

甲基三甲氧基硅烷基 SiO_2 气凝胶骨架尺寸调控及 对有机液体的吸附特性

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摘 要: 骨架尺寸对气凝胶的吸附性能具有显著影响。通过改变十六烷基三甲基溴化铵(CTAB)的含量, 在纯水中合成了骨架尺寸可控的甲基三甲氧基硅烷(MTMS)基 SiO_2 气凝胶(MSA)。结果表明: CTAB 含量的变化对 MSA 的表面化学组成无显著影响, 但 MSA 的骨架尺寸和孔径均随 CTAB 含量的增加而减小。当 CTAB 含量从 0.01 g 增加到 0.03 g 时, MSA 平均骨架直径从 2.39 μm 减小到 0.55 μm , 且 MSA 对有机液体的吸附量下降。当 CTAB 含量为 0.01 g 时, MSA 对醇类和烷烃类表现出良好的吸附性能, 最大吸附量达 10 g/g, 泵吸附速率达到 1.04 g/s, 有机液体毛细上升速率可达 2.1 mm/s。此外, MSA 的高热稳定性(456 $^{\circ}\text{C}$)可确保实现热脱附。合成骨架尺寸可控 MSA 的方法为获取特异性吸附性能的气凝胶材料提供了新途径。

关键词: 二氧化硅气凝胶; 甲基三甲氧基硅烷; 吸附; 毛细上升

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Methyltrimethoxysilane Based Silica Aerogels with Controllable Skeleton Size and Their Adsorption Characteristics for Organic Liquids

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Abstract: Methyltrimethoxysilane (MTMS) based silica aerogels (MSA) with a controllable skeleton size were synthesized in pure water via adjusting the cetyltrimethylammonium bromide (CTAB) content. The results show that the content of CTAB has little effect on the surface chemical composition of MSA, while the skeleton size and pore size of MSA decrease with increasing the CTAB content. The average skeleton diameter (d) of MSA decreases from 2.39 μm to 0.55 μm , and the adsorption capacity for organic liquids decreases simultaneously when the CTAB content increases from 0.01 g to 0.03 g. When the CTAB content is 0.01 g, the as-prepared MSA has good adsorption properties for alcohols and alkanes, where the maximum adsorption capacity reaches 10 g/g, the adsorption rate of the pumping application is 1.04 g/s, and the capillary rise speed of organic liquids can reach 2.1 mm/s. Furthermore, the high thermal stability (456 $^{\circ}\text{C}$) of MSA ensures the realization of thermal desorption. A preparation method of MSA with a controllable skeleton size to obtain aerogels with specific adsorption properties.

Keywords: silica aerogels; methyltrimethoxysilane; adsorption; capillary rise

1 Introduction

With the rapid development of technologies, a variety of organic solvents participate in the production processes with increasingly important roles. Simultaneously, the surge of industrial wastewater and the leakage of those insoluble organic liquids show threats to

the environment and human health^[1]. These circumstances request an urgent need to develop new materials and new technologies for the efficient treatment of organic liquids.

Several methods have been proposed previously to treat industrial wastewater or recycle organic solvents from aqueous solution, such as membrane separation^[2],

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centrifugal separation^[3], adsorption^[4–7], ion exchange^[8], electrodialysis^[9] and biodegradation^[10]. Among these methods, the adsorption recognized as one of the most effective and popular ways to show the advantages of collection, low energy requirement, design flexibility, operational simplicity, and low cost. The materials used for the adsorption include activated carbon^[11–13], expanded graphite^[14], metal oxides^[15], and other porous materials^[16–18].

Due to their fascinating characteristics, such as low density, high specific surface area and high porosity, silica aerogels show great potential for those adsorption applications^[19–21]. For example, Gurav et al^[22] synthesized tetraethoxysilane (TEOS) based silica aerogels and investigated their adsorption capacities of those organic liquids. Guo et al^[6] fabricated methylsilsesquioxane aerogels and employed them for oil/water separation. According to the principle of like dissolves like, hydrophobic and oleophilic silica aerogels are regarded as the ideal adsorbents for those organic liquids.

To obtain the hydrophobic silica aerogels, the common method is surface modification by grafting organic groups onto the network skeletons of silica aerogels. Another method is to adopt some specific silicon sources which carry the non-hydrolytic methyl groups, such as silica aerogels (MSA), which exhibit nice hydrophobicity without further surface modification, creating the chemical and structural basis of absorbing organic liquids. Some studies^[4, 23] have made effort to expand the adsorption application of the MSA. However, the effects of the pore size of MSA on the adsorption capacity of those organic solvents are rarely investigated.

For practical applications, acquiring MSA with controllable skeleton and pore sizes are significant, which means that the adsorption characteristics can be customized. In this study, the MSA were prepared in pure water and the skeleton and pore sizes were tailored by adjusting the cetyltrimethylammonium bromide (CTAB) contents. In order to grasp the adsorption characteristics of as-prepared MSA, the basic physicochemical properties, especially the variation of skeleton and pore sizes with the CTAB content, were studied firstly. Further, the static adsorption and dynamic adsorption (containing pumping application and capillary rise behavior) were also investigated.

2 Experimental

2.1 Materials and preparation

Methyltrimethoxysilane (MTMS, 98%) and cetyltrimethylammonium bromide (CTAB, 99%) supplied by the Aladdin company (China) were used as the precursor and surfactant, respectively. Hydrochloric acid (HCl, 36%–38%) and ammonia water (NH₃·H₂O, 25%–28%) provided by Sinopharm Chemical Reagent Co., Ltd (SCRC, China) were used as the acidic and alkaline catalyst, respectively. Methanol (MeOH, ≥99.5%), ethanol (EtOH, ≥99.7%), isopropanol (IPA, ≥99.7%), n-hexane (≥97.0%)

and n-heptane (≥98.5%) from the SCRC were selected as the adsorbates without further purification. Deionized water (Di-H₂O) was provided by an ultra-pure water machine (Direct-Q 3UV, Merck Millipore).

A typical MTMS aerogel was prepared by using 5 mL MTMS, 30 mL of Di-H₂O, 0.010 ~0.025 g CTAB, 0.3 mL 0.1 mol/L HCl and 1.0 mL 0.6 mol/L NH₃·H₂O. Firstly, MTMS, H₂O and a certain content of CTAB were mixed in a 100 mL beaker and stirred for several minutes, during which 0.1 mol/L HCl was added into the hybrid solvent. And the mixture was then kept in a water bath at 45 °C. After sufficient hydrolysis for 30 min, 0.6 mol/L NH₃·H₂O was dropped into the solvent during stirring, and the gelation usually occurred within 30 min. Subsequently, the gel was directly put into an oven and dried at 100 °C for 4 h to obtain the MSA.

2.2 Adsorption tests

The porous three-dimensional network structure and high hydrophobicity of the MSA make it a potential candidate for absorbing those organic liquids. The static adsorption experiments at room temperature aim to investigate the adsorption capacities and behaviors of the MSA towards organic liquids. During the tests, about 2 g monolithic MSA was put into a beaker with 50 mL organic solvent. After immersing for several minutes, saturated absorbed MSA was taken out and then weighed. The adsorption capacity (Q) is calculated as follows:

$$Q = \frac{m_e - m_0}{m_0} \quad (1)$$

in which m_0 and m_e are the weights before and after adsorption, respectively. For each organic liquid, the adsorption process was repeated 10 times to test the recycling adsorption capabilities of the MSA.

The dynamic adsorption experiments include the pumping applications and the capillary rise behaviors. Therein, the pumping device as shown in Fig. 1(c) consists of a peristaltic pump (LHZW200, China), a silicone tube with an outer and inner diameter of 7 mm and 5 mm, and a plastic screwed union inlaid in cylindrical MSA. During the preparation of the MSA, a plastic screwed union shown in Fig. 1(a) was put into the sol immediately after adding the basic catalyst and was then fixed after the gelation. Fig. 1(b) presents the cylindrical MSA with a screwed union, which is obtained by drying in an oven at

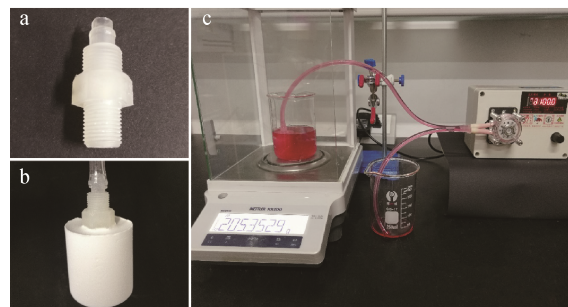


Fig. 1 (a) Plastic screwed union, (b) the cylindrical MSA inserted by a plastic screwed union, and (c) the photo of the pumping system.

100 °C under ambient pressure for about 6 h. The capillary rise behavior is then investigated by inserting the slender cylindrical MSA into the EtOH liquid and measuring the capillary rise height.

2.3 Methods of characterization

The pH values were tested by a waterproof pen tester (7011, EZDO). The bulk density (ρ_b) was measured by the Archimedes principle. And the porosity (ρ_p) was calculated by

$$\rho_p = (1 - \frac{\rho_b}{\rho_s}) \times 100\% \quad (2)$$

where ρ_s is the skeleton density about 2.2 g/cm³ in this study.

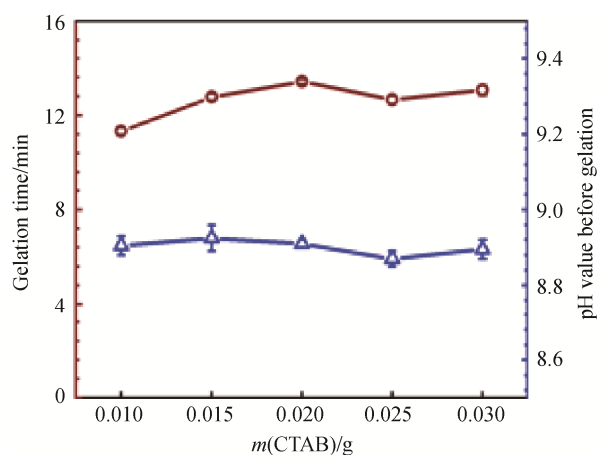
The microstructure of MSA was investigated by a scanning electron microscope (SEM, Nova Nano SEM230, FEI). The hydrophobicity was tested by a contact angle measurement instrument (JC2000D1, Shanghai Zhongchen Instrument), putting a 5 μ L water drop at the surface of the monolithic MSA. The Fourier transform infrared spectroscopy (FTIR) was used to investigate the chemical bonds and chemical groups of MSA by a Nicolet iS50 instrument (Thermo Fisher Scientific) *via* the KBr pellet method. And molecular structure and element content was determined by an X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi, Thermo Fisher Scientific). The thermal stability was evaluated by a thermogravimetry-differential scanning calorimetry (TG-DSC) performed by a simultaneous thermal analyzer (SDT Q600, TA) in the air environment under a heating rate of 20 °C/min.

3 Results and discussion

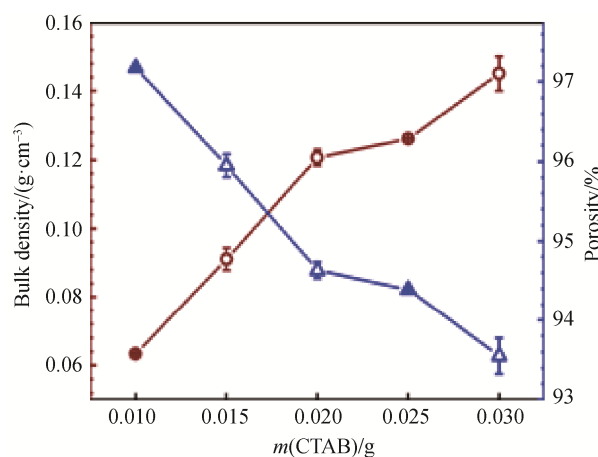
3.1 Basic physicochemical characteristics

As a surfactant, CTAB has been frequently applied to inhibit the phase separation and reduce surface tension in a hybrid solution system^[24]. Fig. 2 exhibits the gelation time, the pH value before gelation, the bulk density and the porosity of MSA along with different CTAB contents. Both gelation time and the pH before gelation vibrates slightly with increased CTAB content. The bulk density increases monotonously with increased CTAB content, while the porosity presents an opposite trend. Furthermore, in Fig. 2(c), the total pore volume decreases significantly along with the CTAB content. These variations have been investigated and reported in our previous work^[25].

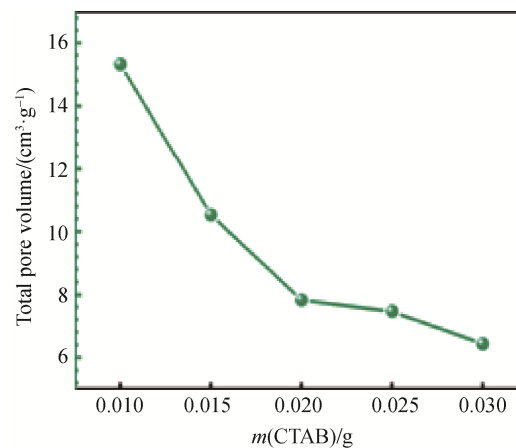
Fig. 3 shows that the porous three-dimensional network structure of the MSA compose of coralloid skeletons. With increased CTAB content, both the skeleton and pore sizes decrease significantly. The skeleton size distribution of the MSA prepared with different CTAB contents were analyzed by ImageJ software^[26], shown in Fig. 4(a)–Fig. 4(e). It further indicates that the increasing CTAB content narrows the skeleton size distribution of the MSA and decreases the average skeleton diameter (d) from 2.39 μ m to 0.55 μ m.



(a) Gelation time and pH values before gelation



(b) Bulk density and porosity of MSA



(c) Total pore volume of MSA

Fig. 2 Basic parameters of MSA prepared with different CTAB contents

Detailed correlation between the CTAB content and the average skeleton size of the as-prepared MSA is plotted in Fig. 4(f), in which the average skeleton size displays a decreasing trend as per the power function along with higher CTAB content. It indicates that the higher CTAB content has an evident inhibitory effect on

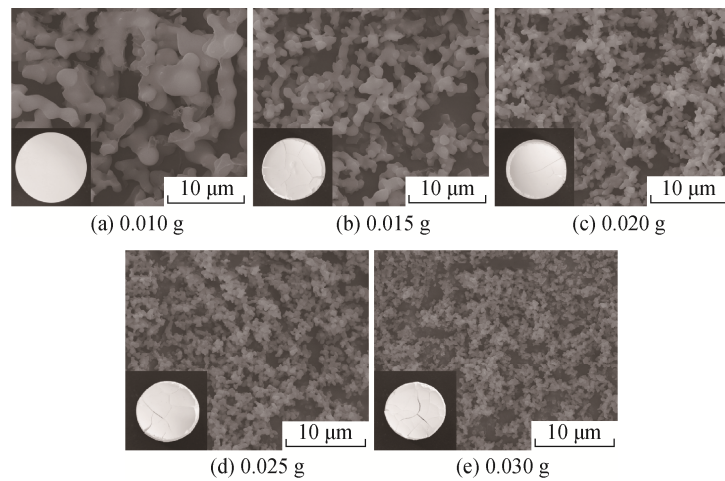


Fig. 3 SEM images of the MSA prepared with different CTAB contents

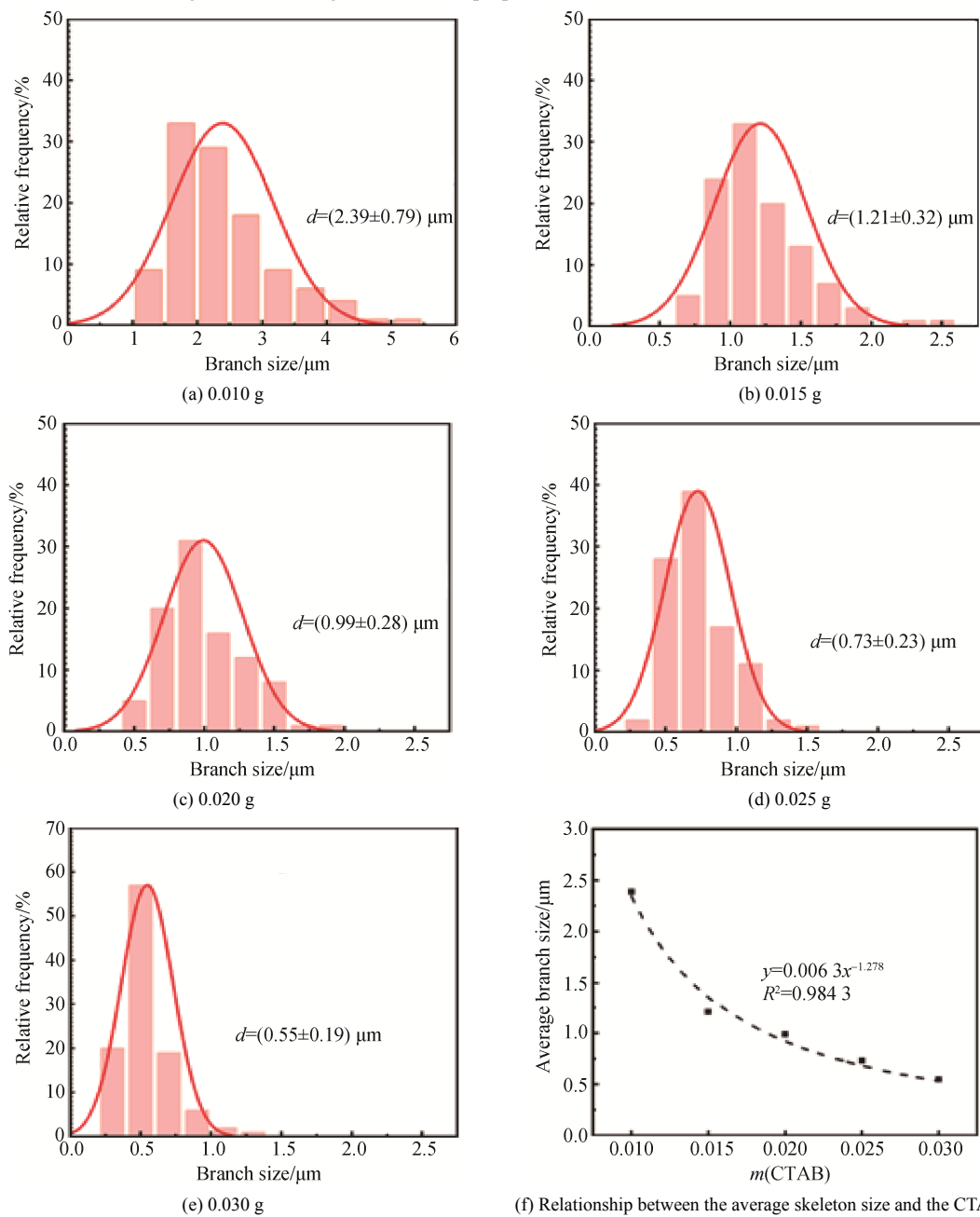


Fig. 4 Skeleton size distribution and the average skeleton sizes of MSA with different CTAB contents

the skeleton size of the MSA. As more CTAB is added into the hybrid solvent, the polycondensation reaction between the hydrolyzed MTMS precursor is intercepted due to the long chain of the CTAB, which further leads to the inhibition of the growth of the skeletons and the Oswald ripening^[27]. As a consequence, the smaller skeleton size is finally generated.

Fig. 5 presents that those MSA prepared with

different CTAB contents all have large contact angles (over 140°), indicating a nice hydrophobicity. The variation of the contact angles illustrates that the CTAB content shows a very limited effect on the hydrophobicity of MSA. To further address the influences of the CTAB on the chemical bonds and surface functional groups of MSA, the FTIR and XPS spectra of the MSA with different CTAB contents are exhibited in Fig. 6.

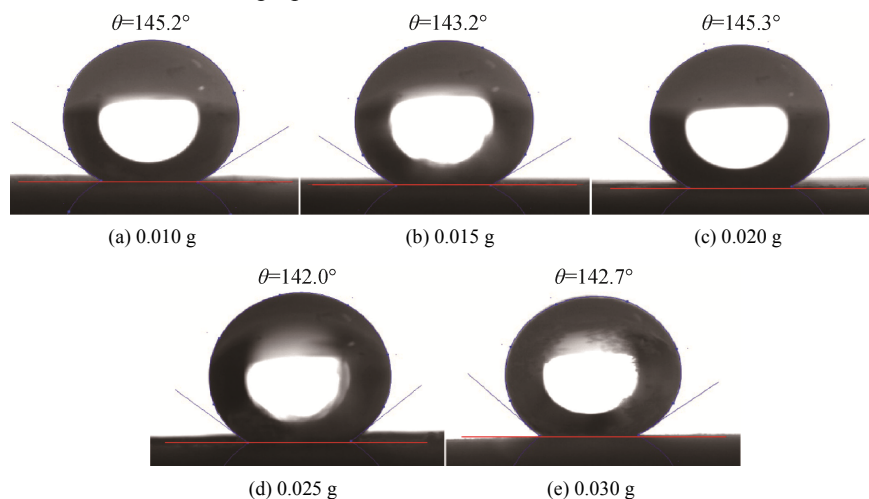


Fig. 5 Contact angles of MSA prepared by different contents of CTAB

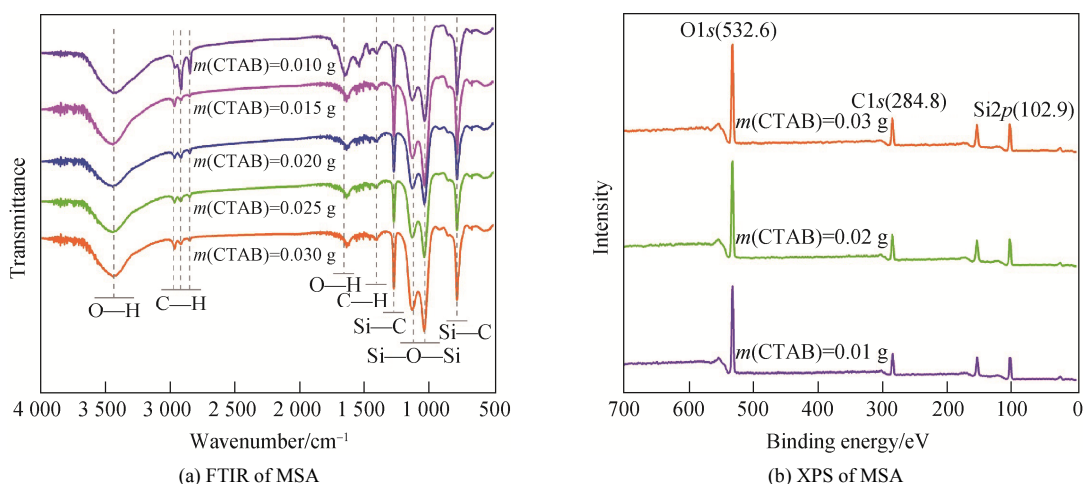


Fig. 6 FTIR and XPS of MSA prepared with different CTAB contents

In Fig. 6(a), two strong peaks observed at $1\,132\text{ cm}^{-1}$ and $1\,035\text{ cm}^{-1}$ are caused by the asymmetric stretching vibration of $\text{Si}-\text{O}-\text{Si}$ bonds^[28]. The broad band around $3\,444\text{ cm}^{-1}$ and the peak at $1\,648\text{ cm}^{-1}$ represent $\text{O}-\text{H}$ bonds from $\text{Si}-\text{OH}$ groups and water, respectively^[29]. The $\text{Si}-\text{C}$ bonds on the aerogel skeletons are confirmed by the narrow peaks appearing at $1\,270\text{ cm}^{-1}$ and 786 cm^{-1} ^[30-31], which are derived from the precursor MTMS. The peaks around at $2\,969\text{--}2\,854\text{ cm}^{-1}$ are attributed to the asymmetric and symmetric stretching of $\text{C}-\text{H}$ bonds, and the peak at $1\,403\text{ cm}^{-1}$ is ascribed to the bending of $\text{C}-\text{H}$ bonds^[32]. The $\text{Si}-\text{C}$ bonds, together with $\text{C}-\text{H}$ bonds, verify the existence of $\text{Si}-\text{CH}_3$ groups, which just constitute the chemical basis for the hydrophobicity of MSA^[33]. In Fig. 6(b), the primary peaks around 532.6 eV is attributed to $\text{O}\,1s$ of oxygen atoms; the peaks around

284.8 eV result from $\text{C}\,1s$ of carbon atoms; and the peaks at 102.9 eV arises from $\text{Si}\,2p$ of silicon atoms^[34]. From the FTIR and XPS spectra, the limited difference was observed among MSA prepared with various CTAB contents. These negligible variations further evidence that CTAB hardly affects the surface chemical composition of the MSA.

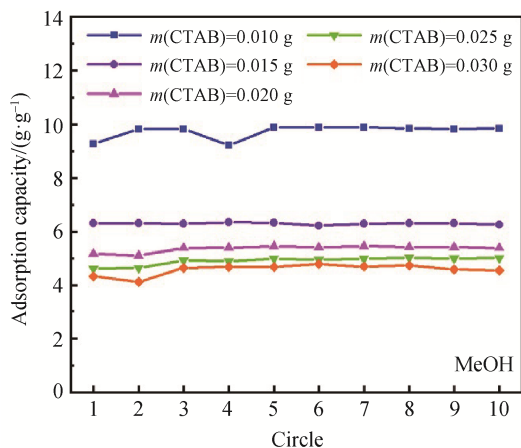
3.2 Static adsorption characteristics

Adsorption which occurs when a solid surface is exposed to a gas or liquid is defined as the enrichment of material or the increase of the density of liquid around the interface^[35]. Unlike that water hardly infiltrate MSA due to the hydrophobicity and low surface energy^[36], organic liquids could wet MSA completely, which can be easily adsorbed by MSA because the organic liquids have lower surface tension and less polarity than water.

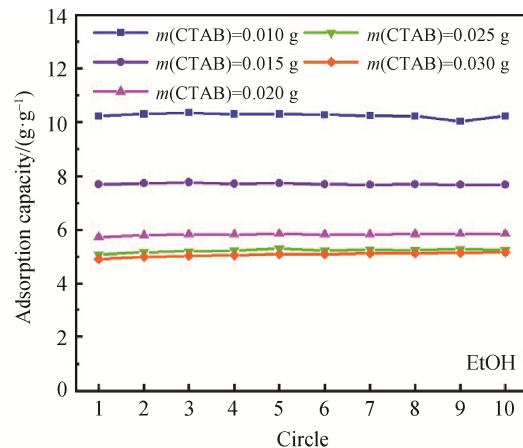
For the static adsorption tests, five organic solvents,

including MeOH, EtOH, IPA, n-hexane and n-heptane, were used in this study, respectively. Fig. 7 shows the cyclic adsorption capacities of MSA prepared with different CTAB contents for the five liquids. It indicates that the adsorption capacities of those MSA among 10 circles are nearly the same without the evident decline of the adsorption capacity, indicating that the MSA shows good recyclability for the adsorption application. As shown in Fig. 7(a)–Fig. 7(e), the adsorption capacity of the MSA decreases obviously with increased CTAB content, because a higher CTAB content could reduce the

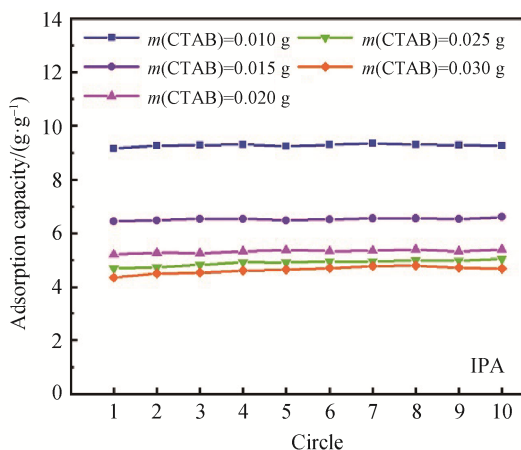
pore volume of MSA significantly (Fig. 2(c)), which results in less accommodation space for the adsorbates. Fig. 7 shows that the adsorption capacity of MSA for the alcohols is higher than that of alkanes. Besides, the adsorption capacities of the MSA with the CTAB of lower than 0.015 g is much larger than those of the MSA with the CTAB of higher than 0.020 g. This indicates the CTAB shows an obvious influence on the adsorption capacity at a certain content. When the CTAB content increases further, the declining degree of the adsorption capacity tends to be flat, as shown in Fig. 7(f).



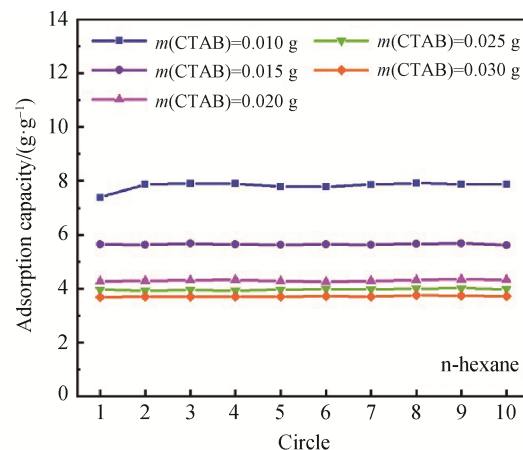
(a) Cyclic adsorption capacities of MSA for MeOH



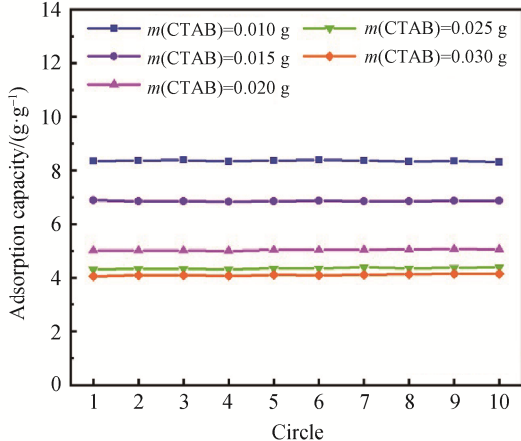
(b) Cyclic adsorption capacities of MSA for EtOH



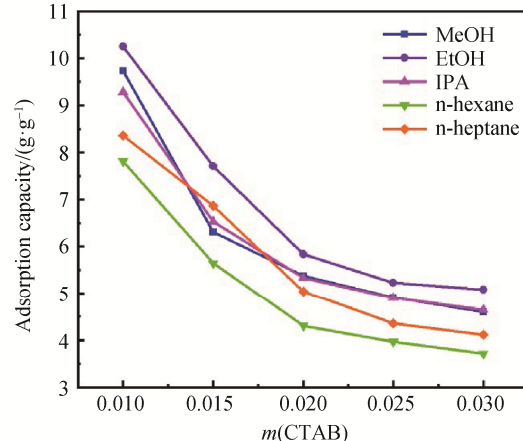
(c) Cyclic adsorption capacities of MSA for IPA



(d) Cyclic adsorption capacities of MSA for n-hexane



(e) Cyclic adsorption capacities of MSA for n-heptane



(f) Cyclic adsorption capacities of MSA for different solvents

Fig. 7 The adsorption capacity of MSA prepared with various CTAB contents for different solvents

Some studies have investigated the adsorption capacities of MTMS based aerogels. For example, Guo et al^[6] prepared the methylsilsesquioxane (MSQ) aerogels, where the adsorption capacity for n-heptane is 5.4~5.6 g/g. Lin et al^[37] synthesized polymethylsilsesquioxane (PSMQ) aerogels, and its maximum adsorption capacity for n-hexane is about 4 g/g. Yun et al^[38] prepared resorcinol-formaldehyde-reinforced silica (RF/ SiO_2) aerogels, and their adsorption capacity for EtOH is 5.8 g/g. Here, we obtained that the adsorption capacities of the as-prepared MSA for alcohols (MeOH, EtOH and IPA) can reach over 9 g/g, and the adsorption capacities for alkanes (n-hexane and heptane) can exceed 7 g/g with 0.010 g CTAB content. This declares that the prepared MSA has an evident improved adsorption capacity for these alcohols and alkanes. Besides, the adsorption capacity of MSA for the alcohols is higher than those for alkanes, which is due to the larger surface tension coefficients of the alcohols (Fig. 7).

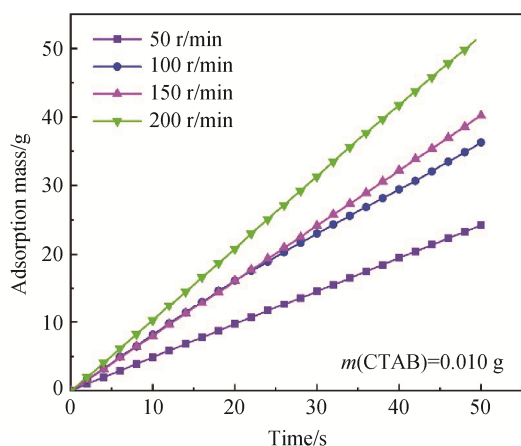
3.3 Dynamic adsorption characteristics

3.3.1 Pumping application The MSA prepared with the CTAB of 0.010 g and 0.015 g are used as adsorbents, while the EtOH acts as the adsorbate in this pumping system. In Fig. 8(a)–Fig. 8(b), the adsorption mass of EtOH increases linearly with the time under the analyzed pumping rates. The slopes of

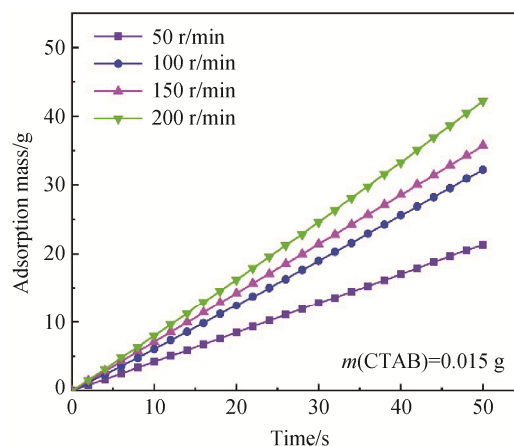
those lines reflect the adsorption rate of the MSA under a specific pumping rate. It is known that the adsorption rate increases with a higher pumping rate. The smooth running of this pumping system also proves that the silica skeleton of MSA is robust enough to maintain structural stability under the negative pressure generated by the peristaltic pump.

Under a given pumping rate, the adsorption rate of the MSA prepared by 0.010 g CTAB is larger than that of the MSA prepared by 0.015 g CTAB. The maximum adsorption rate of the MSA by the 0.010 g CTAB reaches as high as 1.04 g/s under a pumping rate of 200 r/min in Fig. 8(c). As the pumping rate increases, the gap of adsorption rate widens between the MSA prepared with by the 0.010 g and 0.015 g CTAB. All these indicate that the MSA with a larger skeleton and pore size facilitates the liquid transport during the pumping application. This is consistent with He's work^[23], which demonstrates that the liquid mass flux (Q) of the MSA is related to the radius (r), i.e., $Q \propto r^4$.

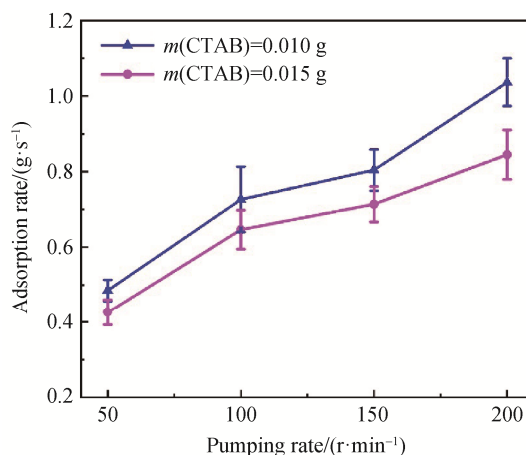
Due to the hydrophobicity and lipophilicity of as-prepared MSA in this study, the MSA can be applied to recover organic liquids with flexible operation and low cost. In the practical pumping applications of the MSA, the pore size of aerogel and pumping rate can be increased to improve the efficiency of liquids collection.



(a) Adsorption mass with the time of MSA prepared with the CTAB of 0.010 g



(b) Adsorption mass with the time of MSA prepared with the CTAB of 0.015 g



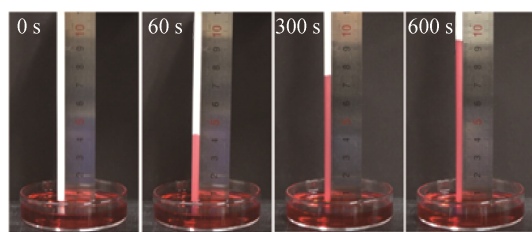
(c) Relationship between pumping rate and adsorption rate

Fig. 8 Adsorption mass with the time of MSA and the relationship between pumping rate and adsorption rate

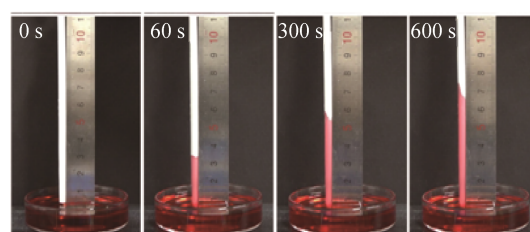
3.3.2 Capillary rise behavior As it is known to all, there are abundant capillaries inside the silica aerogels due to their porous structure, providing the structural basis for the capillary rise. That enables the possibility of delivering liquids without external force under some applications.

Fig. 9 gives the process of capillary rise of the MSA prepared with 0.010 g and 0.015 g CTAB, respectively, and EtOH is still used as the adsorbate. In Fig. 9(a)-Fig. 9(b), at the same time, the capillary rise height for the MSA prepared with 0.010 g CTAB is higher than that of the MSA prepared with 0.015 g CTAB. The detailed capillary rise height has been figured in Fig. 9(c), in

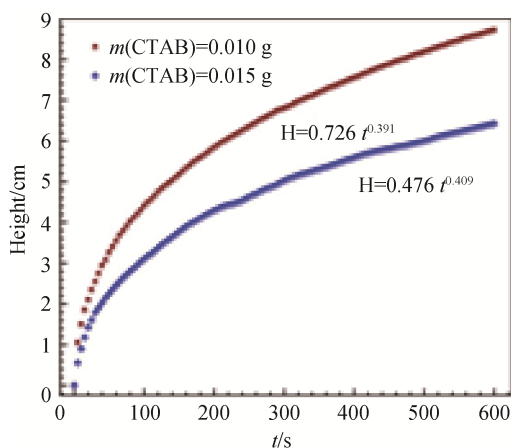
which the capillary rise heights of the two specimens both conform to the power functions of the time. The capillary rise speed is calculated by deriving the capillary rise height as presented in Fig. 9(d). At the first second, the capillary rise speeds of the EtOH in the MSA reached the maximum of 2.1 mm/s and 1.1 mm/s with 0.010 g and 0.015 g CTAB, respectively. It further indicates that the capillary rise speed is higher within the first few seconds and then slows down until becoming constant at a lower value. Comparing the structures of these two aerogels, it shows that the EtOH rises faster and achieves a higher height in the MSA with larger pore diameters, which can be attributed to the larger capillary force.



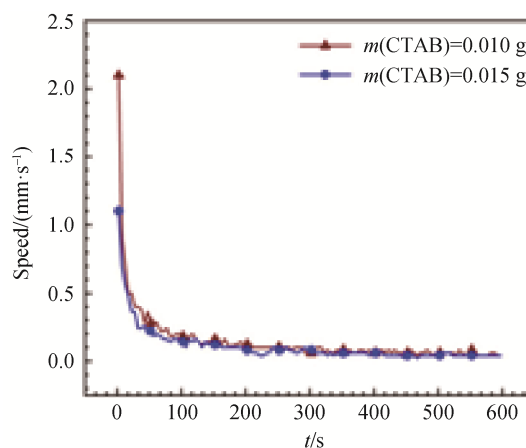
(a) Schematics and capillary rise status at different time points for MSA prepared with CTAB=0.010 g



(b) Schematics and capillary rise status at different time points for MSA prepared with CTAB=0.015 g



(c) Capillary rise height of MSA with the time



(d) Capillary rise speed of MSA with the time

Fig. 9 Process of capillary rise of as-prepared MSA

Therefore, we conclude that less CTAB generate relatively larger skeleton and pore sizes, which result in a higher capillary rise height and a larger capillary rise speed. In a word, the capillary rise speed of organic liquid can be adjusted by the pore size of the MSA, showing a possibility of regulating and controlling the evaporation of perfumes, kerosene and other organic liquids in some applications.

3.4 Desorption by heating

For some practical applications, desorption should be taken into consideration to improve the utilization of adsorbents that could reduce costs. As we know, heating is a prevalent method of desorption^[22], and here, we want to discuss the applicability of thermal desorption for the MSA.

Fig. 10 presents the thermal analysis (TG–DSC) of

the MSA prepared with 0.010 g CTAB. An apparent weight loss was observed between 450–580 °C, corresponding to a prominent exothermic peak that attributes to the thermal oxidation of the Si-CH₃ groups on the silica skeleton of the MSA^[30]. The onset temperature (T_{onset}) and the peak temperature (T_{peak}) of the thermal oxidation reaction are 455.7 °C and 479.2 °C, respectively. These two temperatures indicate that the MSA can maintain thermal stability even under a relatively high temperature.

For the common organic liquids, their boiling points are much lower than the T_{onset} of the MSA, which means that the MSA can keep a good performance after the thermal desorption of the adsorbed organic liquids. From this point, the high thermal stability ensures the applicability of the thermal desorption of the MSA.

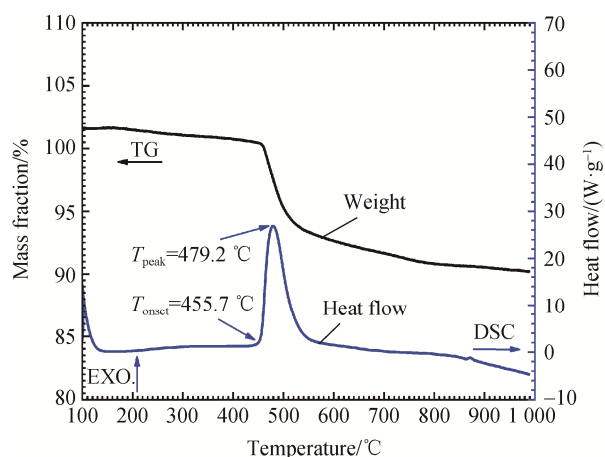


Fig. 10 TG-DSC curves of MSA prepared with 0.010 g CTAB

4 Conclusions

MTMS based silica aerogels (MSA) with controllable skeleton and pore sizes were prepared by adjusting the CTAB contents, and their adsorption characteristics for organic liquids were investigated.

When CTAB content increases from 0.010 g to 0.030 g, the average skeleton diameter decreases monotonously from 2.39 μm to 0.55 μm without significantly affecting the surface chemical composition of the MSA, which simultaneously reduces the pore size and total pore volume. The static adsorption for organic liquids indicates that the MSA is a good adsorbent with an evident improved adsorption capacity for the specific alcohols and alkanes, and the maximum adsorption capacity for the specific organic liquid can reach 10 g/g. The dynamic adsorption experiments demonstrate that the adsorption rate for the pumping application increases to 1.04 g/s, and the greater capillary rise speed of organic liquids can reach 2.1 mm/s with larger skeleton and pore sizes. Furthermore, the thermal analysis proves that the thermal desorption is applicable for the MSA without impairing the good performance. The MSA with controllable skeleton and pore sizes have adjustable adsorption characteristics, enabling abundant adsorption applications.

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