Journal of Colloid and Interface Science 420 (2014) 66–69

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Short Communication

Well-defined plate and hollow disk shaped particles of silica-dialkyldimethylammonium hybrids

Shingo Machida [a], Takaaki Yoshida [b], Ryouya Hashimoto [b], Makoto Ogawa [a,b,*]

[a] Department of Earth Sciences, Waseda University, Nishiwaseda 1-6-1, Shinjuku-ku, Tokyo 169-8050, Japan
[b] Graduate School of Creative Science and Engineering, Waseda University, Nishiwaseda 1-6-1, Shinjuku-ku, Tokyo 169-8050, Japan

ARTICLE INFO

Article history:
Received 3 December 2013
Accepted 6 January 2014
Available online 13 January 2014

Keywords:
Monodispersed particle
Mesoporous silica
Stöber method
Platy particle
Hollow disk
Lamellar mesophase

ABSTRACT

Well-defined plate and hollow disk of silica-dioctadecyldimethylammonium hybrid particles were obtained by the sol–gel reaction of tetraethoxysilane in the presence of dioctadecyldimethylammonium chloride, where synthetic condition was determined based on the Stöber synthesis for micron size silica sphere. The particle size was several hundreds of nm in the radius and several tens of nm in the thickness. X-ray powder diffraction patterns indicated that the products possess layered mesostructures, which were thought to be directed by the lamellar aggregates of dioctadecyldimethylammonium.

1. Introduction

After the discovery of mesoporous silicas prepared by supramolecular templating approach [1,2], their preparation with varied, mesostructure, chemical composition, and morphology have been investigated and their practical application has been proposed [1–5]. Alkyltrimethylammonium salts and block copolymer (such as P123) are surfactants used most extensively as porogen (or template) for the preparation of periodic mesoporous materials, because they give several well-defined mesophases which were used to make porous materials with periodic pore arrangements. In order to obtain hybrid materials with varied structures and properties, various surfactants and polymers have also been complexed with silicas as well as other inorganic solids.

Here, we report the preparation of well-defined anisotropic silica-dioctadecyldimethylammonium hybrid particles. Dialkyldimethylammonium salts were originally developed by Kunitake and co-workers as the very first artificial biomembrane component and are known to give lamellar mesophases due to the packing parameter [6,7]. Lamellar hybrids of dialkyldimethylammonium salts with silicas have been prepared by the hydrolysis and condensation of tetraethoxysilane in the presence of pre-formed lamellar aggregates of dialkyldimethylammonium salts [8–14]. In the present study, the preparation of silica-dialkyldimethylammonium hybrid particles was conducted by Stöber method [15] to find unique platy particle and hollow disk shaped particle, which can be candidate for the novel types of adsorbents, catalysts supports delivery carriers.

2. Experimental section

2.1. Materials

Tetraethoxysilane (abbreviated as TEOS) and dioctadecyldimethylammonium chloride (abbreviated as 2C18) were obtained from Tokyo Kasei Kogyo Co., Ltd. Methanol and 28% aqueous ammonia solution were obtained from Kanto Chemical Co., Inc. All the chemicals were used without further purification.

2.2. Sample preparation

The synthetic procedure, which is similar to those employed in our previous reports on the preparation of nanoporous silica spherical particles using alkyltrimethylammonium salts [16,17], is as follows: 2C18 (260 mg) was dissolved into the mixture of methanol (75 mL) and deionized water (17.7 mL), then, 28% aqueous ammonia solution (7.2 g) were added. The solution was shaken at room temperature. TEOS (0.368 mL) was added to the solution and then the mixture was shaken at room temperature. The mixture was aged at room temperature in a sealed vessel. The composition of the starting solution (TEOS:2C18:H_2O:methanol:NH_3) was 1:0.27:774:1125-375:72 in molar ratio. The samples were

* Corresponding author at: Department of Earth Sciences, Waseda University, Nishiwaseda 1-6-1, Shinjuku-ku, Tokyo 169-8050, Japan. Fax: +81 3 3207 4950.
E-mail address: makoto@waseda.jp (M. Ogawa).

0021-9797/$ - see front matter © 2014 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcis.2014.01.002

named as shown in Table 1. The initial solutions (before TEOS addition) are turbid due to the low solubility as well as aggregation of 2C18 chloride in the solution. The solution became milky within ca. 5 min after the addition of TEOS. Solid products were collected after the aging for 20 h from the milky mixture by vacuum filtration using membrane filter (cellulose acetate, pore diameter: 200 nm, Advantec), washed with methanol and dried at 60 °C for a day. 2C18 was removed by calcination in air at 550 °C for 10 h at a heating rate of 150 °C h^{-1}.

2.3. Characterization

Scanning electron micrographs (SEM) were obtained on a Hitachi S-2380N scanning electron microscope. Prior to the measurements, the samples were coated with gold. Transmission electron micrographs (TEM) were observed on a JEOL JEM-100CX transmission electron microscope. Powder X-ray diffraction patterns were recorded on Rigaku RADI-A diffractometer equipped with monochromatic Cu Kα radiation. The nitrogen adsorption/desorption isotherms of the calcined particles were measured at −196 °C on a Belsorp MINI instrument (BEL Japan Inc.). Prior to the measurements, samples were dried at 120 °C under evacuation for 3 h. Surface area and pore size distribution were determined from the adsorption isotherms by the Brunauer–Emmett–Teller (BET) method [18] and the Barrett–Joyner–Halenda (BJH) method [19], respectively. The pore volume was determined using the adsorption branch of the N_2 adsorption isotherm at the relative pressure of ca. 0.95 single point.

3. Results and discussion

The SEM images of 2C18silica-1 and 2C18silica-2 are shown in Fig. 1(a and c), where disk shaped particles are observed. The TEM images of 2C18silica-1 and 2C18silica-2 are shown as inset of Fig. 1(a and c), which indicated that the disk shaped particle is hollow. The particle size distribution (the diameter and the thickness) were derived from the SEM images (Fig. 1b and d), to showed narrow particle size distribution. The TEM images of 2C18silica-1 and 2C18silica-2 are also shown in Fig. 1(a and c) as insets to show, that the particle is hollow.

On the other hand, 2C18silica-3 possesses platy shape, which is seen in the SEM (Fig. 2) and TEM images (Fig. 2 inset). The difference between plate (2C18silica-3) and hollow disk (2C18silica-1 and 2C18silica-2) shapes are clearly seen in the TEM images (Fig. 1(a and c), insets). The present well-defined plate and hollow disk shaped particles are unique examples of products prepared by the Stöber synthesis. The origin of the anisotropic shapes is thought to be coming from the lamellar and vesicular aggregates

Table 1
Characterization of the products.

Sample name	Particle shape	Composition of the starting solutions					BET surface area ($m^2 g^{-1}$)	BJH pore size (nm)	Pore volume ($cm^3 g^{-1}$)
		TEOS (mL)	2C18Cl (mg)	H_2O (mL)	CH_3OH (mL)	28% aq NH_4OH (g)			
2C18silica-1	Hollow disk	0.368	260	17.7	75	7.2	570	2.4	0.48
2C18silica-2	Hollow disk	0.368	260	17.7	50	7.2	350	1.8	0.26
2C18silica-3	Plate	0.368	260	17.7	25	7.2	540	2.1	0.54

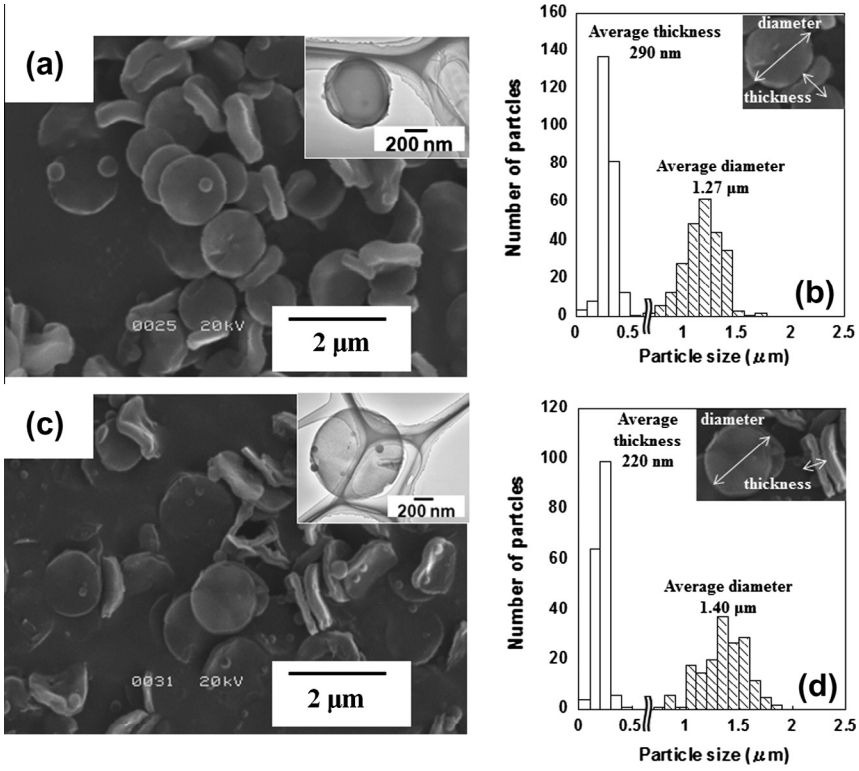

Fig. 1. SEM images of (a) 2C18silica-1 and 2C18silica-2 (c) (inset; TEM image of 2C18silica-1 and 2C18silica-2, respectively). (b and d) are particle size distribution derived from the SEM images (diameter (black) and particle thickness (white)).