Conference materials
UDC 54.057
DOI: https://doi.org/10.18721/JPM.163.232

Hard-template synthesis of monodisperse spherical microporous SiO_2 particles

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Abstract. A simple and facile method for the synthesis of monodisperse microporous spherical silica particles is proposed. The method is based on a traditional Stöber technique with the use of ammonium metavanadate acting as a hard template for the micropore formation. The thus obtained silica particles possess an interconnected system of micropores that determines high values of their specific surface area (up to 320 $m^2 g^{-1}$) and pore volume (up to 0.25 $cm^3 g^{-1}$). The use of the Stöber method allows obtaining highly monodisperse spherical particles with the standard size deviation not exceeding 5%. The particles with an average diameter of 250 nm exhibit high sedimentation and aggregation stability and form stable hydrosol, which is important from the practical point of view.

Keywords: Porous silica, monodispersity, template method, ammonium metavanadate, microporosity

Funding: This work was funded by the Russian Science Foundation, project 23-79-00018.

Citation: Eurov D.A., Kirilenko D.A., Stovpiaga E.Yu., Kurdyukov D.A., Hard-template synthesis of monodisperse spherical microporous SiO_2 particles, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 188–193. DOI: https://doi.org/10.18721/JPM.163.232

Материалы конференции
УДК 54.057
DOI: https://doi.org/10.18721/JPM.163.232

Темплатный метод синтеза монодисперсных сферических микропористых частиц SiO_2

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Аннотация. Предложен простой и технологичный метод синтеза монодисперсных микропористых сферических частиц аморфного кремнезема. Метод основан на традиционной методике Штобера с применением метаванадата аммония в качестве темплата, используемого для формирования микропор. Показано, что полученные частицы содержат внутреннюю систему взаимосвязанных микропор, что обуславливает их большую удельную поверхность (320 $м^2 г^{-1}$) и объем пор (0.25 $см^3 г^{-1}$). Использование метода Штобера позволяет получать монодисперсные сферические частицы со среднеквадратичным отклонением размеров, не превышающим 5%. Частицы со средним размером 250 нм обладают седиментационной и агрегативной устойчивостью и образуют стабильную водную суспензию, что важно с практической точки зрения.

Ключевые слова: пористый кремнезем, монодисперсность, темплатный метод, метаванадат аммония, микропористость

Финансирование: Работа выполнена за счет гранта Российского научного фонда № 23-79-00018.

Ссылка при цитировании: Еуров Д.А., Кириленко Д.А., Стовпяга Е.Ю., Курдюков Д.А., Темплатный метод синтеза монодисперсных сферических микропористых частиц SiO_2 // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 188–193. DOI: https://doi.org/10.18721/JPM.163.232

Introduction

In today's world high-capacity inflammable and ecologically safe microporous materials are in high demand across various industries [1]. Materials of this kind are used, for example, in selective adsorption [2], catalysis [3], and as molecular sieves [4]. Zeolites and $AlPO_4$ are widely used microporous materials possessing a specific surface area (SSA) of up to 600 m^2g^{-1} and pore volume (V_p) of up to 0.4 cm^3g^{-1} [5]. Amorphous silica (a-SiO_2) has a number of advantages such as fast and facile synthesis, high thermal and chemical stability [6], low toxicity [7], which makes it promising as an alternative for creating microporous materials. The main way to synthesize silica particles (SP) is the Stöber method [8], which is based on a hydrolysis of tetraethyl orthosilicate (TEOS) in an NH_3-H_2O-C_2H_5OH medium and allows obtaining highly monodisperse (with standard size deviation less than 3%) spherical particles of a-SiO_2. However, the thus obtained particles are nonporous. There are two approaches to forming micropores within the silica particles: post-synthetic treatment of nonporous SPs or modification of the Stöber process by changing the composition of the reaction mixture. For example, the authors of [9] showed that a treatment of nonporous SPs in alcoholic solutions yields microporous silica particles with micropore V_p of up to 0.16 cm^3g^{-1} and SSA of up to 380 m^2g^{-1}. It was shown in [10] that the replacement of 80% of TEOS with aminopropyltriethoxysilane containing an unhydrolyzable pore-forming aminopropyl group yields microporous silica particles with SSA ~130 m^2g^{-1} and V_p ~0.1 cm^3g^{-1}. Addition of [3-(methacryloyloxy)propyl] trimethoxysilane with an unhydrolyzable methacryloyloxypropyl (MP) group to the reaction mixture made it possible to obtain particles with SSA of up to 950 m^2g^{-1} and V_p of up to 0.8 cm^3g^{-1} [11,12]. Micropores within the particles obtained are frequently isolated from each other, which makes it difficult to obtain large values of specific surface area and pore volume. Molecules of adsorbate (e.g., N_2) cannot penetrate inside the pores and they are not included into the useful volume of the particles. Thus, the development of a method for obtaining microporous silica particles with interconnected pore structure is an urgent technological problem. In the present study, an approach is implemented to synthesizing monodisperse spherical microporous silica particles by Stöber process with the use of ammonium metavanadate as a porogen for the first time.

Materials and Methods

Materials. Vanadium (V) oxide, V_2O_5, 99.95% (Sigma-Aldrich, Germany); tetraethyl orthosilicate, $Si(OC_2H_5)_4$, 99% (Acros Organics, Germany); aqueous ammonia, NH_3, 24 wt%, 99.99%; ethanol, C_2H_5OH, 95 wt%; deionized (DI) water, H_2O with a resistance of 10 MΩ. All the chemicals were of analytical purity grade commercially available. There was no need to additionally purify the reagents.

Methods. The procedure used for synthesis of microporous silica particles with the use of ammonium vanadate as a hard template is similar to that employed for synthesis of submicron monodisperse silica particles (Stöber-Fink-Bohn method [8]). A weighed portion of TEOS (2 g) was added to a concentrated solution (0.5 L) of ammonium metavanadate in a mixture C_2H_5OH–NH_3–H_2O under stirring at room temperature. After 5 h of further stirring, the particles obtained were centrifuged, washed with DI water, and dried under the ambient conditions at 100 °C for 2 h.

Transmission electron microscopic measurements were performed using a Jeol JEM-2100F microscope (accelerating voltage 200 kV, point-to-point resolution 0.19 nm) equipped with Bruker XFlash 6T-30 energy dispersive X-ray (EDX) spectrometer. The nitrogen adsorption was performed using a Micromeritics 3FLEX at a temperature of 77 K. The specific surface area was calculated by the Brunauer – Emmett – Teller (BET) method, and the pore size distribution was found using the nonlocal density functional theory (NLDFT). The hydrodynamic diameter of the particles was determined at 25 °C by dynamic light scattering (DLS) using a Zetasizer Nano ZS analyzer.

Results and Discussion

The silica particles were synthesized by hydrolysis of TEOS in a concentrated solution of ammonium metavanadate in a H_2O-C_2H_5OH-NH_3 mixture traditionally used in Stöber process [8]. To obtain a solution of NH_4VO_3 a weighed portion of commercially available V_2O_5 powder was dissolved in a H_2O-C_2H_5OH-NH_3 mixture heated to 60°C under ultrasonic agitation, which leaded to the formation of saturated aqueous-alcoholic solution of ammonium metavanadate. After that TEOS was added to the obtained solution, as a result of hydrolysis of which spherical particles of amorphous silica were formed.

The synthesis conditions similar to those in the Stöber process (namely reaction mixture composition, temperature and time) allowed obtaining highly monodisperse spherical silica particles. Fig. 1 shows typical TEM images of the particles obtained. It can be seen (Fig. 1,*a*) that the particles have spherical shape and the same size. The large object in the bottom left corner is, most likely, comprised of several particles lying on top of each other. An average diameter of the particles was found to be 250 nm with the size deviation less than 5%. On the enlarged image of a single particle (Fig. 1,*b*) one can clearly see that the synthesized silica particles possess a spongy structure, which indicates the presence of pores. This is confirmed by the results of nitrogen porosimetry.

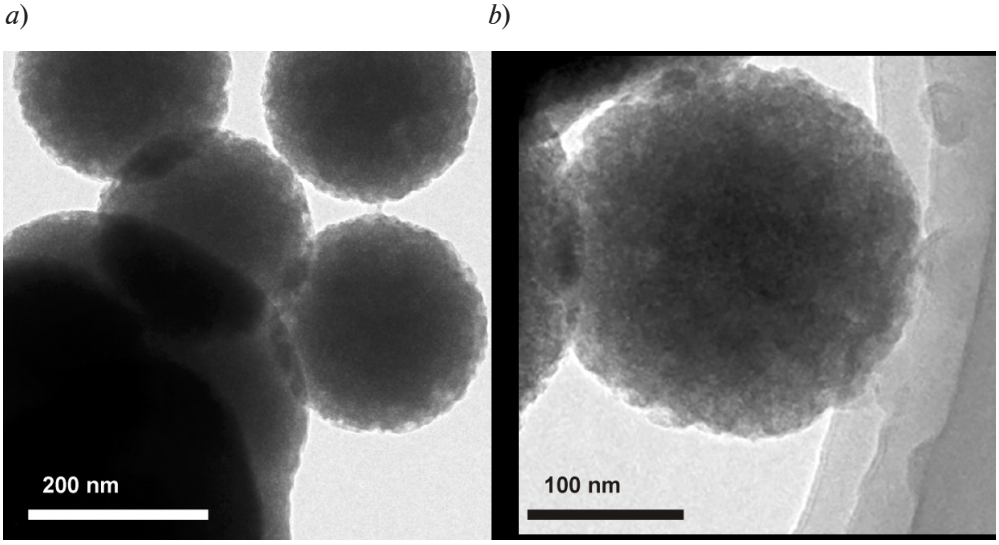

Fig. 1. TEM images of silica particles synthesized using NH_4VO_3 as a hard template

Fig. 2,*a* shows N_2 adsorption-desorption isotherms for the particles obtained. It can be seen that the isotherm has a shape characteristic of microporous materials. The specific surface area of the particles calculated in the pressure range $0.05 \leq p/p_0 \leq 0.20$ by the BET method was found to be 320 $m^2\ g^{-1}$. The pore volume was 0.25 $cm^3\ g^{-1}$. The pore size distribution (Fig. 2,*b*) demonstrates a well pronounced peak with a maximum at ~1 nm. Apparently, NH_4VO_3 present in the solution acts as a template for the formation of micropores. During SiO_2 formation the polycondensation of silicic acid monomers with non-hydrolyzed $\equiv V-O^-$ and hydrolyzed $\equiv V-OH$ groups present in solution, presumably, can take place. In an alkaline medium condensation can proceed as follows:

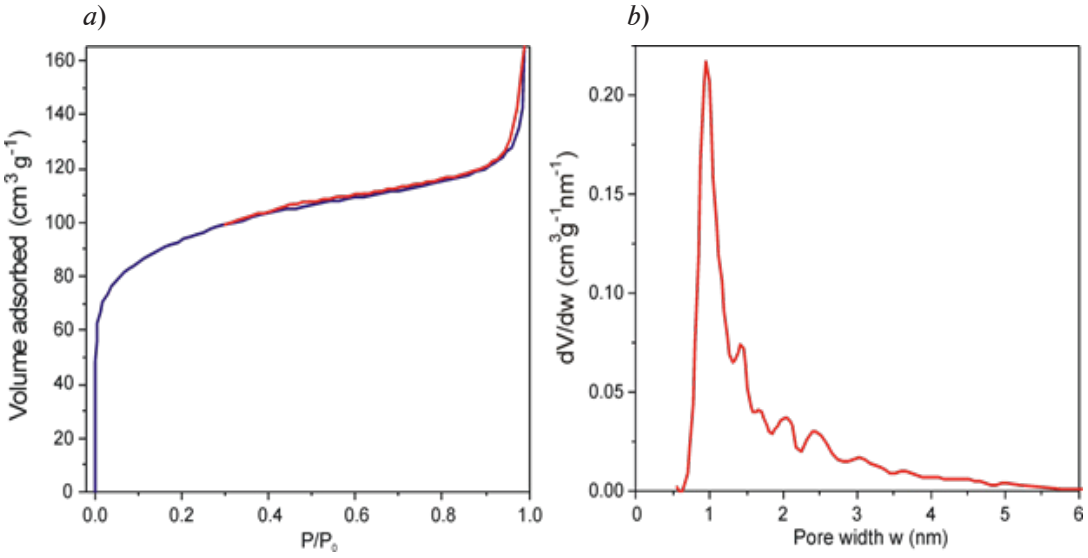

Fig. 2. N_2 adsorption and desorption isotherms at 77 K (*a*) and pore size distribution (*b*) for silica particles synthesized using NH_4VO_3 as a hard template

$$\equiv V\text{–}O^- + H_4SiO_4 \leftrightarrow \equiv V\text{–}O\text{–}Si(OH)_3 + OH^-$$

$$\equiv V\text{–}OH + H_3SiO_4^- \leftrightarrow \equiv V\text{–}O\text{–}Si(OH)_3 + OH^-$$

$$\equiv V\text{–}OH + H_4SiO_4 \leftrightarrow \equiv V\text{–}O\text{–}Si(OH)_3 + H_2O$$

Similar interaction with the formation of V-O-Si bonds was observed for various silica-supported vanadium complexes [13].

Next, the silica produced as a result of TEOS hydrolysis can adsorb ions from a saturated ammonium metavanadate solution with the formation of associates of hydrated amorphous SiO_2 with VO_3^- and NH_4^+. Due to the high concentration of NH_4VO_3 in the reaction mixture the silica contains, apparently, not individual ions but associated complexes of several vanadium-containing species. After the synthesis the obtained particles are washed with water, as a result of which the dissolution of the complexes occurs with the formation of voids in their place – micropores. The results of the elemental EDX analysis confirm the complete removal of the vanadium from the particles at the washing stage. Moreover, the obtained values of specific surface area and pore volume of the particles synthesized allow concluding that they contain not isolated micropores, but their interconnected system.

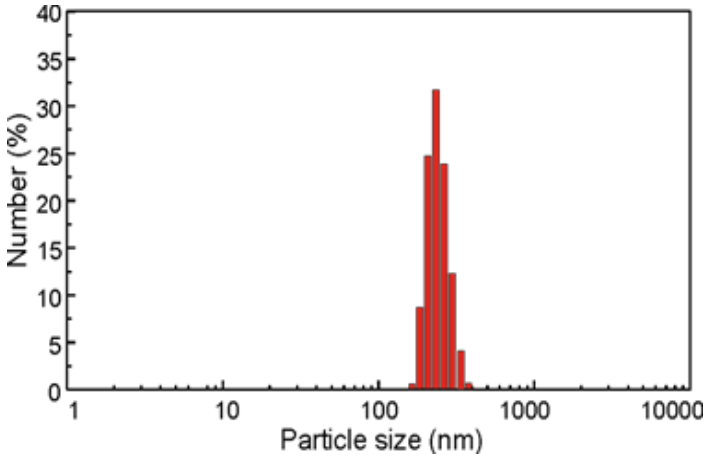

Fig. 3. DLS size distribution for the obtained silica particles

Fig. 3 shows the results of the DLS measurements. An average diameter of the particles was found to be 265 nm, while the PDI value was as low as 0.07. Note, that the value of the particle diameter measured from DLS data correlates with that obtained from TEM measurements. According to DLS the standard size deviation of the fabricated particles does not exceed 5%, which together with the results of TEM and nitrogen porosimetry measurements confirms that the applied approach allows obtaining highly monodisperse spherical silica particles with an interconnected system of micropores.

It is worth noting that the synthesized particles exhibit high sedimentation and aggregative stability, which provides the formation of a stable hydrosol. These advantages together with high monodispersity of the particles make them promising materials for use, for example, as sorbents, which will have identical properties such as adsorption capacity, selectivity, kinetics of adsorption/desorption and hydrodynamic properties.

Conclusion

An approach was proposed for the synthesis of SiO_2 particles by Stöber method with the use of ammonium metavanadate as hard template, which made it possible to obtain highly monodisperse spherical silica particles possessing microporous structure. The standard deviation of the particle diameter does not exceed 5%. Micropores within the particles form an interconnected system resulting in high values of SSA (~320 $m^2 g^{-1}$) and V_p (~0.25 $cm^3 g^{-1}$) of the particles. The monodispersity and the high sedimentation and aggregative stability of the particles provide the formation of a stable hydrosol and allow obtaining materials with identical geometrical and hydrodynamic characteristics, which makes the obtained particles promising, for example, in adsorption or catalytic applications.

Acknowledgments

The TEM study was carried out on equipment of the Federal Joint Research Center “Material science and characterization in advanced technology”.

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Received 07.07.2023. Approved after reviewing 19.07.2023. Accepted 27.07.2023.