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Sorption Characteristics Of The Mesoporous Sorbents Based On Tetraethoxysilane And Titanium Oxide

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Abstract. Samples of mesoporous sorbents based on tetraethoxysilane and titanium dioxide in an acidic medium were obtained using the sol-gel technology. The synthesized mesoporous sorbents are characterized by a large specific surface area of 700-950 m^2 / g, as well as an average diameter of 2.6-6.5 nm and a low pore volume of 0.60-0.90 cm^3 / g. It was found that a hysteresis loop is observed in the mesoporous sorbents during the adsorption of benzene and water vapors. The phase composition of the sorbents was studied by X-ray diffractometry (XRD), surface characteristics by a scanning electron microscope (SEM). The mesoporous sorbents can be used as a sorbent for gas chromatographic separation of light alkanes, olefins, aromatic hydrocarbons, alcohols, aldehydes, ketones, ethers and esters.

Keywords: Sorbent, mesoporous, silica gel, size, texture, Sol-gel technology, diffractometry

1. INTRODUCTION

Mesoporous materials based on silicon oxide with a given structure, geometric characteristics and their modifications have found wide application in chromatography as a sorbent, as well as in catalysis, cosmetics, and photonic crystals due to the unique properties of these materials [1, 2]. The composition of mesoporous materials based on SiO_2 with oxides of various metals expands the possibilities of their application in practical chromatography of sorption materials as sorbents with improved chromatographic characteristics [3, 4].

The specially synthesized silicon materials MCM-41 (Mobile Composition of Matter) and their use as a stationary phase in chromatography have expanded the range of possibilities. Mesoporous siliceous materials MCM-41 were first synthesized by G.A. Ozin et al. [5] in acidic conditions. The materials were synthesized by the interaction of highly dilute tetroethoxysilane solutions with cationic surfactants at low pH values [7]. In addition, in an acidic medium, D. Zhao and colleagues synthesized mesoporous substances SBA-X (Santa Barbara Amorphous) with hexagonal cylindrical pores 30 nm in size using a triblock copolymer of nonionic surfactant P123 (Pluronic asid) [8].

Currently, various representatives of this type of mesoporous materials are successfully used in high performance liquid chromatography as a stable phase, as well as in ion exchange chromatography. In this regard, the synthesis of mesoporous materials based on SiO_2 and their modifications are relevant today.

The aim of this work is to synthesize and study the sorption characteristics of a mesoporous sorbent based on tetraethoxysilane and $TiCl_4$.

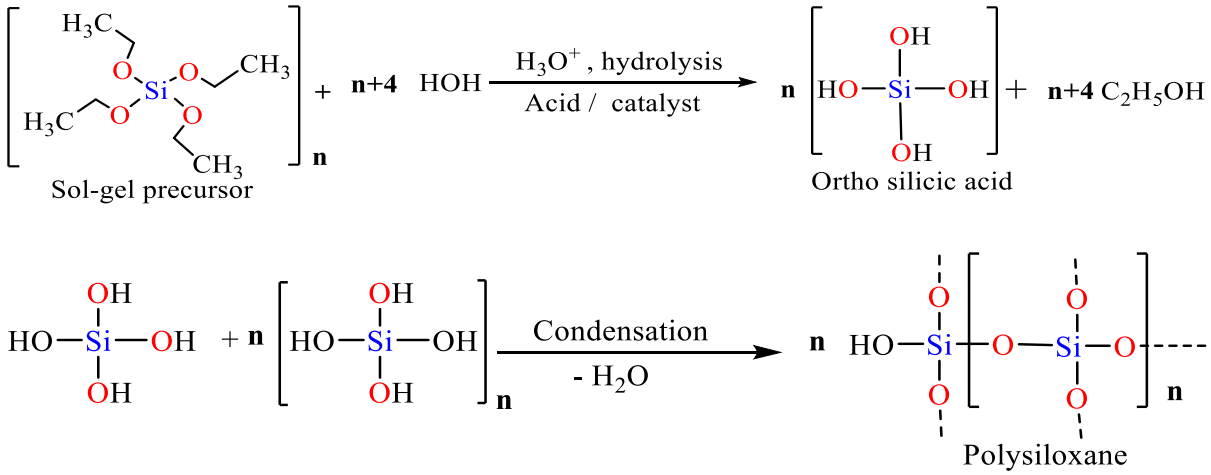
2. MATERIAL AND METHODS

In the process of synthesis, the silicon precursor tetraethoxysilane (98%, Jiangxi, China), ethanol (96.4%), the surfactant polyethylene glycol-6000 (Jiangxi, China) and $TiCl_4$, Al_2O_3 of the chemically pure qualification were used as templates.

Sol-gel technology was used to synthesize sorbent samples from tetraethoxysilane. Sol-gel processes are the most effective methods for producing porous nanomaterials, which have a number of advantages, such as simplicity of the device, efficiency, environmental safety, and low cost. This is also of practical importance due to the possibility of introducing functional monomers, polymers, and metal oxides with variable valence into the reaction system [9, 10].

The preparation of mesoporous sorbent samples is based on the formation of a sol as a result of hydrolysis of tetraethoxysilane in an aqueous solution under acidic conditions and the reaction of its polycondensation with the formation of a polymer with siloxane groups.

The synthesis of a mesoporous material based on SiO_2 was carried out according to the following scheme:



During the synthesis, various reagent samples were obtained at the TEOS: C_2H_5OH: H_2O: HCl = 1: 4: 4: 0.01 mol ratio at temperatures of 35 °C and 50 °C. 5 ml of an alcoholic solution of PEG-6000 was added to distilled water and stirred for 30 minutes until a homogeneous solution was formed. Then, the HCl solution was added to the mixture with stirring until pH = 2. TEOS in ethanol solution was added dropwise to the resulting solution over 10 minutes. 0.75 mol of $TiCl_4$ and Al_2O_3 were added to the solution to ensure thermal stability of the obtained sorbents and increase their surface. The solution was placed in a thermostat and kept until a white suspension was formed. The resulting gel was washed several times with distilled water, dried at 120 °C for 2 h. The dried white powder was calcined in an oven at 600 °C for 8 h. The physicochemical properties of the obtained samples were studied.

3. RESULTS AND DISCUSSION

The phase composition and structure of mesoporous sorbents were studied on a Pananalytical Empyran X-ray diffractometer (XRD). To obtain diffraction patterns of XRD, CuKα-

radiation (β-filter, Cu, current mode 1.5406 A° and voltage applied to the tube 30 mA and 30 kV, respectively) and a detector was used at a constant rotation speed of 4 deg / min with a step of 0.02° (compatibility ω / 2 θ), and the scanning angle was changed from 0° to 90° (Figure 1).

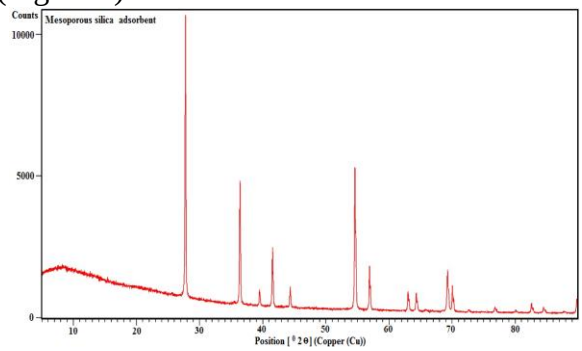


Figure 1. X-ray diffraction pattern of a mesoporous sorbent based on tetraoxysilane and TiO_2

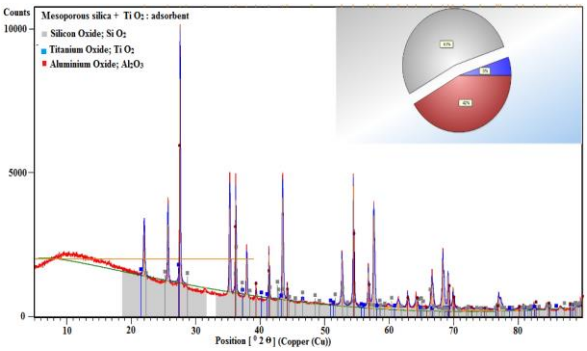


Figure 2. Phase composition of a mesoporous sorbent based on tetraoxysilane and TiO_2

The phase composition of the samples was analyzed by a semi-quantitative method based on calibration standards [11, 12] (Figure 2).

As it can be seen from the data presented, the phase composition of the sample consists of SiO_2, TiO_2, Al_2O_3.

The geometric characteristics of the samples, established by the SEM method, show that, in terms of pore size, they belong to mesoporous materials (D = 2.6 ± 6.5 nm) (Fig. 3, 4). Based on the analysis of the figures, it was found that the mesoporosity of the samples is 85-90%.

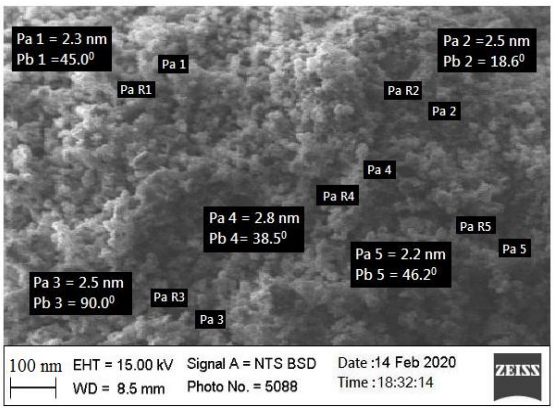


Figure 3. Surface of mesoporous sorbent obtained at 35 °C

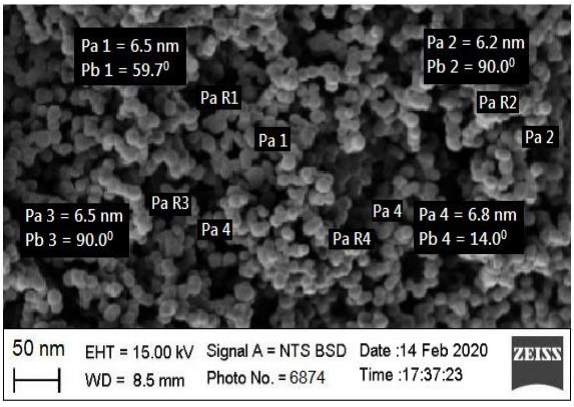


Figure 4. Surface of the mesoporous sorbent obtained at 50 °C

On the basis of the data obtained, the optimal conditions for the synthesis of a mesoporous material were found: the ratio TEOS: C_2H_5OH: H_2O: HCl = 1: 4: 4: 0.01, the temperature 35 °C, the gelation time - 4 hours. In this case, the average pore size of SiO_2 is 2.6 ± 0.8 nm.

Sorption isotherms of benzene and water vapors at a temperature of 473 K and a residual pressure of $1.33 \cdot 10^{-3}$ Pa are shown in figure 5.

Based on the data obtained, it can be stated that the synthesized materials and composites, according to the sorption isotherm of IUPAC, belong to the IV class [13, 14].

The sorption of benzene sharply increases at a relative pressure of P / Ps ≈ 0÷0.2 at P / Ps ≈ 0.8÷1.0 an approach to the maximum saturation of the sorbent is observed. In the case of adsorption of water vapor, a sharp increase in sorption is not observed, but hysteresis immediately begins at P / Ps ≈ 0 and continues up to P / Ps ≈ 0.7.

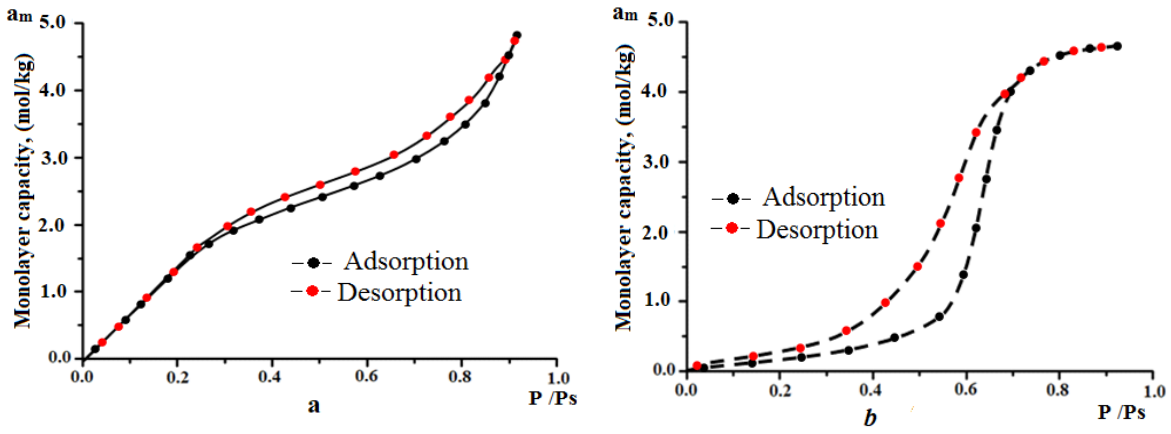


Figure 5. Study of the sorption isotherm of vapors of benzene (a) and water (b) at a temperature of 473 K and a residual pressure of $1.33 \cdot 10^{-3}$ Pa.

Textural characteristics of the synthesized mesoporous sorbents

Synthesis temperature, °C	Ratio of H_2O / TEOS, in moles	Pore volume, V, cm^3 / g	Specific surface, S_{BET}, m^2 / g	Average pore diameter D, nm
35	4:1	0.6 ± 0,3	950 ± 100	2.6 ± 0.8
50	4:1	1.5 ± 0,3	400 ± 30	6.5 ± 0.2

From the above data, it can be seen that at a temperature of 35 °C, the specific surface area is ~ 2 times larger, and the average diameter is 3 times smaller than at 50 °C.

The resulting mesoporous sorbents were used as a sorbent for the gas chromatographic separation of light alkanes, olefins, aromatic hydrocarbons, alcohols, aldehyde, ketones, ethers and esters.

4. CONCLUSION

Thus, the synthesized mesoporous sorbent is characterized by a large specific surface area (700-950 m^2 / g), an average diameter of 2.6-6.5 nm, and a smaller pore volume (0.60-0.90 cm^3 / g). It was found that a hysteresis loop is observed in the mesoporous sorbent during the adsorption of benzene and water vapors. The mesoporous sorbents can be used as a sorbent for gas chromatographic separation and analysis of light alkanes, olefins, aromatic hydrocarbons, alcohols, aldehydes, ketones, ethers and esters.

5. REFERENCES

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