**Effect of reactant molar ratio on the hierarchical morphology of a novel mesoporous silica**

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**Highlights**

* Using MTMS in the synthesis of mesoporous silica produced a novel material (MS-Asym)
* Increasing the silica to template relative molar ratio gave a hierarchical morphology
* All members of the MS-Asym sfamily possess a similar porous structure with the same pore size

**1. Introduction**

Porous materials and specially mesoporous silica particles are commonly used in a number of different applications such as petroleum refining, detergents, medicinal applications and separations [1]. MSP are very promising as they are cheap to synthesize and their surface properties can be tuned to suit specific functionalities [2]. The effect of employing the asymmetric methyltrimethoxysilane (MTMS) as the only silica source on the synthesis of mesoporous silica particles has been scrutinised for the first time in our previous work [3]. The resultant synthesis was a novel MSP, which we named MS-Asym. In the current study, we have focused on analyzing the MS-Asym particle’s morphology, characteristic sizes and crystallinity, when increasing the silica to template relative molar ratio.

**2. Methods**

The novel mesoporous silica, MS-Asym, was synthesised using a triblock copolymer, Pluronic P123 (EO20PO70EO20) in a highly acidic media, and trimethoxy(methyl)silane (MTMS, Sigma-Aldrich) as a new silica source via a sol gel method [3, 4].

To study the morphology transformation of the samples seven different experiments were conducted. The pH and the amount of Pluronic were kept constant in all the tests. The amount of MTMS was increased to reach the desired MTMS/Pluronic P123 molar ratio from 59 to 590. The produced samples were labelled MS-Asym-1 to MS-Asym-10 according to the relative molar ratio of silica/template. As a result, the silica source concentration increased from 0.3 mol/L to 2.24 mol/L, and the concentration of the template decreased from 0.53×10-2 mol/L to 0.38×10-2 mol/L.

The products were characterised using SEM to study the external morphology, TEM to investigate the internal structure and ATR-FTIR spectroscopy to confirm the conformation of the bonds. A Malvern Mastersizer was also employed to measure the particle size by laser diffraction.

**3. Results and discussion**

In the first three samples (MS-Asym-1, MS-Asym-2 and MS-Asym-3), the solid products were not discrete and they formed a structure with the characteristics of continuous solids [3]. However, according to the SEM results shown in Figure 1, MS-Asym-2 and MS-Asym-3 included many tiny spherical particles that were packed together. MS-Asym-4, MS-Asym-6, MS-Asym-8 and MS-Asym-10 were quite similar in shape, and consisted of spherical and rod-like individual particles, completely different from the first three samples.



Figure 1 SEM and TEM results of MS-Asym-1, MS-Asym-2 and MS-Asym-3

From the size measurements of these samples demonstrated in Figure 2, it could be suggested that the outer diameter of the particles was mostly controlled by varying the concentration of the silica source. The higher the concentration of MTMS, the larger the characteristic sizes of the produced particles were, which is in accordance with what Neville et al. (2016) observed in the synthesis of nonporous PEI-MTMS particles [5].

Figure 2 Comparison of the characteristic sizes of the samples

On the other hand, the pore size of all these samples obtained from their TEM images, proposes that all the porous samples from MS-Asym-2 to MS-Asym-6 have a similar pore size range. This similarity could be attributed to their similar process conditions such as pH and temperature as well as the employment of the same template in their fabrication. By further increasing the amount of MTMS and decreasing the concentration of Pluronic, MS-Asym-8 and MS-Asym-10 were produced, which were much less porous than the previous members of the family. MS-Asym-6, MS-Asym-8 and MS-Asym-10 also presented crystallinity, which did not appear in the other samples.

**4. Conclusions**

Altering the amount of MTMS resulted in a combined change in both MTMS and Pluronic concentration. By considering SEM and TEM results of the samples, a distinct pattern was identified as described in the results section. This study also found that the combined effect of MTMS and P123 concentrations played a crucial role in controlling the particle morphology of MS-Asym mesoporous material. With the increase in the MTMS concentration and decrease in the P123 concentration, the morphology of the spherical-like MS-Asym particles changed from aggregated nanoparticles to micrometre size granules.

The new developed porous silica family offers the possibility to be processed in a shorter time, which is beneficial in commercial applications since it undergoes a faster reaction and makes the project more feasible. It is also large and inert and its density covers a range which is lower than that of water density in MS-Asym-6. These characteristics could open up new horizons to enquire into different novel applications.

**References**

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