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Preparation of monodispersed microporous SiO_2 microspheres with high specific surface area using dodecylamine as a hydrolysis catalyst

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Abstract

A novel and simple method for the synthesis of monodispersed microporous SiO_2 microspheres with high specific surface area was developed by hydrolysis of tetraethoxysilane (TEOS) in a water–ethanol mixed solution and using dodecylamine (DDA) as hydrolysis catalyst and template. The as-prepared products were characterized with differential thermal analysis–thermogravimetry, scanning electron microscopy, high-resolution transmission electron microscopy, small angle X-ray diffraction and nitrogen adsorption. The effects of experimental conditions including hydrolysis temperatures, calcination temperature and concentrations of TEOS and DDA on the morphology and pore parameters of the as-prepared SiO_2 microspheres were investigated and discussed. The results showed that hydrolysis temperature and concentrations of TEOS and DDA are important parameters for the control of size and morphology of particles. The specific surface area and specific pore volume of the as-prepared SiO_2 microspheres increased with increasing DDA concentration and calcination temperature. DDA may act not only as a good hydrolysis catalyst but also as a template for the formation of monodispersed SiO_2 microspheres with high specific surface area. This research may provide new insight into the synthesis of monodispersed microporous SiO_2 microspheres.

Keywords: SiO_2 microspheres; Microporous; Monodispersed; TEOS; Dodecylamine

1. Introduction

The preparation and characterization of oxide particles with a specific size and morphology are of primary importance for the development of advanced functional materials [1–4]. Micrometer spheres of ceramic materials are of particular interest for fundamental research in order to explain physical properties or surface interactions quantitatively [5]. Especially, monodispersed SiO_2 microspheres have received much attention owing to its wide application potential, not only in the field of physical chemistry but also in such industries involving catalysts, chromatography, ceramics, pigment, photographic emulsion, etc. [6–9]. Therefore, a great deal of effort has been devoted in recent years to obtain porous SiO_2 spheres with defined size and pore structure [10–15].

Micrometer-sized SiO_2 microspheres have been synthesized by many experimental methods such as spray gelling, coacervation process, sol–gel and hydrolyzing silicon esters in an emulsion system [16,17]. However, the tailoring of the pore size, pore volume and surface texture of the silica spheres prepared by these methods remain questionable. So the synthesis of porous SiO_2 microspheres in the presence of organic templates and/or additives has been intensively investigated in recent years. For example, Vacassy et al. [18] used 3-aminopropyltriethoxy-silane and glycerol as templates to prepare microporous SiO_2 spheres. Qi [19] used double-hydrophilic block copolymers (PEO-b-PMMA) as template under strong acidic conditions to form microporous SiO_2 spheres. Ma et al. [20] used a triblock copolymer $EO_{20}PO_{70}EO_{20}$ as template in combination with a co-surfactant CTAB to prepare SiO_2 microspheres via a two-step synthesis process. Yano and Fukushima [21] discovered that microporous SiO_2 spheres were prepared using CTAB as template under basic

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condition. Although a variety of porous SiO_2 spherical particles have been synthesized so far, almost all the SiO_2 spheres have been obtained by using a triphasic system of a quaternary ammonium surfactant with an additional auxiliary organic solvent and co-surfactant.

1-alkylamines as templates for the preparation of porous materials were first reported by Pinnavaia and co-workers [22–24] in 1994. Recently, some researchers used 1-alkylamines as templates to synthesize microporous or mesoporous silica materials [25–27]. However, the effects of experimental conditions on the morphology and pore parameters of the prepared SiO_2 microspheres using dodecylamine (DDA) as hydrolysis catalyst and template have not been clear. In this work, monodispersed microporous SiO_2 microspheres have been successfully prepared by the hydrolysis and condensation of tetraethoxysilane (TEOS) in a water–ethanol mixed solution and using DDA as hydrolysis catalyst and template. Accordingly, the effects of experimental conditions including concentrations of TEOS and DDA, temperatures of hydrolysis and calcination on the resulting particle size, morphology and pore parameters were investigated and discussed.

2. Experimental and characterization

2.1. Experimental procedure

TEOS, DDA and ethanol were purchased from Shanghai Chemical Reagent Factory and were analytical reagent grade. Distilled water was used as the water source in all cases.

In a typical procedure, DDA was dissolved in a mixed solution of ethanol (0.16 L) and distilled water (0.1 L). Then TEOS was added dropwise to the above solution at different temperatures under magnetic stirring. After the addition of TEOS, the clear solution gradually turned opaque owing to the formation of a white precipitate. After continuous stirring for 4 h, the white precipitate was filtrated. The products were repeatedly washed with water and ethanol for four times, then dried in a vacuum oven at 80 °C for 4 h, finally calcined at 200, 400 and 600 °C for 4 h in a muffle furnace to remove the templates, respectively. In the experiments, the concentration of TEOS was varied from 0.11 to 0.25 mol L^{-1}, the concentration of DDA was varied from 0.016 to 0.030 mol L^{-1}, the temperature of the solution was varied from 5 to 35 °C, and the calcination temperatures were kept at 80, 200, 400 and 600 °C for 4 h, respectively.

2.2. Characterization

The as-prepared SiO_2 microspheres were characterized by scanning electron microscopy (SEM) (type JSM-5610LV) with an accelerating voltage of 20 kV. Differential thermal analysis (DTA) and thermogravimetric (TG) were performed with a Netzsch STA 449C thermal analyzer in an air flow of 100 mL min^{-1} at a heating rate of 10 $°\text{C min}^{-1}$ from room temperature to 600 °C. The high-resolution transmission electron microscopy (HRTEM) was carried out with a Philips TECNAL-10 at 100 kV. The small angle X-ray diffraction (XRD) pattern was obtained on an HZG41B-PC X-ray diffractometer using Cu $K\alpha$ radiation with a 2θ range of 1–5°. The Brunauer–Emmett–Teller (BET) specific surface area (S_{BET}) and pore parameters of the SiO_2 products were analyzed by nitrogen adsorption–desorption isotherm measurements on an AUTOSORB-1 (Quantachrome Instruments, USA) nitrogen adsorption apparatus. For the samples obtained at 80 °C, the samples were degassed at 70 °C prior to actual measurements. However, for the samples calcined at high temperatures (from 200 to 600 °C), the degassing temperature was 180 °C. The BET specific surface area was determined by the multipoint BET method using the adsorption data in the relative pressure (p/p_0) range of 0.05–0.25. The desorption branch of the nitrogen isotherm was used to determine the micropore size distribution using the Horvath–Kawazoe (HK) method [28]. The porosity was calculated according to the following equations (the skeleton specific volume of SiO_2 is taken as 0.37 $\text{cm}^3\,\text{g}^{-1}$) [29]:

$$P = V_p/(V_p + 0.37), \qquad (1)$$

$$V_p = 1.547 \times 10^{-3}\, V_d, \qquad (2)$$

where V_p is the volume of the liquidated nitrogen corresponding to the total pore volume, which was calculated from the saturation adsorption volume at STP, V_d.

3. Results and discussion

3.1. Thermal analysis

Fig. 1 shows DTA/TG curves of the SiO_2 microspheres obtained at 15 °C under the standard synthesis conditions

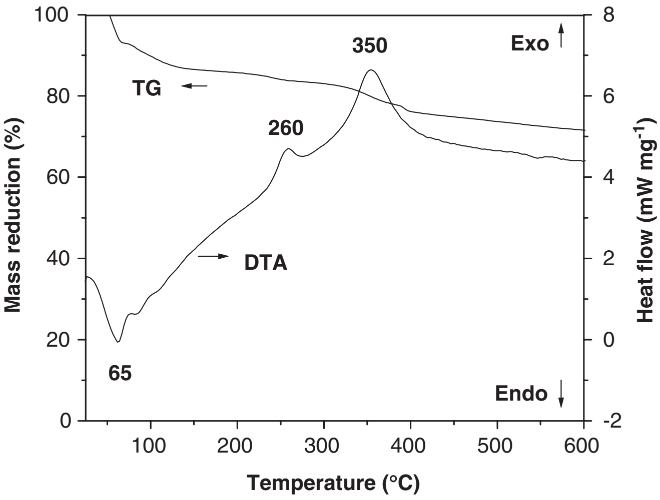

Fig. 1. DTA/TG curves of SiO_2 microspheres obtained at 15 °C and dried at 80 °C for 4 h. [DDA] = 0.024 mol L^{-1} and [TEOS] = 0.18 mol L^{-1}.

and dried at 80 °C for 4 h. A broad endothermic peak at below 100 °C is due to the evaporation of the physically adsorbed water and ethanol solvent. The two exothermic peaks at 260 and 350 °C come from the decomposition of organic substances contained in the SiO_2 microspheres. The TG curve in Fig. 1 can be roughly divided into three stages. The largest weight loss (18%) occurs in the temperature range from room temperature to 100 °C. This is attributed to the evaporation of the physically adsorbed water and ethanol. The second stage is from 100 to 400 °C, a mass loss of about 10% is observed, which can be assigned to the combustion and carbonization of a large amount of organic residues. The third stage is from 400 to 600 °C, where the mass loss is about 6% due to the dehydration and condensation of silanols.

3.2. Effect of DDA concentration

Fig. 2 shows the influences of DDA concentration on monodispersity and sizes of SiO_2 microspheres obtained under standard synthesis conditions. It can be seen that DDA concentration had an obvious influence on the diameters and morphologies of SiO_2 microspheres. At $[DDA] = 0.016\,mol\,L^{-1}$, monodispersed SiO_2 microspheres with a diameter of about 500 nm were obtained (as shown in Fig. 2(a)). With increasing DDA concentration, the diameters of SiO_2 microspheres obviously increase. When DDA concentration increases to $0.030\,mol\,L^{-1}$, the diameters of SiO_2 microspheres reach 1.2 μm (see Fig. 2(c)). However, the monodispersity of SiO_2 microspheres decreases. Some SiO_2 microspheres aggregate together. Why do DDA concentrations obviously influence the diameters and monodispersity of SiO_2 microspheres? This may be ascribed to the fact that with increasing DDA concentration, the basicity (or $[OH^-]$ concentration) of the solution increases. This results in the increase in the rate of the hydrolysis of TEOS. Also, the rate of hydrolysis relative to the rate of condensation also increases. The stability of small particles decreases as the concentration of OH^- ions increases, and a dissolution and reprecipitation process occurs, resulting in the formation of larger SiO_2 particles [30].

3.3. Effect of TEOS concentration

In order to examine the influence of TEOS concentration on the monodispersity and sizes of SiO_2 particles, the experiments were carried out at different TEOS concentrations. Fig. 3 shows the influence of TEOS concentration on the monodispersity and sizes of SiO_2 particles. It can be seen that TEOS concentration also had an obvious influence on the diameters and morphologies of SiO_2 microspheres. At $[TEOS] = 0.11\,mol\,L^{-1}$, monodispersed SiO_2 microspheres with a diameter of about 800 nm were obtained (as shown in Fig. 3(a)). With increasing TEOS concentration, the diameters of SiO_2 microspheres obviously increase. When TEOS concentration increases to $0.25\,mol\,L^{-1}$, the diameters of SiO_2 microspheres reach 1.4 μm (see Fig. 3(d)). However, the monodispersity of SiO_2 microspheres decreases. Some SiO_2 microspheres

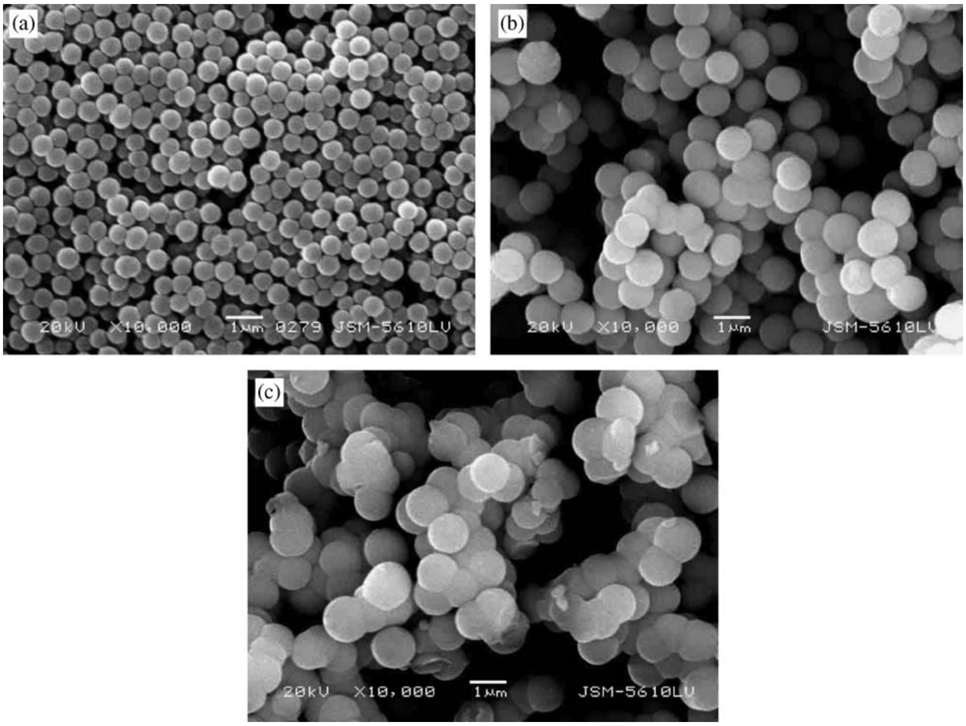

Fig. 2. SEM micrographs of SiO_2 microspheres obtained at different DDA concentrations at 15 °C and calcined at 600 °C for 4 h. $[TEOS] = 0.18\,mol\,L^{-1}$ and $[DDA]$ = (a) 0.016, (b) 0.024 and (c) $0.030\,mol\,L^{-1}$.

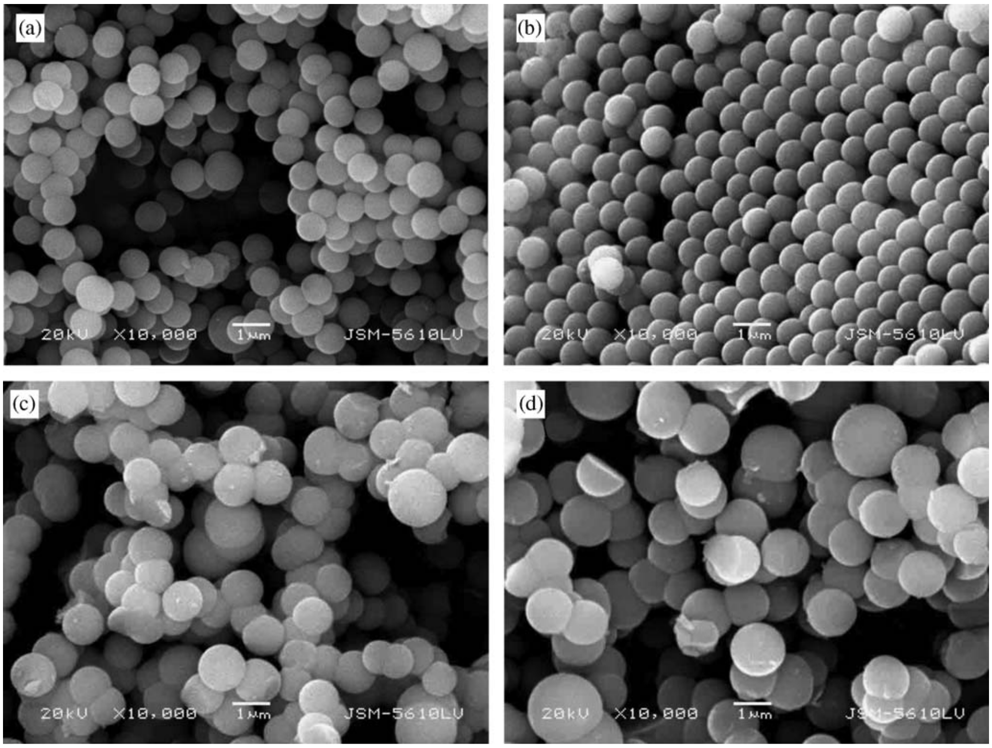

Fig. 3. SEM micrographs of SiO_2 microspheres obtained at different TEOS concentrations at 15 °C and calcined at 600 °C for 4 h. [DDA] = 0.024 mol L^{-1} and [TEOS] = (a) 0.11, (b) 0.14, (c) 0.22 and (d) 0.25 mol L^{-1}.

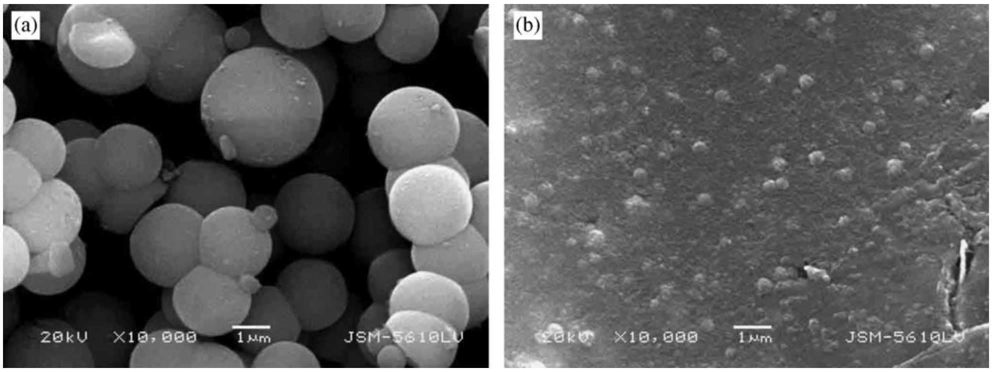

Fig. 4. SEM micrographs of SiO_2 microspheres obtained at (a) 5 and (b) 35 °C. [DDA] = 0.024 mol L^{-1} and [TEOS] = 0.18 mol L^{-1}.

aggregate together. DDA acts as a basic catalyst for the hydrolysis and condensation of TEOS. The rate of hydrolysis is remarkably enhanced with an increase in the TEOS concentration. However, there is only a minimal change for the rate of condensation relative to the variation of TEOS concentration [31]. Thus, with increasing TEOS concentration, the SiO_2 particles become larger and polydispersed. Therefore, increasing TEOS concentration has a result similar to that of increasing DDA concentration.

3.4. Effect of hydrolysis temperature

Figs. 4(a) and (b) show SEM micrographs of SiO_2 particles synthesized at 5 and 35 °C, respectively. It can be seen that the hydrolysis temperature has an obvious influence on the monodispersity and sizes of SiO_2 particles. According to the nucleation and growth theory, nucleation rate (J) can be expressed as $J = J_0\exp(-\Delta G_D/kT)\exp(-\Delta G^*/kT)$, where J stands for nucleation rate ($m^3\,s^{-1}$), J_0 is the initial nucleation rate ($m^3\,s^{-1}$), ΔG_D denotes diffusion activation free energy change (J), ΔG^* represents critical nucleation rate energy change (J), κ the Boltzman constant ($J\,K^{-1}$) and T the temperature (K) [32]. Thus, the temperature (T) increases and the value of nucleation rate (J) of SiO_2 can increase. Therefore, the nucleation rate of SiO_2 at a higher hydrolysis temperature is obviously higher than that at a lower temperature. This results in a fast appearance of opaque solution of SiO_2 due to an increase of nucleation rate. Therefore, it is not

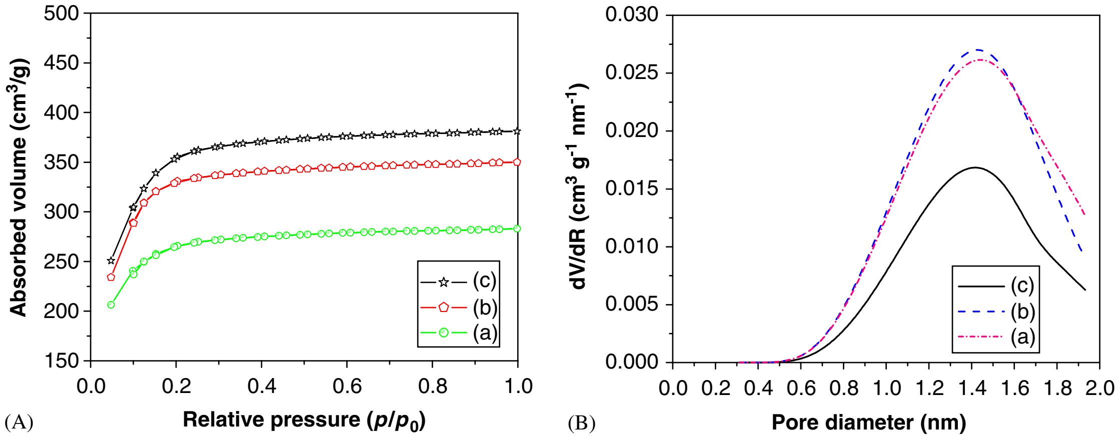

Fig. 5. (A) N_2 adsorption–desorption isotherms of SiO_2 microspheres obtained at different DDA concentrations at 15 °C and calcined at 600 °C for 4 h. [TEOS] = 0.18 mol L^{-1} and [DDA] = (a) 0.016, (b) 0.024 and (c) 0.030 mol L^{-1}. (B) The corresponding pore size distribution curves calculated from desorption branch of the nitrogen isotherms by HK method.

surprising that the particle size of SiO_2 decreases with increasing hydrolysis temperature. SEM observations show that the SiO_2 obtained at low temperature (5 °C) is (some) larger aggregated particles (as shown in Fig. 4(a)). However, with a further increase in hydrolysis temperature from 5 to 15 °C, monodispersed SiO_2 microspheres are produced (Fig. 2(b)). When hydrolysis temperature reached 35 °C, the obtained particles are so small that they are embedded into the SiO_2 gel (as shown in Fig. 4(b)). This might be due to the fact that higher temperature increased nucleation rate. The older nuclei will not grow to become larger than the younger ones, leading to the formation of many small microspheres. Hence, it can be inferred from the above results that high-quality SiO_2 microspheres can be only formed at about 15 °C under the present synthesis conditions.

3.5. Nitrogen adsorption

Fig. 5(A) shows the nitrogen adsorption–desorption isotherms of microporous SiO_2 microspheres obtained at different DDA concentrations under standard synthesis conditions and calcined at 600 °C for 4 h. All isotherms of the as-prepared products are type I nitrogen adsorption–desorption isotherms according to the IUPAC classification [33], characteristic of microporous materials. Although the shapes of the isotherms do not change much with increasing DDA concentration, the amount of adsorbed nitrogen greatly increases. The micropore size distribution curves of SiO_2 microspheres are determined from desorption branch of nitrogen isotherms via HK method (as shown in Fig. 5(B)). The maximum pore diameters of these samples are observed at around 1.4 nm, which is in the microporous range (pore diameter less than 2 nm). With increasing DDA concentration, micropore size distribution curves become wide. Table 1 lists BET specific surface areas and pore parameters of microporous SiO_2 samples obtained at different DDA concentrations and calcined at 600 °C. It can be seen that the specific surface area, porosity, specific pore volume and the average pore diameter increase with increasing DDA concentration.

Table 1
Effects of DDA concentration on BET specific surface areas and pore parameters of SiO_2 microspheres[a]

[DDA] (mol L^{-1})	BET specific surface area[b] (m^2 g^{-1})	Porosity[c] (%)	Specific total pore volume[d] (mL g^{-1})	Average pore size[e] (nm)
0.016	828	54.2	0.44	1.42
0.024	965	59.0	0.54	1.43
0.030	1223	61.4	0.59	1.44

[a] SiO_2 microspheres were prepared at 15 °C and calcined at 600 °C for 4 h. [TEOS] = 0.18 mol L^{-1}.

[b] BET specific surface area calculated from the linear part of the BET plot ($P/P_0 = 0.05$–0.25).

[c] The porosity is estimated from the pore volume determined using the adsorption branch of the N_2 isotherm at the $P/P_0 = 0.997$ single point.

[d] Specific total pore volume, taken from the volume of N_2 adsorbed at $P/P_0 = 0.997$.

[e] Average pore size, estimated using the desorption branch of the isotherm and the HK method.

Figs. 6(A) and (B) show the adsorption–desorption isotherms and the corresponding HK micropore size distribution curves of the microporous SiO_2 microspheres calcined at 80, 200, 400 and 600 °C for 4 h, respectively. Increasing the calcination temperature causes the capillary condensation steps to become more remarkable and shift to lower relative pressure. This indicates that the pore sizes slightly decrease. At the same time, the amount of adsorption nitrogen increases with increasing calcination temperature due to the decomposition of organic chemical components contained in the SiO_2 microspheres. This tendency can be seen clearly from the corresponding HK pore size distributions. Micropore size distribution curves become narrower with increasing calcination temperature. Further observation shows that the maximums in pore size

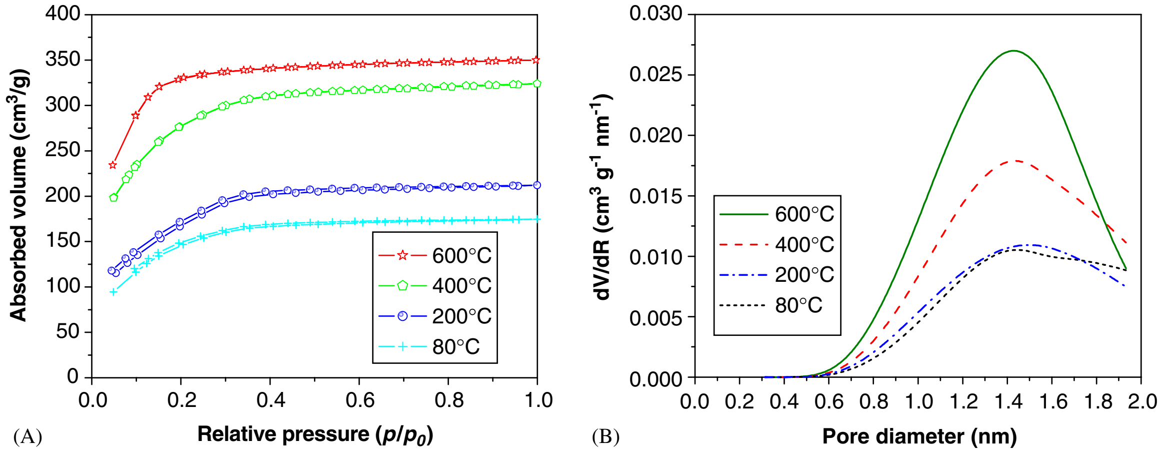

Fig. 6. (A) N_2 adsorption–desorption isotherms of SiO_2 microspheres obtained at 15 °C and calcined at 80, 200, 400 and 600 °C for 4 h, respectively. $[DDA] = 0.024\,mol\,L^{-1}$ and $[TEOS] = 0.11\,mol\,L^{-1}$. (B) The corresponding pore size distribution curves calculated from desorption branch of the nitrogen isotherms by HK method.

Table 2
Effects of calcination temperature on BET specific surface areas and pore parameters of SiO_2 microspheres[a]

T (°C)	BET specific surface area ($m^2\,g^{-1}$)	Porosity (%)	Specific total pore volume ($mL\,g^{-1}$)	Average pore size (nm)
80	513	42.2	0.27	1.50
200	617	47.0	0.33	1.48
400	986	57.5	0.50	1.46
600	1121	59.4	0.54	1.43

[a] SiO_2 microspheres were obtained at 15 °C and calcined at different temperatures. $[DDA] = 0.024\,mol\,L^{-1}$and $[TEOS] = 0.11\,mol\,L^{-1}$.

distributions are slightly shifted toward smaller pore size, indicating the shrinkage of pores due to the densification of the skeleton structure. The BET specific surface areas and pore parameters of microporous SiO_2 samples obtained at different calcination temperatures are summarized in Table 2. It can be seen from Table 2 that the specific surface area, porosity and specific pore volume steadily increase with increasing calcination temperature. However, the average pore diameter slightly decreases with increasing calcination temperature. This is due to the fact that organic template is removed from the SiO_2 microspheres at high temperature. This causes the gradual densification and shrinkage of SiO_2 microspheres.

3.6. *Formation mechanism of monodispersed microporous SiO_2 microspheres*

We believe that the microporous SiO_2 microspheres were formed by the agglomeration of SiO_2 primary nanoparticles via a neutral self-assembly mechanism. The rapid synthesis of SiO_2 microspheres may be due to the formation of initial SiO_2 nuclei using DDA as a hydrolysis catalyst, which is like the formation of initial SiO_2 nuclei in the Stöber et al. [34] method using ammonia as a hydrolysis catalyst, then the SiO_2 particles may further grow by undirectional agglomeration of primary particles on the surface of primary SiO_2 particles, resulting in the formation of submicrometer-sized silica spheres. It is well known that the difference between the nucleation and growth rates is an important factor for the formation of monodispersed particle [35]. Usually, a high degree of separation between nucleation and growth process is beneficial for the formation of monodispersed SiO_2 particles.

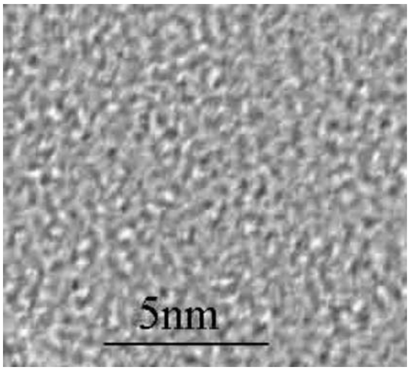

Fig. 7. HRTEM image of microporous SiO_2 microspheres obtained at 15 °C and calcined at 600 °C for 4 h. $[DDA] = 0.024\,mol\,L^{-1}$ and $[TEOS] = 0.11\,mol\,L^{-1}$.

The internal structures of monodispersed SiO_2 microspheres can be clearly observed using HRTEM. Fig. 7 shows the HRTEM image of monodispersed SiO_2 microspheres obtained under the standard synthesis conditions and calcined at 600 °C. It can be seen that the sample has wormhole-like pore structure, which is connected randomly and lack discernible long-range order in the pore arrangement among the small SiO_2 particles. Fig. 8 shows the corresponding small-angel XRD pattern of the as-prepared SiO_2 microspheres. A single broad XRD peak for the as-prepared SiO_2 microspheres in the low angle range also indicates that no discernible long-range order in the pore arrangement exists in the as-prepared SiO_2

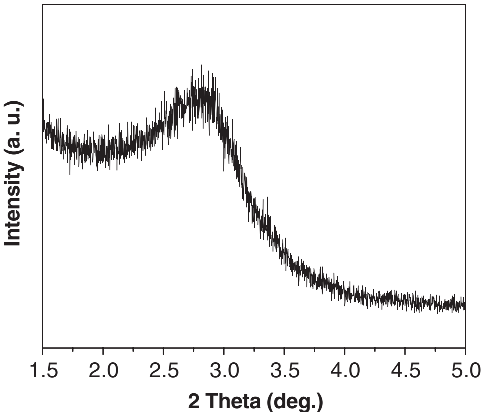

Fig. 8. Small angle XRD pattern of microporous SiO_2 microspheres obtained at 15 °C and calcined at 600 °C for 4 h. [DDA] = 0.024 mol L^{-1} and [TEOS] = 0.11 mol L^{-1}.

microspheres, consistent with the HRTEM image. The formation of such disordered structure can be explained through self-assembly between neutral organic surfactant and neutral inorganic ions (SI) [36,37]. The SI assembly relies on hydrogen bonding between DDA (S) and SiO_2 oligomer (I) at the micelle interface. The SI assembly will proceed during the formation of the silica oligomer generated by the hydrolysis of silica precursor. Finally, the microporous structure in SiO_2 microspheres is formed by high temperature calcination treatment to remove organic template.

4. Conclusions

Monodispersed microporous SiO_2 microspheres with high specific surface area have been prepared directly by the hydrolysis of TEOS using DDA as hydrolysis catalyst and template in a water–ethanol mixed solution, and followed by calcination at 600 °C for 4 h. The morphology, size and the pore structure of SiO_2 microspheres depend on the concentrations of the reactants and temperature of hydrolysis. The optimal synthesis conditions are as follows: [TEOS] = 0.11–0.18 mol L^{-1}, [DDA] = 0.016–0.024 mol L^{-1} and hydrolysis temperature is about 15 °C. The specific surface area, specific pore volume and average pore size of SiO_2 microspheres obviously increase with increasing DDA concentration. The higher calcination temperature, the larger are the specific surface area and pore volume, and the smaller are the pore size for SiO_2 microspheres. The small angle XRD and HRTEM results confirmed that SiO_2 microspheres had disordered pore structures.

Acknowledgments

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