V International Scientific and Technical Conference Actual Issues of Power Supply Systems

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AIPCP25-CF-ICAIPSS2025-00546 | Article

Energy-efficient mesoporous sorbent materials based on silicon dioxide

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Abstract. In this study, a local biowaste-derived product—namely, pure silicon dioxide obtained from rice husk—was utilized. Using the extracted high-purity silicon dioxide and a selected tetraethylammonium hydroxide reagent, the optimal conditions for obtaining a mesoporous sorption material were determined by applying the sol–gel synthesis process. Silicon contained in rice husk was isolated in the form of amorphous silicon dioxide with a high purity of 99.8%, and ordered and controllable mesoporous sorbents were synthesized by introducing the SiO_2–TEAH reagent system. The synthesis was carried out under controlled pH conditions with values of 4, 6, and 9. Regulation of the reaction medium pH during the synthesis—specifically under acidic (pH = 4), neutral (pH = 6), and alkaline (pH = 9) conditions—made it possible to determine the optimal parameters for achieving ordered and controllable mesoporous sorption materials. The incorporation of quaternary alkylammonium salts into silicon dioxide enabled the synthesis of mesoporous sorption materials, thereby expanding the range of new sorbents suitable for industrial applications.

INTRODUCTION

Mesoporous sorbents based on silicon dioxide are distinguished by their well-defined geometric structure, high porosity, and the presence of active sites on their surface [1–5]. The high efficiency of such materials with large specific surface areas lies in their ability to interact with active media at both micro- and macro-scales, enabling their use not only as adsorbents but also as sensors and catalysts. In particular, their application in oil and gas processing industries for the adsorption of active contaminants, water purification, and as carrier platforms for biosensors fully meets current technological demands [6–11]. Another important direction of the research conducted within the framework of this scientific study is the development of modified mesoporous silicate sorbents and their application across various industrial sectors. These include, in particular, the chemical, oil and gas, metallurgical, food, pharmaceutical, and other industries, especially for the treatment of industrial wastewater [12–17]. These sorbents are expected to demonstrate high efficiency in adsorption processes by reducing the concentrations of heavy metal ions (Pb^{2+}, Cd^{2+}, Zn^{2+}, etc.), organic substances (petroleum products, phenol, benzene), as well as mineral salts (NO_3^-, SO_4^{2-}, and others) [18–22].

METHODOLOGY

In this study, scientific and practical approaches were developed for obtaining primary materials with high added value from secondary raw resources. Rice husk, considered a renewable agro-industrial waste, was selected as a source of silicon dioxide, and the optimal conditions for isolating high-purity SiO_2 were determined. The sol–gel process is based on the hydrolysis and polycondensation reactions of silicon-containing compounds, leading to the formation of a colloidal sol and its subsequent transformation into a three-dimensional gel structure. The synthesis process

according to the sol–gel method was carried out under laboratory conditions, and the reagents and auxiliary materials used were selected in compliance with current state standards. In particular, distilled water meeting GOST 6709–72, alkaline reagents conforming to GOST 4328–77, laboratory glassware complying with GOST 25336–82, and measuring and weighing instruments satisfying GOST 24104–2001 requirements were employed. This method enables the synthesis to be conducted at relatively low temperatures and allows precise control over the structural and textural properties of the material. Tetraethylammonium hydroxide (TEAOH) was used as a structure-directing agent (template). TEAOH ions promote the ordered assembly of Si–O–Si units, facilitating the formation of a hierarchical mesoporous structure. The hydrolysis and condensation processes were carried out under strict control of the medium pH, temperature, and reaction time. In subsequent stages, the samples were subjected to drying and thermal treatment to remove organic components and stabilize the mesoporous structure. In addition, a modified form of the sol–gel method, namely the Stöber method, was applied to obtain spherical and monodisperse silicon dioxide particles. This method is based on the controlled hydrolysis and condensation reactions of silicon compounds in an alcoholic medium in the presence of an alkaline catalyst. The Stöber method allows effective control over particle size, morphology, and uniform distribution. During the synthesis, the effects of catalyst concentration, solvent composition, and reaction time on the nucleation and growth mechanisms of the particles were investigated. The obtained products were purified through repeated centrifugation and washing with distilled water and ethanol, followed by drying. The synthesized mesoporous silicate sorbents were analyzed using physicochemical and colloid-chemical methods. All experiments were conducted under standard laboratory conditions, ensuring the reproducibility and reliability of the results.

EXPERIMENTAL RESEARCH

Silica (SiO_2) and sodium carbonate (Na_2CO_3) were selected as the initial reagents. By heating them in a muffle furnace at 1100°C with a molar ratio of 1:1.17, a glassy melt, namely sodium silicate (Na_2SiO_3), was obtained (fig.1). During this reaction, the release of CO_2 gas was observed, which enhances the thermodynamic driving force of the process.

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2\uparrow \quad (1)$$

Subsequently, a 6 wt.% Na_2SiO_3 solution was prepared from the obtained glassy melt. For this purpose, 48 g of the glassy melt was added to 752 g of distilled water and stirred on a magnetic stirrer at 90–100°C until complete dissolution of the melt. The resulting clear silicate solution was then filtered. The filtered Na_2SiO_3 solution was mixed with the template tetraethylammonium hydroxide (TEAOH) at 40°C for 30 minutes using a magnetic stirrer. At this stage, TEAOH acts as an organic template, controlling the size and structure of the mesopores, while the formation of silicic acid gel (H_2SiO_3) is targeted, which constitutes the main structure-forming phase of the mesoporous framework. As a result of the reaction, the following products are formed:

$$TEAOH \rightleftharpoons TEA^+ + OH^-$$

$$\equiv Si–OH + TEAOH \rightleftharpoons \equiv Si–O^- \cdot TEA^+ + H_2O \quad (2)$$

The basic nature of TEAOH helps to maintain the stability of the pH of the reaction medium. Subsequently, acetic acid (CH_3COOH) is added dropwise in order to reduce the pH of the medium and to promote structure formation

$$Na_2SiO_3 + 2CH_3COOH \rightarrow 2CH_3COONa + H_2SiO_3 (\approx H_4SiO_4) \quad (3)$$

$$TEAOH + CH_3COOH \rightarrow TEA^+CH_3COO^- + H_2O \quad (4)$$

H_2SiO_3 is a silicon oxide gel with an amorphous structure, and its modification is widely used for the preparation of sorbent materials. At this stage, proper gel formation is of decisive importance for ensuring the stability and uniformity of the pore structure in subsequent steps. To further optimize the reaction medium, an aqueous ammonia solution (NH_4OH) was introduced in a 1:1 ratio. This mixture ensures continuous structure development and the formation of a porous framework.

$$CH_3COOH + NH_4OH \rightarrow NH_4CH_3COO + H_2O \quad (5)$$

$$H_4SiO_4 \rightarrow SiO_2 \cdot nH_2O + (2-n)H_2O \quad (6)$$

The acetates present in the solution, namely $TEA^+CH_3COO^-$ and NH_4CH_3COO, are soluble in water, resulting in purification of the gel. After repeated filtration, the material was dried at 25°C and subsequently washed with aqueous solutions of $[(C_2H_5)_4N^+CH_3COO^-]$ and NH_4OH, as well as with distilled water at 60°C. At this stage, excess ions, impurities, and residual organic species were removed. In the final stage of the synthesis, the obtained material was calcined in a muffle furnace at 400°C for 2 hours. During this process, the template (TEAOH) was completely decomposed, leaving a stable mesoporous structure.

$$[\equiv Si–O^- \cdot TEA^+] + O_2 \rightarrow \equiv Si–O^- + CO_2 + H_2O \quad (7)$$

$$(CH_3COO^- salts) + O_2 \rightarrow CO_2 + H_2O \quad (8)$$

As a result, a mesoporous sorbent material (MSM) with high porosity and an active surface was successfully synthesized. The acetates present in the solution ($TEA^+CH_3COO^-$ and NH_4CH_3COO) are readily soluble in water, leading to effective purification of the gel. In the subsequent stage, a calcination process is carried out, during which the following transformations occur:

$$[\equiv Si–O^-\cdot TEA^+] + O_2 \rightarrow \equiv Si–O^- + CO_2 + H_2O + \text{volatile amines},$$

$$CH_3COO^- \text{ (including its salts)} + O_2 \rightarrow CO_2 + H_2O + \text{volatile decomposition products.}$$

Pure-composition silicon dioxide obtained via the sol–gel method, together with tetraethylammonium hydroxide selected as an ionic structure-directing agent, served as the key templating component in the synthesis of silicate sorbents featuring a hierarchically organized mesoporous structure.

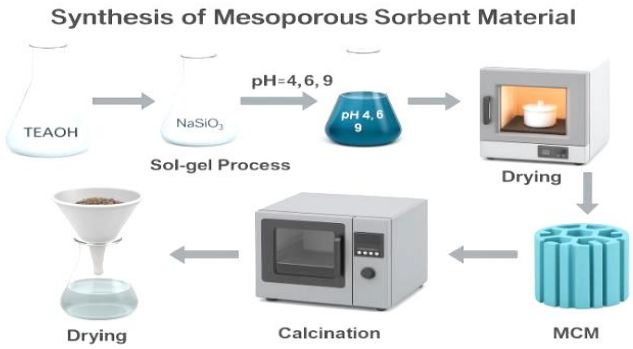

FIGURE 1. Synthesis of a mesoporous silicate material in the presence of silicon dioxide and a template

1.5–6 wt.% Na_2SiO_3 solution; 2. Addition of TEAOH as a template; 3. Mixing using a magnetic stirrer; 4. Filtration of the mixture; 5. Washing of organic species from the pores; 6. Formation of an ordered mesoporous silicate material framework.

RESEARCH RESULTS

During the synthesis process, the pH of the reaction medium was controlled under three different conditions: initially at pH 4 (acidic), pH 6 (neutral), and pH 9 (alkaline) (fig.2). The purpose of this approach was to regulate the structure of the silicic gel, its interaction with the selected template agent, and the degree of crystallinity by studying the influence of the reaction environment. The mechanism of interaction between SiO_2 and TEAOH as a function of the pH of the medium is shown in Figure 1. At pH 4, hydrolysis proceeds rapidly while condensation occurs more slowly, which promotes the formation of an ordered arrangement of mesoporous silicate materials.

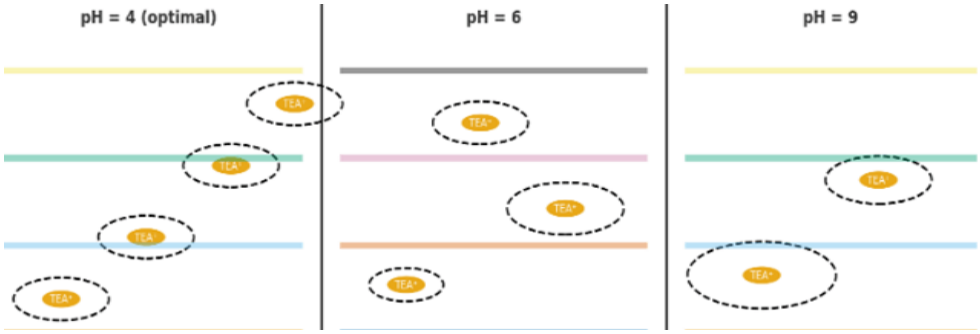

FIGURE 2. Mechanism of interaction between SiO_2 and TEAOH depending on the pH of the medium

In the subsequent stages of the study, hydrolysis and condensation at pH 6 proceeded at a moderate rate, resulting in a mesoporous silicate material structure with randomly arranged ordering. At a critical pH of 9, condensation occurred very rapidly, leading to the formation of heterogeneous porosity. Overall, during the sol–gel synthesis process, the interaction mechanism between SiO_2 and TEAOH under acidic conditions (pH 4) favored the formation of ordered mesoporous materials, which was therefore selected as the optimal synthesis condition. Throughout the study, the synthesized sorbent materials were analyzed to determine their physicochemical and colloid-chemical characteristics. Physicochemical analysis included X-ray phase analysis, FTIR spectroscopy, as well as morphological examination using TEM and SEM imaging. Additionally, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were conducted to evaluate mass loss and the effect of temperature on the mesoporous sorbents.

CONCLUSIONS

Thus, based on the method of obtaining amorphous silicon dioxide from rice husk waste, high-purity amorphous silicon dioxide was successfully extracted and used for the synthesis of mesoporous silicate materials. A technology was developed for the synthesis of ordered and controllable mesoporous sorbents by applying the SiO_2–TEAOH template to amorphous silicon dioxide with a purity of 99.8%, isolated from rice husk as the silicon source. The incorporation of quaternary alkylammonium salts into silicon dioxide enabled the production of mesoporous sorbent materials capable of effectively removing petroleum products from industrial wastewater, thus creating opportunities for environmental remediation applications in various industries.

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