Preparation of Physical-modified Mesoporous Silica

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Abstract. Based on the concept of molecular design, mesoporous silica materials with different physical structure and morphology were prepared by adjusting the molecular chain length of surfactants and the mass ratio of anion-cationic surfactants. The composition and morphology of the prepared silica materials were characterized by FTIR, SEM, N₂ adsorption and desorption. By adjusting the carbon chain length of surfactants and the mass ratio of anion-cationic surfactants, the preparation of mesoporous silica was carried out, and the effects of mesoporous silica on the internal structure of mesoporous silica were analyzed.

Keywords: Mesoporous silica, hydrothermal synthesis, Physical modification, Surfactant.

1. Introduction
Mesoporous silica materials have performances in the fields of photochemistry, catalysis, adsorption and separation due to their large specific surface area, rich pore volume, continuously adjustable pore size, active surface properties and environmental compatibility[1]-[5] Outstanding application value. In order to improve the selectivity and pertinence of mesoporous silica to the target substance in application, the mesoporous silica is physically modified to adjust its pore structure.

In this paper, based on the concept of molecular design, a variety of mesoporous silica materials with different physical structures and morphologies were prepared by adjusting the molecular chain length of the surfactant and the mass ratio of the anionic and cationic surfactants by the "hydrothermal method". The composition and morphology of the prepared silica materials were characterized by Fourier Transform Infrared (FTIR) spectrometer, scanning electron microscopy (SEM), N₂ adsorption and desorption.

2. Experimental

2.1. Reagents and Instruments:
Cationic surfactants: Decadecyltrimethylammonium bromide, dodecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide, cetyltrimethylammonium bromide; orthosilicone Tetraethyl acid (TEOS); sodium hydroxide; absolute ethanol; sodium dodecyl sulfate. Spectrophotometer (721, Shanghai Tsinghua Science and Technology Co., Ltd.), collector type constant temperature heating magnetic stirrer (DF-101S, Gongyi Yuhua Instrument Co., Ltd.), intelligent timing digital display magnetic heating sleeve (ZNCLD, Xi’an Taikang Bio Technology Co., Ltd.), high-pressure reaction kettle (KH-50, Shanghai Leighton Industrial Co., Ltd.), infrared spectrometer (T27, Bruker, Germany),
scanning electron microscope (Quanta 200, US FEI), N$_2$ adsorption desorption analyzer (Autosorb IQ, Connaught Corporation).

### 2.2. Preparation of silica with different carbon chain lengths

Under the condition of 37°C water bath, add 0.5555g NaOH in 50mL deionized water, and then 4.2952 g cetyltrimethylammonium bromide (CTAB) / 2.6424 g decaalkyltrimethylammonium bromide (FSM 20) / 2.9068 g twelve Methyl trimethyl ammonium bromide (DTAB) / 3.1712 g tetradecyl trimethyl ammonium bromide (TTAB) was added to the alkaline solution accurately. After slowly stirring to completely dissolve, 20.6623g of tetraethyl orthosilicate (TEOS) was added gradually, and then stirred vigorously for 2h. The solution was transferred into a stainless steel self-pressurizing reactor with polytetrafluoroethylene lining, crystallize at 110°C for 72 h, wash repeatedly with deionized water and ethanol, suction filter, calcination at 550°C for 6h. The four kinds of silica materials were finally named as Sixteen-MCM, Ten-MCM, Twelve-MCM, and Fourteen-MCM.

### 2.3. Preparation of mesoporous silica with different anion-cation mass ratio

Under a 37 °C water bath, add 0.5555 g of NaOH in 50 mL of deionized water, and slowly add sodium dodecyl sulfate under stirring. After it is completely dissolved, add a certain amount of cetyltrimethylammonium bromide to control the anion surface. The total mass of the active agent sodium dodecyl sulfate and the cationic surfactant cetyltrimethylammonium bromide is always 4 g. When cetyltrimethylammonium bromide is completely dissolved, add 20mL of positive Tetraethyl silicate, vigorously stirred for 2h, transfer the solution to a stainless steel self-pressurizing reactor with polytetrafluoroethylene lining, crystallization reaction at 110°C for 72h, repeatedly wash the product with deionized water and absolute ethanol, pump filtration and calcination at 550 °C for 6h.

The mass ratio of sodium dodecyl sulfate to cetyl trimethyl ammonium bromide is expressed as $k$, and the mass ratio $k$ of sodium dodecyl sulfate and cetyl trimethyl ammonium bromide is controlled. The order is 0.1:1.9, 0.2:1.8, 0.3:1.7, 0.4:1.6. The four materials prepared were named 0.1-MCM, 0.2-MCM, 0.3-MCM, 0.4-MCM in sequence.

### 3. Results and discussion

#### 3.1. Effect of Surfactant Carbon Chain Length on the Structure of Mesoporous Silica

(1) Infrared analysis

(a) Ten-MCM, (b) Twelve-MCM, (c) Fourteen-MCM, (d) Sixteen-MCM.

It can be seen from Figure 1 that the infrared spectra of the four materials have absorption peaks at the corresponding functional group positions. It showed that the above four alkyl trimethylammo-nium bromide surfactants can successfully synthesize silica.

(2) Morphological characterization
Figure 1. SEM spectra of silica prepared with four carbon chain lengths

(a): Ten-MCM, (b): Twelve-MCM, (c): Fourteen-MCM, (d): Sixteen-MCM.

It can be seen from the SEM spectrum that as the length of the alkyl carbon chain in the alkyltrimethylammonium bromide increases, the grooves and pores on the surface of the prepared mesoporous silica gradually increase. Local magnification of the 16-MCM SEM image shows that the surface pores are relatively abundant and orderly, which provides sufficient adsorption sites for wastewater adsorption.

(3) Characterization of N\textsubscript{2} isothermal adsorption and desorption.

(a): Ten-MCM, (b): Twelve-MCM, (c): Fourteen-MCM, (d): Sixteen-MCM

Table 1. Structure parameters of silica pores prepared with four carbon chain lengths

| Serial number | SBET (m\textsuperscript{2}/g) | Pore diameter (nm) |
|---------------|-----------------|------------------|
| Ten-MCM       | 30.12           | 60.79            |
| Twelve-MCM    | 641.111         | 18.41            |
| Fourteen-MCM  | 1059.188        | 23.79            |
| Sixteen-MCM   | 1023.845        | 32.52            |

It can be seen from Fig. 3(a) and Table 1 X-MCM that X-MCM has not formed an effective channel structure, and that grooves with different widths are distributed on its surface, and X-MCM does not meet the requirements of mesoporous materials. The pore diameters of the remaining three materials are all distributed in the range of mesopores. The reason for the analysis may be that the concentration of decaalkyltrimethylammonium bromide did not reach the critical micelle concentration. In the solution, decaalkyltrimethylammonium bromide did not form micelles, resulting in deca-MCM it does not meet the requirements of mesoporous materials; with the remaining three materials, as the length of the surfactant carbon chain increases, the specific surface area and pore size gradually increase.
3.2. **Effect of the ratio of anionic-cationic surfactants on the structure of mesoporous silica**

(1) Infrared analysis

(a): 0.1-MCM, (b): 0.2-MCM, (c): 0.3-MCM, (d): 0.4-MCM.

It can be seen from Fig. 4 that the infrared spectra of the four materials have absorption peaks at the positions of the corresponding functional groups. It shows that the silica material can be synthesized by adjusting the mass ratio k of different anionic surfactants sodium dodecyl sulfate and cationic surfactant cetyltrimethylammonium bromide.

(2) Morphological characterization

![SEM images of silica prepared by the mass ratio of four anionic and cationic surfactants](image)

*Figure 2. SEM images of silica prepared by the mass ratio of four anionic and cationic surfactants*

(a): 0.1-MCM, (b): 0.2-MCM, (c): 0.3-MCM, (d): 0.4-MCM.

It can be seen from the SEM spectrum that the surface of mesoporous silica prepared by adjusting the change of the mass ratio k of anionic and cationic surfactants has more grooves and pores.

(3) Characterization of N₂ isothermal adsorption and desorption

(A): 0.1-MCM, (b): 0.2-MCM, (c): 0.3-MCM, (d): 0.4-MCM.

**Table 2.** Silica pore structure parameters prepared by the mass ratio of four anionic and cationic surfactants

| Serial number | SBET (m²/g) | Pore diameter (nm) |
|---------------|-------------|--------------------|
| 0.1-MCM       | 745.903     | 15.79              |
| 0.2-MCM       | 674.295     | 18.27              |
| 0.3-MCM       | 679.216     | 21.18              |
| 0.4-MCM       | 375.296     | 23.37              |

Table 2. Silica pore structure parameters prepared by the mass ratio of four anionic and cationic surfactants

It can be seen from the above N₂ adsorption and desorption characterization results that the pore diameter of the silica material prepared by adjusting the mass ratio of anionic and cationic surfactant k is distributed in the range of mesopores, and with the quality of anionic and cationic surfactant As the
ratio $k$ increases, the pore size of the prepared silica material gradually increases, and the specific surface area tends to decrease.

4. Conclusion
In this paper, mesoporous silica was mainly prepared by hydrothermal synthesis method, and the purpose of regulating the structure and morphology of mesoporous silica was achieved by adjusting the molecular structure and composition of the surfactant. The prepared materials were characterized by FTIR spectroscopy, SEM, and N$_2$ adsorption and desorption analysis.

(1) Preparation of mesoporous silica (10-MCM, 12-MCM, 14-MCM, 16-MCM) using alkyl trimethylammonium bromide with different carbon chain lengths (C10–C16) as surfactants MCM, FTIR characterization showed that the synthesized four materials are silica. The N$_2$ adsorption and desorption characterization showed that the Ten-MCM has the smallest specific surface area, the smallest mesoporous structure, and contains a part of micropores, and The remaining three silicas with carbon chain lengths all have obvious mesoporous structures. As the carbon chain length of the surfactant increased, the mesoporous pore diameter and specific surface area gradually increased.

(2) Four mesoporous silica materials were prepared by adjusting the mass ratio $k$ of anionic surfactant (sodium dodecyl sulfate) and cationic surfactant (hexadecyltrimethylammonium bromide) (0.1-MCM, 0.2-MCM, 0.3-MCM, 0.4-MCM). As the mass ratio of anionic and cationic surfactants increases, the pore size of the prepared silica material gradually increased, and the specific surface area tends to decreased.

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