Journal of the Taiwan Institute of Chemical Engineers 62 (2016) 307–312

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Rapid synthesis of morphology-controlled mesoporous silica nanoparticles from silica fume

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ARTICLE INFO

Article history:
Received 30 October 2015
Revised 2 January 2016
Accepted 31 January 2016
Available online 14 March 2016

Keywords:
Mesoporous silica materials
Rapid synthesis
Silica fume
Morphologies
Adsorption

ABSTRACT

A very short-time synthesis of morphology-controlled MCM-41 molecular sieve was formulated by using industry by-product silica fume as the silica source. In this synthesis, only by regulating the dose of ethyl acetate, we can well-realize the silica nanoparticle morphological transformation from worm-like to sphere, and popcorn-like shapes. The structure and morphology of the as-fabricated silica nanoparticles were quantitatively investigated by powder X-ray diffraction, Brunauer–Emmett–Teller (BET), scanning electron microscopy and transmission electron microscopy. Owing to the specific surface area and regular morphology, the bimodal mesoporous silica material MSF1 shows a better adsorption property for methylene blue. It was also demonstrated that it is possible to employ silica fume as an ideal silica source in 90 min self-assemble synthesis for large scale production.

1. Introduction

Since their discovery in the year of 1992 [1], MCM-41 and related mesoporous molecular sieves have attracted much attention. Narrow pore size distribution with size controllable pores over micrometer length scales make the MCM-41 materials attractive to many applications, such as the separation of proteins, selective adsorption of special molecules, catalyst support, sensors and drug delivery [2-4].

Generally, MCM-41 is synthesized under alkaline conditions by using various tetraalkoxysilane organics as the silica source, surfactant as the template under high temperature [5]. The synthesis procedure usually takes about 24–72 h or even longer [6,7] . The process suffered from the drawbacks of the expensive, toxic silica sources as well as long reaction time, it makes the practical application of this material severely hampered because it is quite unfavorable to the large scale production [8]. It is of great emergency to develop an economically feasible method for large scale synthesis of MCM-41. And seeking for a proper silicon source alternative with shorter synthesis time will be the most applicable approach.

Silica fume (SF), an industrial solid waste, is produced by an electric arc furnace as a by-product of the smelting process in the production of metallic silicon or ferrosilicon in the alloys industry [9]. The content of silica (SiO_2) can reach up to 85–99% and the submicron particles of silicon dioxide which occur as almost-perfect spheres with diameters ranges from 20 to 500 nm [10]. It is estimated that current global output of SF is, at most, between 1 and 1.5 million tonnes per year [11].

Due to the high specific surface area and highly reactive pozzolanic properties, SF is normally utilized as a substitute for fine aggregates in cement and concrete, additives in refractory, as well as filler in plastics and paints [12]. In consideration of the amorphous phase of silica in SF, it would be a viable alternative for the synthesis of MCM-41 mesoporous material. Other silicious industrial solid waste silica precursors such as coal fly ash [7,13,14], rice hull [15,16] and sedge [6] have been widely reported to produce mesoporous silica materials (MCM-41). Only Wenjie Zhu et al. [10,17] reported the synthesis of mesoporous silica by using silica fume as silica source but the reaction time is rather long. It was reported that the mesoporous silica material was synthesized by one step with the mixture of silica fume and CTAB in alkaline liquor under 90 °C for 48 h for hydrothermal reaction. Also, the product obtained in his paper is a gray powder with the small particle of 100–200 nm.

In this paper, the reaction process was occurred in a portable pressure steam sterilizer which was usually used in the sterilization of medical supplies and food industry. The pressure would reach to 0.125 MPa when the temperature rose up to 125 °C, which accelerated the reaction process, shortening the aging time to only 1.5 h instead of 48 h. What's more, only by regulating the dose of the catalyst ethyl acetate, we could well-realize the silica

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http://dx.doi.org/10.1016/j.jtice.2016.01.031
1876-1070/

Table 1
Chemical composition of raw coal fly ash (wt. %).

Component	Content	Component	Content
SiO_2	96.903	K_2O	0.350
Al_2O_3	0.146	MnO	0.012
Fe_2O_3	0.038	TiO_2	0.005
MgO	0.145	P_2O_5	0.011
CaO	0.112	LOI	2.210
Na_2O	0.065	Total	99.997

[a] Loss on ignition

nanoparticle morphological transformation from worm-like to sphere, and popcorn-like structures with nanoparticle of 5 to 20 μm, which is much bigger than reported. Also, we formulated a two-step method for the synthesis of mesoporous silica to remove the impurities brought by silica fume, resulting in a white product. Our method used in this study features much more advantage and provide more variety of morphology.

2. Materials and methods

2.1. Materials

Cetyltrimethylammonium bromide (CTAB), sodium hydroxide (NaOH), ethyl acetate ($CH_3COOC_2H_5$), and acetic acid (CH_3COOH) were supplied by Tianjin Fuyu Fine Chemical Co., Ltd., PRC. Methylene blue (MB) was chosen in this study because of its well-known adsorption characteristics. Methylene blue has a molecular weight of 373.9 g/mol, which corresponds to methylene blue hydrochloride with three molecules of water. All reagents were analytical reagent grade and were used without further purification.

Silica fumes (SF) used in this research was obtained from Shanghai Archi Silica Fume Material Co., Ltd, and it was used as silica source. The chemical compositions of the as received silica fume are shown in Table 1, and the content of silica reaches up to 96.903%. To further know the mineral phases, powder X-ray diffraction was done. Only a broadened peak at around $2\theta = 22°$ can be observed in Fig. 1a, indicating an amorphous phase, which makes it a suitable silicon source for mesoporous silica synthesis. The morphology of silica fume was also studied with SEM and TEM, illustrated in Fig. 1b and c. From the images it is clear to see that the silica fume is consisted with spherical particles with the size ranging from 20 to 400 nm.

2.2. Preparation of mesoporous silica materials

In a typical synthesis procedure, the mesoporous silica materials were synthesized by using cetyltrimethylammonium bromide (CTAB) as the template, silica fume (SF) as the silica source while ethyl acetate as a catalyst. Exactly, 9.8 g of CTAB, 2.59 g of SF and 8 g NaOH were dissolved in 100 mL deionized water in a 250 mL erlenmeyer flask and were vigorously stirred for 5 min. Then the erlenmeyer flask was transferred in a portable pressure steam sterilizer and kept at 125 °C for 1 h for silica extraction and the solution was separated from the mixture by a filtration process. Afterwards, different amount of ethyl acetate ($V = 8$, 15 and 35 mL) was quickly added to the solution and stirred for 30 s. Subsequently, the reaction mixture was aged at 125 °C for 1.5 h in the steam sterilizer after a standing process at room temperature for 1 h. The solid was then filtered, washed twice with deionized water, dried at 90 °C for 12 h, and finally the template was removed by calcination at 550 °C for 5 h with a heating rate of 1 °C/min in air atmosphere. The materials obtained accordingly were hereafter denoted as MSF1, MSF2 and MSF3, respectively.

2.3. Characterization

The chemical composition was analyzed by the $Li_{12}B_4O_4$ method using the X-ray fluorescence spectrometer (XRF) technique (PANalytical B.V. AXIOS^{mAX}). The powder X-ray diffraction (XRD) measurements were recorded on a Germany Bruker D8 Advance powder X-ray diffractometer, using CuKα radiation ($\lambda = 0.154$ nm) with a step width of 10°/min. The surface area, pore size and pore volume of mesoporous samples were analyzed by N_2 adsorption/desorption method using automatic surface area analyzer (ASAP2020, Micromeritics, US). The sample morphology was examined using a Hitachi SU8010 field emission scanning electron microscopy (FE-SEM) system and a JEOL JEM-2100F high resolution transmission electron microcopy (TEM) system. The initial and final concentrations of the dye were analyzed by using a Mapada, UV-1800 PC UV–vis spectrophotometer.

2.4. Sorption and desorption experiments

To evaluate the adsorption properties of the synthesized mesoporous samples, the cationic dye methylene blue (MB) was chosen as an adsorbate to conduct the adsorption experiments. Typically, 10 mg of dry mesoporous silica materials were placed in a series of 50 mL flasks containing 20 mL of MB stock solution with concentration of 125 mg/L, and then the mixture was shaken with speed of 200 shakes per min in a shaker at 298 K for 12 h. After that, the MB-adsorbed solid adsorbent was separated from the solution by centrifugation. The residual concentration of the dye was determined spectrophotometrically at 664 nm as λ_{max} of MB. The adsorption capability (q_e, mg/g) of MB in mesoporous silica material was calculated by the following equation:

$$q_e = (C_0 - C_e)\frac{V}{m} \quad (1)$$

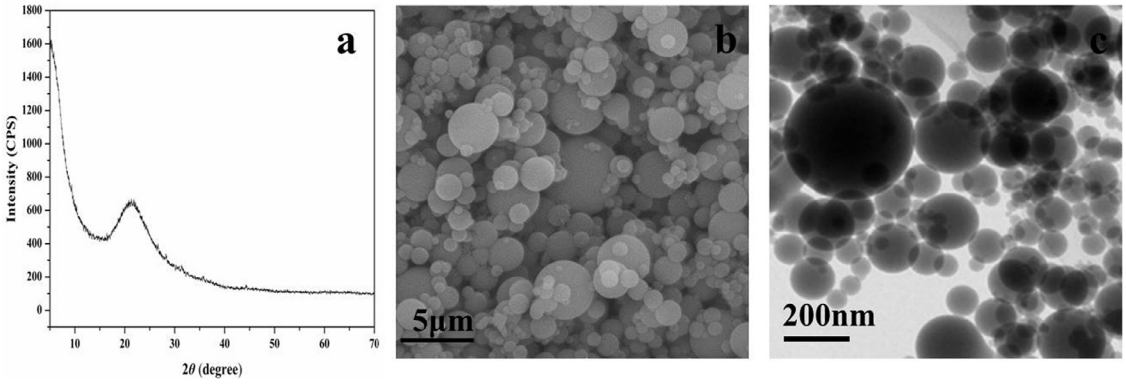

Fig. 1. High-angle XRD pattern (a), SEM image (b), and TEM image (c) of silica fume.