in the first bottle, two substances in the second bottle and third bottle, while the fourth and fifth bottles are not detected. As shown in Figure 9:

CKT - 130 separated six bottles of liquid by TLC method to detect each bottle has several substances. There is one substance in the first bottle, two substances in the second bottle, while the third, fourth and fifth bottles are not detected. As shown in Figure 10:

CKT - 150 separated five bottles of liquid by TLC method to detect each bottle has several substances. There are two substances in the first bottle, the second bottle of a substance, while the third bottle, the fourth bottle and the fifth bottle is not detected. As shown in Figure 11:

The results of the above experiments and the observation of the flow rate of the reagent during the separation process show that the best results are CKT - 130 in the three kinds of CKT - T. The homogeneous stability of CKT - 130 can effectively separate three kinds of organic matter.

4. Conclusion

In this experiment, the preparation of cage nanoporous silica at different hydrothermal reaction temperatures was studied. The samples were calcined at 550 ℃, while their structures, lattice parameters and so on were scanned by XRD. The morphology of the samples was observed by electron microscopy, the distribution of pore size was observed by TEM transmission electron microscopy, and the specific surface area and volume of N2 adsorption and desorption were measured. Finally, the mesoporous materials obtained after calcination are separated and mixed with the standard
stock solution, and two kinds of silica gel are taken in the separation process. The experimental results show that the separation effect of CKT-130 is the best, and the temperature of hydrothermal reaction is moderate. Therefore, CKT-130 is able to separate the above four kinds of organic matter.

References