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奈米孔徑環保吸附材之製備與其應用於室內 VOCs 微污染控制研究(1/3)

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PROGRESS REPORT (1/3)
Synthesis of nano-porous environmental adsorbents and their application to control VOCs from indoor air micro-contamination
奈米孔徑環保吸附材之製備與其應用於室內VOCs微污染控制研究

NSC Project No.: NSC 94-2211-E-009-046
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Abstract

Mesoporous silica particles such as MCM41 have reached wide attention because of its well-defined ordered porous structure with very high specific surface area and hydrophobic property. In this study, meso-structured silica particles were produced via aerosol route. The effects of surfactant concentration on the pore structure and the acetone adsorption capacities were investigated. The results indicated that the values of specific surface area (754 ~ 1337 m2/g) were increased with increasing the molar ratio of surfactant / silica (Surf / Si) for test range of Surf / Si = 0.10 to 0.22. The pore size distributions were in the range of 2.0 to 2.6 nm. An increase in the specific surface area led to an increase in the acetone adsorption capacities for Surf / Si ranged from 0.10 to 0.18. But this was not the case for the Surf / Si = 0.22 sample, even though its specific surface area was the highest, its acetone saturated adsorption capacity could be less than that at Surf / Si = 0.18.

Keywords: nano-structured materials, porosity, tetraethoxysilane (TEOS), M41S, evaporation-induced self-assembly (EISA), aerosol pyrolysis.

中文摘要

中孔洞矽質材料具有高度開發潛力，材料本身不但具有高勻度的孔洞結構組成，其高比表面積與超疏水之物理特性，更讓它受到產學業界的青睞。中孔洞矽質材料的表面物性與孔洞結構深受製備程序變化的影響，本研究針對了其前驅液的組成，改變界面活性劑之比例，並以氣膠合成程序，成功的快速製備出不同物性之中孔洞矽質材料，並以半導體常見揮發性有機物丙酮進行吸附能力分析。

結果指出，中孔洞矽質材料之比表面積隨著前驅液中界面活性劑比例的增加，呈現大幅度上升的效果，其比表面積甚至高達1337 m2/g。在材料表面孔洞式樣部份，隨著界面活性劑之比例改變，孔洞孔徑分佈則介於2.0~2.6 nm之間，其孔洞形狀亦有六角

晶型與蟲洞結構變化。丙酮吸附能力分析結果，在界面活性劑之比例0.10~0.18中，顯現高比表面積之中孔洞矽質材料對於丙酮吸附上優於低比表面積者，但於本研究中亦發現界面活性劑之比例0.22所製備之中孔洞矽質材料，雖然具有最高的比表面積，但其對丙酮之吸附能力卻遜於界面活性劑比例0.18之中孔洞矽質材料，顯示當比表面積高於一固定值後，比表面積的大小已不是影響丙酮吸附能力的主要限制，取代之受限因子可能中孔洞孔徑因素。

關鍵字：奈米結構材料，中孔洞，分子自組裝

1. Introduction

The mesoporous materials such as zeolite and M41S family have been synthesized [1-5] and attracted high attention in the past decade due to their unique properties and potential applications[6, 7]. These materials are typically synthesized by conventional hydrothermal or sol-gel methods which are time-consumed. A newly developed method of evaporation induced self-assembly (EISA) to synthesize ordered mesoporous materials was developed by Lu et al.[8]. The EISA route combines the simple sol-gel process and the aerosol-assisted process with the efficiency of surfactant self-assembly, thus allowing rapid synthesis of mesoporous materials.

But up to the present there is limited information on the surfactant molar ratio effect on the morphology and physical properties of the mesoporous materials manufactured by the EISA method. The surface area and pore diameter distribution of synthesized materials are important factors for their applications as adsorbents and catalytic supports. Therefore, the purpose of this study was to investigate on the effect of Surf / Si precursor molar ratio on the physical properties of the hexagonal mesoporous silica powder synthesized via aerosol route. Their effect on the acetone adsorption capacity was also studied.

2. Experimental

Mesoporous silica particles with various molar ratios of Surf / Si were prepared by aerosol route. The reagents used in this study were TEOS, CTAB, EtOH, H2O, and HCl. The reagents were nebulized by an ultrasonic atomizer as carried by high pressure air. The reactor was consisted of two heating zones, the first zone was operated at a temperature of 150 ^{o}C and the second zone was at a temperature of 550 ^{o}C. The total residence time of the reaction system ranged from 6 to 8 seconds depending on system flow rate. The synthesized samples were collected downstream of the reactor with a high efficiency filter which was maintained at a temperature of 150 ^{o}C to avoid water condensation. They were then placed in an oven for four hours at a calcination temperature of 550 ^{o}C.

The morphology and mesoporous structures of the particles were characterized using transmission electron microscopy (TEM, Hitachi H-7100) and X-ray diffraction (XRD, Rigaku D/MAX-B, using Cu Kα radiation source at 1.54 Å). Nitrogen adsorption isotherms, surface area, and pore diameter distribution were determined using a surface area and porosimetry system (Micromeritics ASAP 2020). The average pore diameter and the pore distribution were obtained with the Brunauer-Emmett-Teller (BET) equation.

Mesoporous silica particles were tested for application as adsorbents via the saturated adsorption study of acetone vapors. The adsorption temperature was set to 25 ^{o}C. Approximately 0.1 g of adsorbents prepared by aerosol route were loaded into the adsorption column (with inner diameter of 1.0 cm) and the inlet flow-rate was operated at 500 cm^3/min in each adsorption experiment. The saturated adsorption capacities of adsorbents were calculated by the breakthrough curves of the adsorbents, which were obtained by the variation of acetone concentrations before and after the adsorption system. The acetone concentration in the gas stream was measured using a gas chromatography / flame ionization detector (GC/FID, SRI 8610C).

3. Results and Discussion

The synthesized samples were denoted as N-X-T-W, where X corresponded to the 100 × molar ratio of (Surf / Si) and W was the calcined temperature. Table 1 lists the physical properties of pore volume, surface area, BJH pore diameter, and pore structure. The samples exhibited high surface area of 753, 1152, and 1337 m2/g, respectively, for the Surf / Si molar ratios of 0.10, 0.18, and 0.22.

Table 1. Physical properties characterized by XRD and BET analysis

Sample code	Synthesized temp (℃)	Surfactant/Si ratio	Pore volume (cc/g)	Surface area (m2/g)	BJH desorption pore diameter (nm)	Pore sturcture
N10T550	550	0.10	0.606	754	2.5	disorderd
N18T550	550	0.18	0.895	1153	2.4	hexagonal
N22T550	550	0.22	0.935	1337	2.5	worm-like

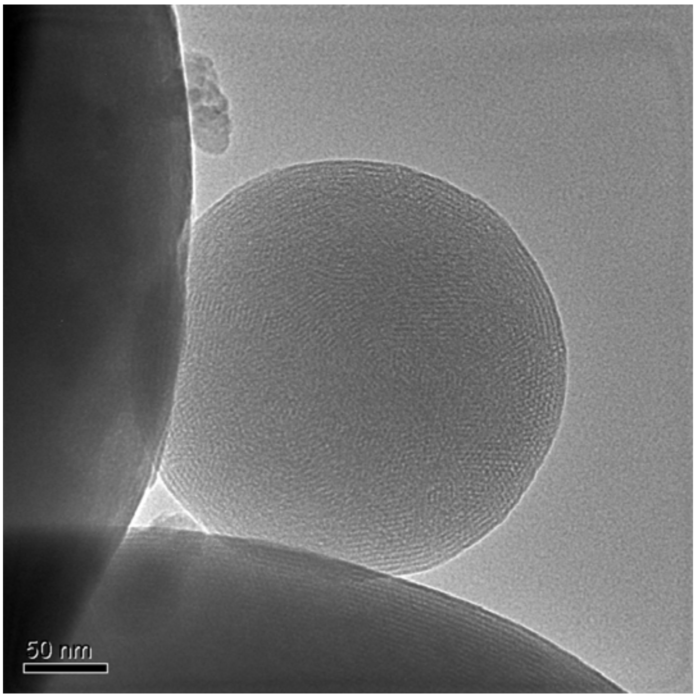

Figure 1. TEM image of mesoporous silica particles of N18T550

The TEM image of a typical sample of the N18T550 adsorbents manufactured in this study was shown in Figure 1. It is clear that the sample exhibited a porous structure, which is better ordered in the N18T550 sample as compared to other Surf / Si molar ratio samples. The ordered mesoporous structures of the samples were also confirmed by small angle x-ray diffraction patterns. A strong intensity diffraction peak located at about $2\theta = 2.5°$ representing (100) orientation was appeared for the N10T550, N18T550 and N22T550 samples.

The nitrogen adsorption isotherms and pore diameter distributions of the hexagonal mesoporous silica powder prepared with various molar ratio of Surf / Si are shown in Figure 2 and Figure 3. The nitrogen adsorption isotherm were of type IV for all samples, typical of mesoporous solid particles. All samples revealed a rapid adsorption at a relative pressure range of 0.2 to 0.3, which was the evidence of capillary condensation into uniform mesopores.

The BJH pore diameter distributions of the N10T550, N18T550, and N22T550 samples showed a narrow pore diameter distribution centered at around 24 Å. However, it was noted from Figure 3 that the peak intensity for pore diameter distribution of N18T550 sample was higher than those of N10T550 and N22T550 samples. It may be dut to the rigid and uniform mesoporous structure of N18T550 sample.

Figure 4 displays the acetone saturated adsorption capacity of the hexagonal mesoporous silica particles prepared with various molar ratios of Surf / Si. Regardless of any acetone inlet concentrations analysis, one can see the saturated adsorption capacity of N10T550 sample was inferior to the other two adsorbents. On the other hand, at a relatively high acetone inlet concentration of 300 ppm, the N22T550 adsorbent has the highest adsorption capacity. But at a relatively low acetone inlet concentration of 100 ppm, the N18T550 adsorbent has the highest adsorption capacity. With almost the same chemical components and BJH pore diameter distribution for these samples, the difference of saturated adsorption capacity between different adsorbents may be due to surface area and mesoporous structure uniformity. The higher surface area indicated the more active site on surface structure which can be provided for adsorption. Although N22T550 sample has the highest surface area, the saturated adsorption capacity of it was nearly the same as or even less than that of the sample N18T550. Therefore, it was possible that the structure uniformity restrained the diffusion of adsorbate while with almost the same mesopore diameter for N10T550 and N18T550 adsorbents, one can see that the surface area was the key factor that affected the saturated adsorption capacity.

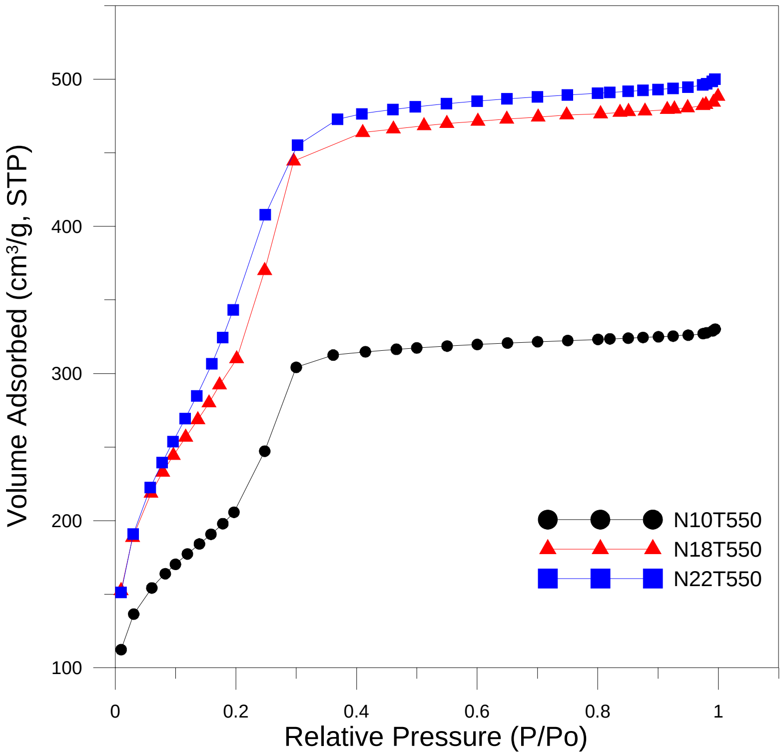

Figure 2. Nitrogen adsorption isotherms of mesoporous silica particles of N10T550, N18T550, and N22T550.

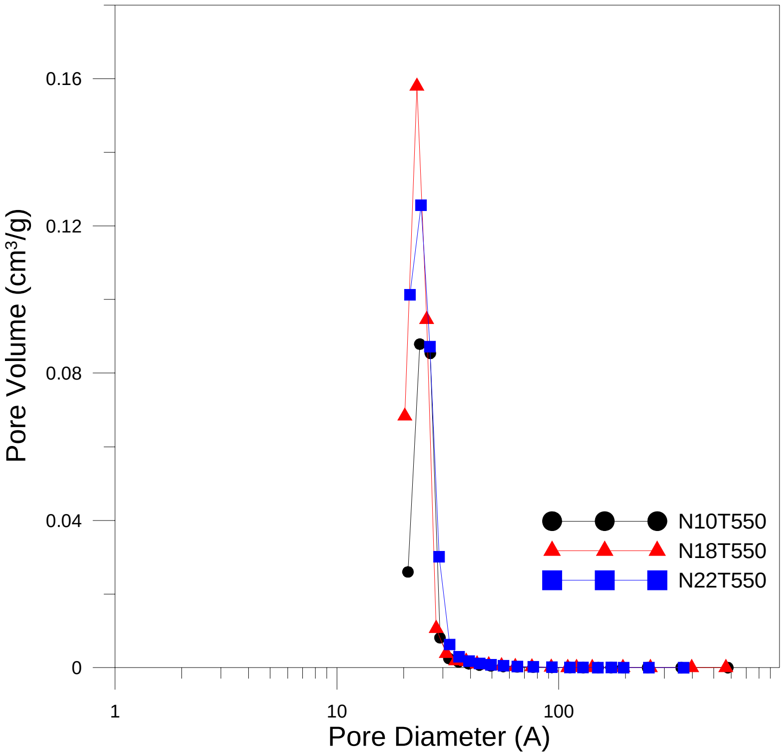

Figure 3. BJH pore diameter distributions of mesoporous silica particls of N10T550, N18T550, and N22T550.

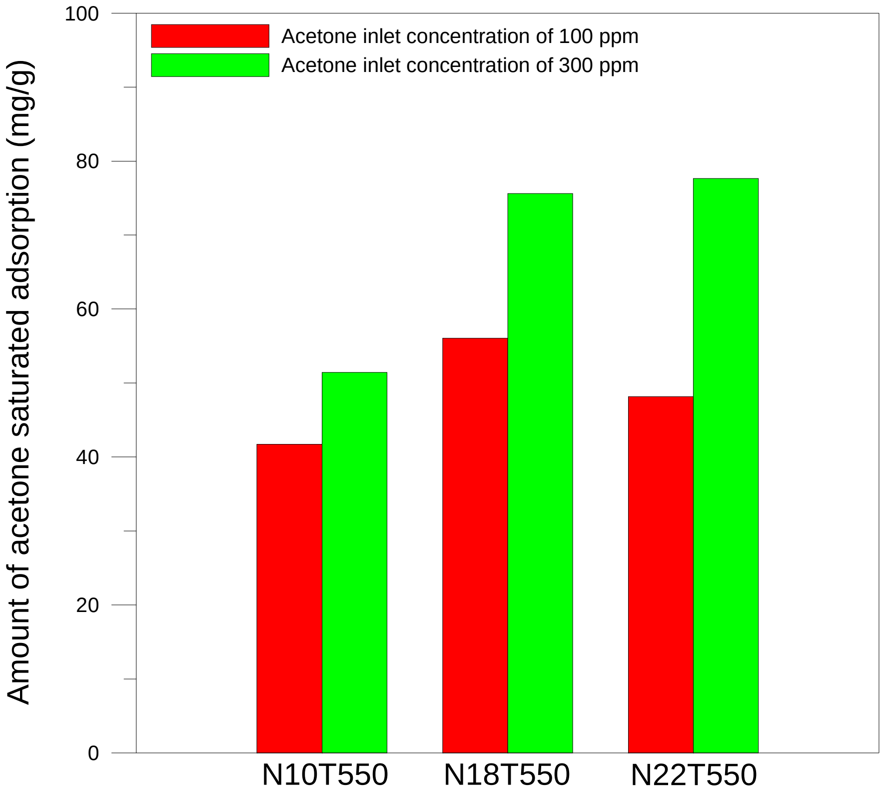

Figure 4. Saturated adsorption capacity of acetone via N10T550, N18T550, and N22T550 adsorbents

4. Conclusion

Mesoporous silica particles with various molar ratios of Surf / Si have been synthesized via aerosol route. The results indicated that the molar ratio of Surf / Si was a key parameter on the surface area and the pore structure. Highly uniform pore diameter distribution and ordered pore structure of synthesized materials which exhibited high saturated adsorption capacity for acetone removal can be achieved for molar ratio of Surf / Si = 0.18. Mesoporous silica particles have a potential to be used as a highly efficient adsorbent in organic vapor concentrators for controlling VOCs emitted from semiconductor and optoelectronic manufacturing plants. This has been demonstrated by the adsorption of commonly encountered organic vapors, acetone, in this study.

5. Project Achievement

So far we have published two conference papers supported from this project, one in the international conference, Asia aerosol conference (AAC), and the other one in the 3rd Environmental protection and nanotechnology conference:

1. Hsunling Bai and Chin-Te Hung, "Synthesis of mesoporous silica materials via aerosol process and application as adsorbents" 4th Asia Aerosol Conference, 2005.
2. Hsunling Bai and Chin-Te Hung, "Production of meso-structured silica particles via aerosol route for acetone adsorption: effect of surfactant concentration" 3rd Environmental protection and nanotechnology conference, 2006.

And currently we are writing a journal paper and will submit it to a referred SCI journal for possible review and publication at the end of the first year project.

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