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SYNTHESIS OF HIERARCHICAL STRUCTURED POROUS $\text{MoS}_2/\text{SiO}_2$ MICROSPHERES BY ULTRASONIC SPRAY PYROLYSIS

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Hierarchical structure porous $\text{MoS}_2/\text{SiO}_2$ microspheres were prepared by ultrasonic pyrolysis technique. The nanostructured $\text{MoS}_2/\text{SiO}_2$ materials were characterised by scanning electron micrograph (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), high-resolution transmission electron microscope (HRTEM), as well as nitrogen isotherm. The $\text{MoS}_2/\text{SiO}_2$ microspheres, synthesised using polystyrene latex spheres as a template, showed two pore sizes: 5.8 and 68 nm. The micro-, meso- and macropore volume was also calculated. Effect of PSL:SiO₂ ratio on the hierarchical structure was also investigated.

Keywords: hierarchical structure, $\text{MoS}_2/\text{SiO}_2$, ultrasonic spray pyrolysis, hydrotreating

INTRODUCTION

Hierarchical structured materials have attracted significant interest because of their wide applications including catalysis and separation process. Their multiscale porosity has advantages of rendering size and shape selectivity with micro- and mesopores and favouring the diffusion and accessibility to the active sites by large molecules with the macropores. A variety of hierarchical structured materials have been developed (Lin et al., 2010; Lemaire and Su, 2011; Stevens et al., 2011; Wang et al., 2011), and a recent excellent review summarised these results (Yang et al., 2011).

Molybdenum sulfides-based catalysts have been extensively used in hydrodesulfurisation (HDS) for several decades (van Veen and Colijn, 1993; Meille et al., 1997; Breyse et al., 2003; Egorova and Prins, 2004; Topsoe, 2007). Having the potential to enhance its catalyst activity, nanostructured MoS_2 -based catalysts have attracted significant interests in recent years. As the conventional sweet light crude oils dwindle, the utilisation of extra heavy oils, which contain large molecules with molecular size ranging from tens of nm up to 100 nm, such as asphaltenes and resins, is becoming more common. Also extra heavy oil contains high

level of contaminants. Upgrading and refining of extra heavy oil is more complicated than those of conventional light crude oil. To upgrade extra heavy oil, these molecules must have contact with the catalyst's active sites, which can be achieved either by using nanosized catalysts or using nanostructured catalysts with different pore sizes that can facilitate the diffusion of different sized reactants. As the upgrading and refining processes involve reactants and products with different sizes from H_2 to asphaltenes, catalysts with multiscale porous structure are expected to facilitate the processes.

Ultrasonic spray pyrolysis (USP) is able to convert different types of liquid and solid precursors into nanostructured, highly dispersed and uniform materials. A series of nanostructured materials have been developed with this technique (Bang and Suslick,

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2010). However, these materials usually possess single pore size. For example, Skrabalak prepared porous MoS_2 microspheres with pore size of ~ 20 nm using the USP technique (Skrabalak and Susslick, 2005). In this work, we report the synthesis of hierarchically porous $\text{MoS}_2/\text{SiO}_2$ microspheres using USP. SiO_2 is a common support for MoS_2 in hydrotreating processes. It has shown that by using polystyrene latex (PSL) microspheres as a template for creating the macropores and colloidal silica nanospheres as a support for the formation of both meso- and micropores, hierarchically structured porous $\text{MoS}_2/\text{SiO}_2$ could be successfully synthesised.

EXPERIMENTAL

Materials

Ammonium tetrathiomolybdate, LUDOX[®] SM-30 colloidal silica (30 wt.% suspension in H_2O , 8 nm in diameter) were purchased from Sigma-Aldrich, Oakville, Canada. PSL microsphere (0.05 μm , 2.5 wt.% dispersion in water) were obtained from Alfa-Aesar, Ward Hill, MA.

Synthesis of Mesoporous $\text{MoS}_2/\text{SiO}_2$

The $\text{MoS}_2/\text{SiO}_2$ particles were synthesised with the following method. A designated amount of LUDOX[®] SM-30 colloidal silica was dissolved into 50 mL distilled water followed by adding certain amount of PSL microsphere dropwise. The solution was then diluted to 100 mL. Proper amount of $(\text{NH}_4)_2\text{MoS}_4$ was dissolved into 100 mL distilled water to form a Mo containing solution. The silica-PSL solution was then dropped into the Mo containing solution slowly with stirring. The mixture was then loaded to the ultra-sonic cell and nebulised with an ultrasonic atomiser (2.4 MHz, Sonaer Inc., Farmingdale, NY). The smog containing small droplets generated from the nebuliser was carried through a horizontal quartz tube at 700°C with a continuous flow of argon (99.999%, 5.0 dm^3/min). The products were collected, filtered, washed with DI water and dried at room temperature.

For comparison, SiO_2 microspheres were also prepared according to a literature procedure (Iskandar et al., 2001, 2002, 2003; Thill and Spalla, 2005; Okuyama et al., 2006; Chang et al., 2008; Widiyastuti et al., 2010). Typically, a designated amount of LUDOX[®] SM-30 colloidal silica was dissolved into 100 mL of distilled water. Then, a designated amount of PSL microsphere was slowly dropped into the solution. The solution was then diluted to 200 mL with distilled water and stirred for 1 h. The solution was loaded into the ultrasonic cell, subject to USP. The USP condition and product collection are the same as described for $\text{MoS}_2/\text{SiO}_2$.

Physical Characterisation

The synthesised materials were characterised by scanning electron microscopy (SEM)/energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), high-resolution transmission electron microscope (HRTEM) and N_2 adsorption/desorption isotherm. High-resolution images of the $\text{MoS}_2/\text{SiO}_2$ microspheres were taken with a Strata DB235 field emission SEM. EDX was carried out using a Oxford EDX system. HRTEM observations were conducted using FEI Titan 80–300 transmission electron microscope (TEM) equipped with a CEOS-designed hexapole-based aberration corrector for the image-forming lens and one for the probe-forming lens. This instrument achieves sub-Ångstrom resolution. Scanning transmission electron microscopy (STEM) high-angle annular dark-field (HAADF) images (Nan et al., 2011), intensity of which is sensitive to the atomic number of the atoms

in the sample (also known as Z-contrast), were obtained while operating the TEM at the accelerating voltage of 200 kV. The XRD measurements were carried out with a Bruker D8 X-ray diffractometer equipped with a graphite monochromator and a vertical goniometer, using $\text{Cu-K}\alpha$ radiation at 40 kV and 40 mA. The phases were identified by comparison with the data of the (JCPDS) files or International Centre for Diffraction Data (ICDD). The specific surface area measurement was carried out by the BET method in a surface area analyser (SA3100, Beckman Coulter, Mississauga, ON, Canada).

RESULTS AND DISCUSSION

Figure 1 shows SEM images of $\text{MoS}_2/\text{SiO}_2$ microspheres (Figure 1a) and SiO_2 microspheres (Figure 1b), obtained with PSL: SiO_2 ratio of 1:2. The particle size for both materials was around 500 nm. Pores with pore size of about 50–100 nm were clearly observed. The sphere shape was formed from the spray drying process. Ultrasonic nebuliser produced small droplets containing PSL microspheres, SiO_2 nanoparticles and MoS_2 precursor. These droplets shrank, and the constituent particles and precursor assembled into solid through evaporation via capillary forces and electrostatic forces (Sen et al., 2009).

Figure 1. SEM images of (a) $\text{MoS}_2/\text{SiO}_2$ microspheres and (b) SiO_2 microsphere prepared by USP with a PSL: SiO_2 ratio of 1:2.

It has been reported that drying rate affected the shape of the solid particles. Too fast drying of the droplets could lead to the formation of non-spherical solids. In this work, non-spherical shaped particles were not observed with SiO_2 , indicating that the carrier gas flow rate is not fast enough to trigger the deformation. However, a few doughnut-like particles were observed for $\text{MoS}_2/\text{SiO}_2$ as shown in Figure 2. Two different doughnut shapes were shown in Figure 2a and b. Similar morphologies have been reported in the literature (Leonard et al., 2002; Sen et al., 2009). Since the carrier gas flow rate for both $\text{MoS}_2/\text{SiO}_2$ and pure SiO_2 is the same, this deformation was not caused by the drying rate. Sen et al. (2009) found that doughnut-like transition was formed at moderate drying rate during evaporation driven self-assembly of colloidal alumina, which was dependent on the volume fraction of the colloids. With high alumina colloid volume fraction (5% alumina colloid), spherical shaped materials were obtained, while low alumina volume fraction (2%) led to the formation of doughnut-like particles (Sen et al., 2009). In this work, the same SiO_2 and PSL concentration was used for both materials. However, in the synthesis of $\text{MoS}_2/\text{SiO}_2$, certain amount of MoS_2 precursor existed in the solution, which might dilute the solution. However, this concentration decrease was extremely minor, which might not be sufficient to contribute to any morphology change. Most possibly, the morphology change was due to the temperature gradient at the droplet surface. Sen et al. (2009) explained that the thermophoretic force originated from this temperature gradient moved the colloid at the air–water interface, forming a viscoelastic shell of densely packed particles, which might buckle after a sol–gel type transition, forming the doughnut-like morphology. In this work, MoS_2 precursor condensed on the silica nanoparticles gradually, forming MoS_2 -coated SiO_2 . Presence of MoS_2 on the silica surface might have led to a non-uniform temperature distribution, creating a temperature gradient. However, this gradient only occurred in some droplets, thus only a few doughnut-like particles were observed.

The MoS_2 content in the $\text{MoS}_2/\text{SiO}_2$ materials was determined by EDX. Mo content in the material was found to be 10%, an optimal content for a supported MoS_2 catalyst (van Veen and Colijn, 1993; Meille et al., 1997; Breyse et al., 2003; Egorova and Prins, 2004; Topsøe, 2007).

Figure 3a presents the STEM-HAADF image at relatively low magnification of a typical MoS_2 - SiO_2 catalyst particle prepared by USP method, suggesting that MoS_2 (brighter area) is highly dispersed within the SiO_2 sphere template. High resolution STEM-HAADF micrograph (Figure 3b) indicates nanocrystalline MoS_2 was grown within the crevices of densely packed template spheres. Plane stacking of 2–7 layers of MoS_2 crystallites were observed, the length of which ranges from 6 to 12 nm. Furthermore, the MoS_2 interlayer spacing is $6.34 \pm 0.3 \text{ \AA}$, which is consistent with the XRD measurement.

Figure 4 shows the XRD pattern of $\text{MoS}_2/\text{SiO}_2$. The broad peak of 2-theta around 24° is attributed to the SiO_2 . Three broad diffraction peaks at 2-theta of 14.1° , 33.6° and 59.4° , are attributed to the (002), (100) and (110) planes of the poorly crystalline MoS_2 , respectively. The corresponding d spacing was 6.4, 2.7 and 1.2 $\text{\AA}$ respectively (Skrabalak and Suslick, 2005). This material might exhibit some low stacking of layers on the SiO_2 surface along different directions, as evidenced from the HRTEM image. The intensity of MoS_2 diffraction peaks is rather low, suggesting that the MoS_2 is well dispersed along the surface of the SiO_2 .

Figure 5 shows the nitrogen isotherms of $\text{MoS}_2/\text{SiO}_2$ (Figure 5a) and SiO_2 (Figure 5b). Three steps, at the relative pressure range of <0.02 , $0.5\text{--}0.8$ and >0.85 , were observed on both curves,

Figure 2. SEM images of doughnut-like $\text{MoS}_2/\text{SiO}_2$ showing different morphology (a,b) prepared by USP with a PSL: SiO_2 ratio of 1:2.

corresponding to micro-, meso- and macropores in the materials. The inset in each figure showed the pore size distribution. The micro-, meso- and macropore volume was calculated from the adsorbed volume obtained by extrapolating the plateau after each step. The porous properties were summarised in Table 1.

The BET surface area of $\text{MoS}_2/\text{SiO}_2$ was found to be $235 \text{ m}^2/\text{g}$, smaller than that of pure hierarchical SiO_2 ($280 \text{ m}^2/\text{g}$). The pore size of $\text{MoS}_2/\text{SiO}_2$ was 5.8 and 68 nm, while for the SiO_2 microspheres, pore sizes of 4.3 and 70 nm were obtained. This is not unexpected. In the synthesis process, small droplets containing PSL, SiO_2 nanoparticles and MoS_2 precursor were formed by the ultrasonic nebuliser and were taken into the heating zone by the carrier gas; then PSL particles rearranged quickly inside the silica nanoparticles and MoS_2 precursor depositing on the SiO_2 nanoparticles during the evaporation of the droplets, forming particles containing PSL, SiO_2 nanoparticles and MoS_2 precursor stacked together. The well-ordered PSL particles would occupy fixed positions after the droplets were transformed into solid particles. At higher temperature, PSL were decomposed, leaving ordered pores at their original position. The PSL microspheres used were 50 nm, thus the macropore size created is around this value. Actually $\sim 70 \text{ nm}$ pore size was observed for both $\text{MoS}_2/\text{SiO}_2$ and SiO_2 . This pore size is comparable with the molecular size of asphaltene,

Table 1. Properties of the hierarchical structure porous MoS₂/SiO₂ and SiO₂

Properties	MoS ₂ /SiO ₂		SiO ₂	
	PSL:SiO ₂ = 1:2	PSL:SiO ₂ = 1:4	PSL:SiO ₂ = 1:2	PSL:SiO ₂ = 1:4
BET (m ² /g)	235	191	280	232
Pore size (nm)				
Meso	5.8	6.8	4.3	4.3
Macro	68	87	70	55
Pore volume (cm ³ /g)				
Micro	0.077	0.064	0.080	0.065
Meso	0.270	0.137	0.235	0.220
Macro	0.243	0.245	0.203	0.119
Total	0.590	0.446	0.518	0.404

Figure 3. (a) Overview of a typical MoS₂ catalyst particle supported on SiO₂ template at relative low magnification in STEM-HAADF mode; (b) high-resolution STEM-HAADF image of the particle with lattice fringe details of MoS₂.

which may facilitate the diffusion of asphaltenes to get access to the inner active sites.

The mesopores were created from the packing of SiO₂ nanoparticles and MoS₂/SiO₂ nanoparticles formed in the USP process. In this work, 8 nm SiO₂ nanoparticles were used and the packing of these nanoparticles into microsphere shape created mesopores, producing SiO₂ microspheres with mesopore size of 4.3 nm. For MoS₂/SiO₂, MoS₂ deposited on the SiO₂ nanoparticles, resulting in increased SiO₂ nanoparticle size. Therefore, packing of larger-sized nanoparticles led to the formation of larger pores. This is what was observed experimentally. The mesopore size of MoS₂/SiO₂ microspheres (5.8 nm) is larger than SiO₂ (4.3 nm).

The micro-, meso- and macropore volume was calculated by extrapolating the plateaus after each step. The intercept at the y-axis was the adsorbed N₂ volume in gas form. Converting the adsorbed N₂ gas volume into liquid N₂ volume, the pore volume for each pore size could be obtained. The results are also listed in Table 1. The total pore volume of MoS₂/SiO₂ is larger than that of SiO₂, which is due to the larger mesopore and macropore volumes of MoS₂/SiO₂. The microspore volume of MoS₂/SiO₂ and SiO₂ is close to each other.

The PSL:silica ratio determined the hierarchical porous structure of the product. Increasing PSL concentration resulted in the formation of brittle spheres that were easily collapsed. Increasing silica nanoparticles concentration produced microspheres with less porosity. Table 1 also presents the results obtained with MoS₂/SiO₂ and SiO₂ microspheres prepared with a PSL:SiO₂ ratio of 1:4. The total pore volume, micro-, meso- and macropore volume were smaller than their corresponding counterparts prepared using a PSL:SiO₂ ratio of 1:2. However, the change in pore size

Figure 4. XRD profile of the MoS₂/SiO₂ microspheres.

Figure 5. N₂ adsorption/desorption isotherm of (a) the MoS₂/SiO₂ microspheres, (b) SiO₂ microspheres prepared by USP, inset: pore size distribution from the adsorption section.

with increased SiO₂ concentration was different for MoS₂/SiO₂ and SiO₂. For MoS₂/SiO₂, both mesopore and macropore size increased with the PSL:SiO₂ ratio of 1:4. For SiO₂, the mesopore size did not change, while the macropore size decreased. Slight decrease in BET surface area was observed for both materials. This difference might be due to the stacking of PSL, SiO₂ and MoS₂ precursor, and due to the decomposition of PSL during the USP process (Iskandar et al., 2001, 2002).

CONCLUSIONS

Hierarchical structured porous MoS₂/SiO₂ microspheres were successfully prepared using USP technique with PSL as a template to create the macropores and with silica nanoparticles as support to create meso- and micropores. The microspheres had high BET surface area, with macropore size of 68 nm, matching the molecular size of asphaltenes, and mesopore size of 5.8 nm. PSL:SiO₂ ratio affected the hierarchical porous structure. More PSL produced easily collapsed microspheres and high SiO₂ concentration led to a product with less pore volume. The hierarchical structured MoS₂/SiO₂ can facilitate the diffusion of different sized molecules, and have the potential as catalyst component in extra heavy oil upgrading.

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