Mesoporous silica nanoparticles synthesized by using templating technique

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Abstract. Mesoporous silica nanoparticles (MSNs) were synthesized in this research. TEOS was used as a precursor and two types of surfactant including CTAB and TTAB, to be used as a main structure directing agent. DMHA, PVP and S770 were employed as co-templates. To compare the effect of template type on the characteristics of synthetic nanoparticles, molar ratio of precursor to template is equally controlled. The co-condensation method combined with water-CHX biphasic condition was utilized for this synthesis. The as-synthesized particles were incinerated to remove the directing agent at about 550 °C under atmospheric pressure for 5 h. To confirm the quality of synthesized nano-silica, characteristics of nanoparticles are characterized by several analytical techniques. Morphology, particle size and composition are analyzed by SEM and TEM. Surface area, pore volume and pore size distribution are determined by BET and BJH techniques through N_2 adsorption-desorption isotherm, while phase of particles was analyzed by XRD technique. Results showed that specific surface area (SSA) of MSNs synthesized by using TTAB, TTAB+DMHA, TTAB+PVP and TTAB+S770 is about 672.30, 477.60, 431.91 and 259.71 m^2/g, respectively. Pore size distribution of the obtained MSNs are quite uniform. XRD results indicate the amorphous phase of MSNs synthesized in this work. N_2 adsorption-desorption isotherm shows microporous size on each particles. Experimental results confirm the effect of structure directing agent type on the characteristics of synthesized MSNs.

Keywords: Characteristics, Mesoporous, SiO_2, Nanoparticles, Synthesis.

1. Introduction

Mesoporous silica nanoparticles (MSNs) are one of the most important materials that many research groups around the world pay attention to research and develop. This because they have high potential to apply in different fields. To synthesis of MSNs, many of an approaches are introduced. One of the most important synthesis method is co-condensation combined with biphasic condition and using of directing agents. Using this synthesis method can resulted a high monodisperse and high surface area MSNs that is suitable for application in different fields such as drug delivery, enhancement of membrane performance and environmental problem mitigation. This research attempted to synthesized monodisperse MSNs with high surface area by using the directing agent method. Different types of surfactant that is used as directing agent or template, were employed. Co-condensation method combined with water-CHX biphasic condition was utilized in this research.

2. Materials and Methods

Tetraethylorthosilicate (TEOS, $C_8H_{20}H_4Si$, M_W: 208.33 g/mol, Density of 0.932-0.934 at 20 °C) was supplied by Merck. Cetyldimethyl ammonium bromide (CTAB, $C_{19}H_{42}BrN$, M_W: 364.45 g/mol), Tetradecyltrimethyl ammonium bromide (TTAB, $C_{17}H_{38}BrN$, MW: 336.39 g/mol, 97.5% purity) and Ryoto Sugar Ester S770 manufactured by Mitsubishi-Kagaku Foods Corporation, were supported by Merck (USA), Sigma-Aldrich (Singapore) and Caltech Corp., Ltd (Thailand), respectively. Ethanol (EtOH; C_2H_5OH, M_W: 46.07 g/mol, 99.9%) and cyclohexane with purity of 99.5% (CHX, C_6H_{12}, M_W: 84.16 g/mol)

were purchased from RCI Labscan. L-Arginine (LAG, $C_6H_{14}N4O_2$, M_W: 174.20 g/mol) that is used as catalyst, was supplied by Himedia (India). Dimethylhexylamine (DMHA, $CH_3(CH_2)_4CH_2N(CH_3)_2$, MW:129.24 g/mol) and polyvinyl pyrrolidone (PVP, M_W: 360,000 g/mol) were purchased from Sigma-Aldrich (Singapore). Deionized water (DI-water, 18.2 MΩ) was produced by a Sartorius H2OPRO-DI-T Arium Pro DI Ultrapure Water System.

Scientific community intensive attend to micro and meso-porous silica nanoparticles due to its high potential applications in various industrial fields. In this study, the high surface area mesoporous silica nanoparticles (MSNs) were attempted to synthesize. Characteristics of the obtained particles were evaluated. Co-condensation method that is modified from Stöber process [1] combined with water-CHX biphasic condition [2] was utilized for the synthesis of silica nanoparticles. Main templates including CTAB and TTAB, and co-templates including DMHA, PVP and S770, and catalyst; L-Arginine (LAG), were dissolved in DI-water under stirring and then CHX was slowly poured into the solution to create a second phase on the template and DI-water mixtures. About 15-20 min after CHX was added, TEOS was added dropwise and continued stirring for 20 h. Silica nanoparticles were collected by centrifugation and washed three times with ethanol-DI-water solution. Afterwards, as-synthesized particles were washed again with RO-water and dried in electric oven at 80 °C overnight. The process of the synthesis was shown in figure 1. Synthesized particles were characterized by an analytical techniques. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed to study the external and internal morphology and porous structures appeared on the particles. While Brunauer-Emmett-Teller (BET) Surface Area Analysis and Barrett-Joyner-Halenda (BJH) through the resulted N_2 absorption-desorption isotherm were utilized to analyze the surface area and pore size and volume, respectively. X-ray diffraction spectroscopy was used to evaluate the phase of particles.

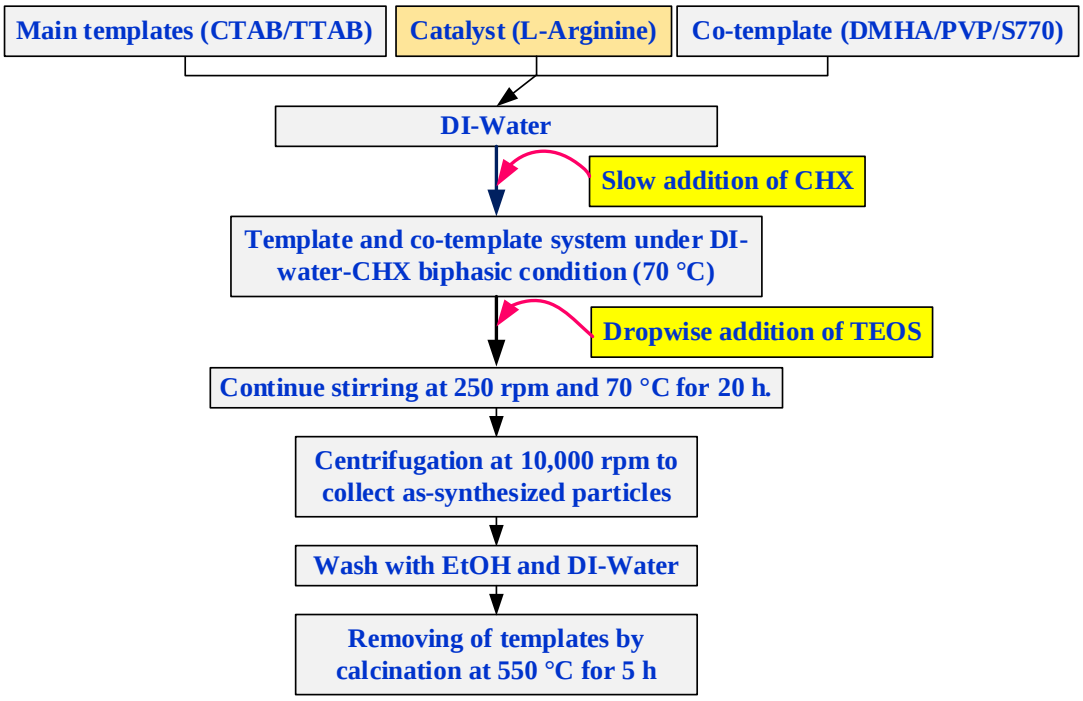

Figure. 1 Synthesis process of MSNs.

3. Results and discussion

As shown in figure 1, three types of co-template (DMHA, PVP and S770) used in this research affect external morphological structure of synthesized MSNs particles. Smallest and biggest particle size was obtained when S770 and DMHA are used as co-template, respectively. However, external nano-structure of MSNs not well define when S770 is employed.

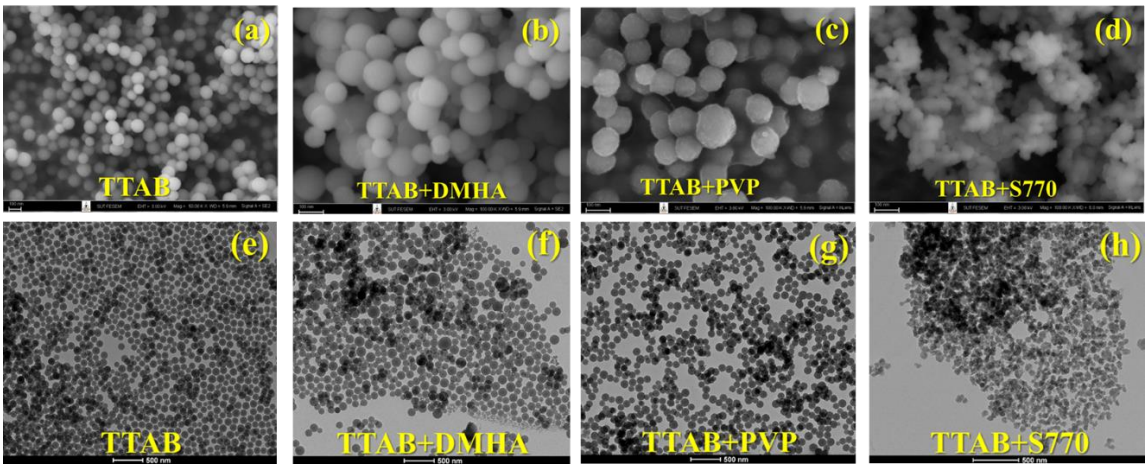

Figure 2. (SEM) External morphology of synthesized MSNs using, (a) TTAB, (b) TTAB+DMHA, (c) TTAB+PVP, TTAP + S770 and (d) CTAB, as templates and (TEM) porous structure of synthesized MSNs using, (e) TTAB, (f) TTAB +DMHA, (g) TTAB+PVP and (h) TTAB+S770.

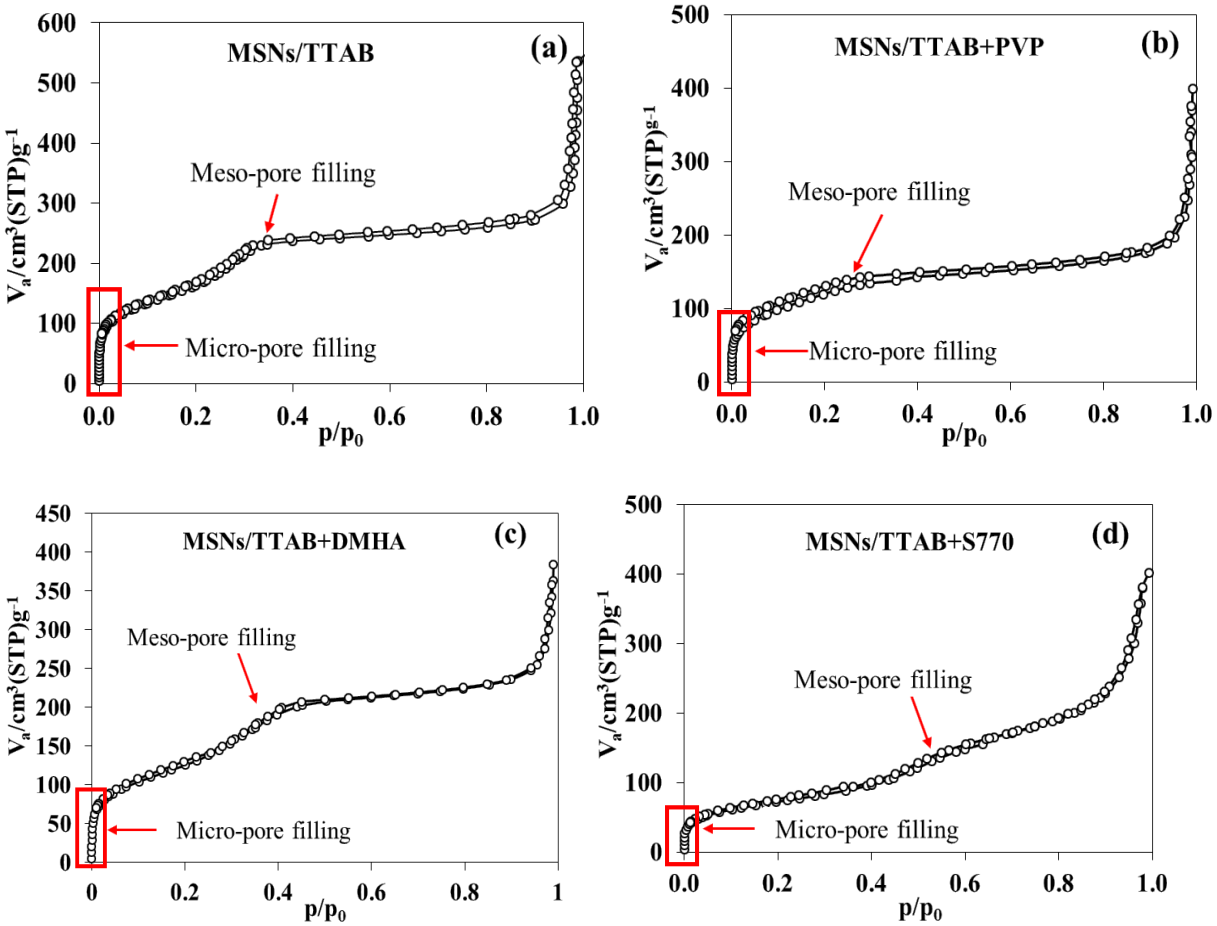

Figure 3. Nitrogen adsorption-desorption isotherm of synthesized MSNs using TTAB, (b) TTAB+PVP, (c) TTAB + DMHA and (d) TTAB+S770, as template and LAG as catalyst.

Porous silica nanoparticles were completely synthesized. Profile of N_2 adsorption-desorption isotherm as illustrated in figure 2 shows clearly pore characteristics on the particles and corresponds to the type IV

adsorption-desorption isotherm published by IUPAC [3]. Type IV adsorption-desorption isotherm shows micro/meso-porous on the particles. Specific surface area (SSA) of the synthesized MSNs was about 477.60, 431.91 and 259.71 m^2/g when DMHA, PVP and S770 are used as co-template, respectively. While SSA of MSNs that is synthesized by no use of co-template, was about 672.30 m^2/g. Total pore volume (p/p_0 = 0.990) and mean pore diameter of resulted MSNs/TTAB, MSNs/TTAB+DMHA, MSNs/TTAB+PVP and MSNs/TTAB+S770 were about 0.8301, 0.5788, 0.5722, 0.6156 cm^3/g and 4.94, 4.85, 5.30, 9.48 nm, respectively. Pore size distribution ($d_{p,peak}$) which is analyzed by Belsorp Adsorption/Desorption Data Analysis Software (Ver. 6.1.0.4, BEL, Japan, Inc.,), of MSNs/TTAB, MSNs/TTAB+DMHA and MSNs/TTAB+PVP was about 2.43 nm while pore distribution of MSNs/TTAB+S770 was about 3.71 nm. Effect from particle size, pore volume and pore size distribution as well as micro-pore and meso-pore filling (as shown in figure 3) [4] lead to the highest and lowest SSA of MSNs/TTAB and MSNs/TTAB+S770, respectively.

4. Conclusion

In summary, mesoporous silica nanoparticles (MSNs) or micro/meso-porous silica nanoparticles (MMSNs) with quite high SSA were completely synthesized by co-condensation method combined with a biphasic condition and templating technique. Co-template types affect the morphological nano-structure, surface area, pore volume and particle size of synthesized MSNs. SSA of MSNs decrease when DMHA, PVP and S770 is utilized as template.

Acknowledgements

This research work was financially supported by the Science Research and Innovation Fund (budget year of 2020), Thailand Science Research and Innovation (TSRI). We would like to thank to the Science Center and Department of Physics, Faculty of Science and Technology for infrastructure support. We also thank to Mr. Wirachai Meesuk for helps.

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