Mesoporous Silica Nanosheets with Tunable Pore Lengths Supporting Metal Nanoparticles for Enhanced Hydrogenation Reactions

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Abstract: The channel lengths of mesoporous materials have a crucial impact on the catalytic performances of as-loaded active components. However, it remains a challenge to precisely tune the mesochannel length in a wide range from ≤50 nm to 200 nm. In this paper, we developed a top-down strategy, that is to say, crushing hollow microspheres, for preparing mesoporous silica nanosheets (MSSs) with perpendicular mesochannels and tunable thicknesses. Owing to the heterogeneous growth of the mesoporous silica layer on the surfaces of polystyrene microspheres (hard template), it was achieved to regulate the mesochannel length continuously in the range of 20–200 nm. The obtained materials were characterized by X-ray diffraction (XRD), nitrogen sorption, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The effect of channel lengths on the catalytic activity of metal nanoparticles was then investigated in the selective hydrogenation reaction of nitroarenes. It was found that a short channel not only favored dispersing metal nanoparticles uniformly and then avoiding pore blocking, but also improved the accessibility of metal nanoparticles largely during reactions.

Keywords: mesoporous silica; nanosheet; channel length; molecular diffusion; hydrogenation

1. Introduction

Owing to the high surface area, tunable pore structures and diverse surface functionalization, mesoporous silicas have been widely employed as a solid support to immobilize catalytic active metal nanoparticles for heterogeneous catalysis [1–6]. Their uniform mesochannels can not only provide a confined nanospace for protecting the metal nanoparticles from sintering and leaching out, but also afford an efficient mass transport for reactants and intermediates as well as products [7–9]. Over the past decades, a variety of metal nanoparticles, including bimetallic and even multimetallic catalysts, have been loaded inside mesoporous silicas for improving their catalytic performances largely [10–19]. However, for the conventional order mesoporous silicas such as MCM-41 and SBA-15, their micrometer-sized bulk morphology and parallel channels often lead to limited pore accessibility [20]. This lowers the molecular diffusion rate significantly and produces an issue of pore blocking during the process of loading metal nanoparticles. Therefore, designing new mesoporous materials with short mesochannels is desirable to optimize the diffusion process and the pore accessibility, and then to further enhance the catalytic properties of metal nanoparticles.

An alternative strategy to shorten the mesochannel lengths is to prepare mesoporous materials with two-dimensional (2D) morphologies of platelet/sheet and perpendicular mesochannels [21–23].
In 2004, Chen and co-workers reported the fabrication of SBA-15 platelets with vertical channels via using a ternary surfactant system as the structure-directing agent [24]. Inspired by their success, different surfactants and additives were attempted to prepare mesoporous silica platelets with uniform morphology and tunable channel length. For example, Tomczk et al. reported a biomimetic approach for synthesizing hexagonal silica platelets [25], in which a polypeptide was employed as the soft template. NH4F and Zr(IV) ions were also used as the additive to tailor the coassembly process of surfactants and inorganic precursors, then guiding the formation of SBA-15 platelets [26]. Although great progress has been achieved, however, the mesoporous silica platelets prepared via aforementioned bottom-up methods still showed a mesochannel length of ≥150 nm. More importantly, it is still very difficult for these bottom-up approaches to precisely adjust the channel length from ≤50 nm to 200 nm due to the limit in tuning the coassembly between the surfactants and the inorganic precursors in nanoscale.

In comparison to the bottom-up approaches, top-down routes often show advantages in simplifying the fabrication procedures and tailoring the structure parameters of as-obtained materials [27–30]. Very recently, we reported Janus mesoporous silica nanosheets with two distinct surfaces via a top-down strategy of crushing hollow microspheres [31]. In this work, such a simple strategy was extended to precisely tune the channel lengths of mesoporous silica nanosheets (MSSs) and the effect of channel lengths on the catalytic performance of as-loaded active components was investigated. Because the co-assembly process of the surfactants and the inorganic precursors occurred on the surfaces of polystyrene microspheres (hard template), the thickness of the formed mesoporous silica layer could be easily adjusted in the range of 20–200 nm. Then a precise modulation can be achieved on the mesochannel length. The obtained materials were characterized by X-ray diffraction (XRD), nitrogen sorption, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Finally, the Pd nanoparticles were introduced into MSSs and the effect of the channel lengths was studied on the catalytic performance of Pd nanoparticles in the selective hydrogenation reaction of nitroarenes.

2. Results and Discussions

The synthetic route for the mesoporous silica nanosheets (MSSs) with tunable thicknesses is shown in the Figure 1a. Firstly, mesoporous silica with vertical channels was coated on the surfaces of polystyrene microspheres via a well-defined, wet-chemistry method (Figure 1b,c), in which hexadecyltrimethylammonium bromide (CTAB) and ammonia were respectively used as the surfactant and the base catalyst. Then a calcination process was performed to remove the surfactant molecule (CTAB) and the hard template (polystyrene), presenting mesoporous silica hollow microspheres with open mesochannels. Figure 1d shows the SEM image of broken hollow microspheres. Finally, a simple grinding results in the formation of MSSs. Because the thickness of the mesoporous silica layer on the polystyrene microspheres is highly controllable due to its heterogeneous growth, the channel length of MSSs can be facilely tailored. As shown in Figure 1e, the as-obtained sample (denoted as MSSs-40) has a morphology of an irregular nanosheet. The diameter of these nanosheets broadly distributes in the range of 200–800 nm. The irregular morphology and the broad particle size distribution are the typical feature of top-down strategy for preparing nanomaterials. The cross-sectional SEM image further indicates that the nanosheet thickness is nearly 40 nm (the inset in Figure 1e), in good agreement with the shell thickness of the hollow microsphere. Moreover, the TEM image confirms the morphology of irregular nanosheet, and reveals that a uniform mesoporous structure appears in these nanosheets (Figure 1f). The HRTEM image further indicates that the mesochannels are perpendicular to the nanosheets, as evidenced by the distinct hexagonal pattern (indicated by a white box in Figure 1g), which is similar to the (110) direction of MCM-41 materials [32]. In addition, it must be noted that these nanosheets also possess many defect structures (indicated by a yellow cycle in Figure 1g), which are likely resulted from the drastic grinding process. Such a defect structure is expected to assist the mesochannels to further improve the molecule diffusion.
Figure 1. (a) Schematic illustration for the preparation of mesoporous silica nanosheets with tunable channel lengths. Scanning electron microscopy (SEM) images of the sample polystyrene microspheres (b), polystyrene@mesosilica microspheres (c) and mesosilica hollow microspheres (d). SEM (e) and transmission electron microscopy (TEM) (f,g) images of mesoporous silica nanosheets with a channel length of 40 nm. The inset in SEM images (e) is the corresponding cross-sectional SEM image.

Figure 2 shows the SEM and TEM images of the sample MSSs with a bigger thickness (denoted as MSSs-75 and MSSs-120) prepared via increasing the amount of tetraethylorthosilicate from 0.3 mL to 0.5 mL and 0.8 mL under the same conditions. It is clear that both of these samples show a morphology of an irregular nanosheet with a broad particle size distribution (Figures 2a,d), which is identical to that of MSSs-40. Whereas, the cross-sectional SEM images show that their thicknesses are respectively 75 nm and 120 nm (the inset in Figure 2a,d). The TEM and HRTEM images further confirm the uniform mesoporous structures of MSSs-75 and MSSs-120. Their mesochannels are also perpendicular to the nanosheets, keeping consistent with that of MSSs-40. Additionally, it is worth mentioning that the defect structures of MSSs-75 and MSSs-120 are less than that of MSSs-40. This is likely due to their bigger thicknesses that can avoid being destroyed during the drastic grinding process. All these results demonstrate that we have successfully obtained mesoporous silica nanosheets with tunable channel lengths via a facile top-down strategy.
The mesoporous structure of three MSSs samples were further characterized by X-ray diffraction (XRD) and nitrogen sorption. As shown in the Figure 3a, the small-angle XRD patterns of three MSSs samples all display one sharp diffraction peak and one weak diffraction peak at 2θ values of approximately 2.2 and 4.0 degrees, which can be indexed as the (100) and (110) reflections of a hexagonal mesophase (space group p6mm). This suggests that they have a partly ordered mesopore array. Moreover, a gradually increased structure order can be seen along with the increase of nanosheet thickness, which may be caused by the domain-size increase of the ordered mesostructure [33]. The nitrogen adsorption–desorption isotherms of three MSSs samples show a type IV curve according to the IUPAC classification (Figure 3b). A sharp capillary condensation step can also be clearly observed in the P/P0 range of 0.1–0.4. These results indicate that three MSSs samples have a uniform mesoporous structure. Furthermore, their corresponding Barrett–Joyner–Halenda (BJH (1951)) pore size distribution curves reveal a sharp distribution (Figure 3b), suggesting a uniform mesoporous structure. The average pore diameter is approximately 2.54 nm. Meanwhile, the sample MSSs-40 distinctly shows a secondary mesopore centered at 4.2 nm, which could be assigned to the defect structure of nanosheets. This mesopore is gradually disappeared in the pore size distribution curves along with the increase of the nanosheet thickness, indicating that the defect structure is gradually decreased and even disappeared. The Brunauer–Emmett–Teller (BET (1938)) surface areas of MSSs-40, MSSs-75 and MSSs-120 are 927.2 m² g⁻¹, 923.9 m² g⁻¹ and 1016.1 m² g⁻¹ (Table 1), respectively. Their total pore volumes are 0.75 cm³ g⁻¹, 0.68 cm³ g⁻¹ and 0.66 cm³ g⁻¹, respectively. These results further confirm the partly ordered mesoporous structures of MSSs samples, keeping highly consistent with the results of the TEM images.

Figure 2. SEM (a,d) and TEM (b,c,e,f) images of mesoporous silica nanosheets with different channel lengths: 75 nm (a–c) and 120 nm (d–f). The inset in SEM images (a,d) is their corresponding cross-sectional SEM image.
Whereas, the sample Pd with di-As shown in Figure 5a, the sample Pd producing anilines which are key intermediates for the manufacture of fine chemicals, pharmaceuticals and agrochemicals [34–37]. In the current study, the catalytic performances of Pd-loaded MSSs in the conventional MCM-41 under the same conditions.

The metal Pd nanoparticles were introduced into the mesochannels of MSSs via a simple impregnation-reduction route. In order to anchor the Pd nanoparticles uniformly inside the channels, the –NH₂ group was modified on the mesopore surfaces by a post-grafting process. From the TEM images in Figure 4a,b, we can see that the Pd nanoparticles are uniformly loaded in the sample MSSs, and the metal loading process has no obvious influence upon the morphology of MSSs. The HRTEM image further reveals that the particle size of Pd nanoparticles distributes in the range from 1–6 nm with an average size of 3.0 nm (Figure 4b). It is distinct that there is no aggregation of metal nanoparticles occurring on the mesochannels of MSSs, which should be attributed to the short pore channels and as-provided fast molecule diffusion. Although the large Pd nanoparticles (e.g., ≥5 nm) cannot be immobilized inside the mesochannels of MSSs, their defect structures are big enough to accommodate the large Pd nanoparticles, as indicated by the white box (Figure 4a). The high-angle, annular dark-field scanning TEM (HAADF-STEM) image confirms that the ultrafine Pd nanoparticles are uniformly loaded in the sample MSSs-40, MSSs-75 and MSSs-120.

- MSSs-40  927.2  0.75  2.54, 4.2
- MSSs-75  923.9  0.68  2.68, 4.2
- MSSs-120  1016.1  0.66  2.53

| Sample   | \(S_{\text{BET}}\) (m² g⁻¹) | \(V_t\) (cm³ g⁻¹) | \(D_p\) (nm) |
|----------|--------------------------|-----------------|------------|
| MSSs-40  | 927.2                    | 0.75            | 2.54, 4.2  |
| MSSs-75  | 923.9                    | 0.68            | 2.68, 4.2  |
| MSSs-120 | 1016.1                   | 0.66            | 2.53       |

* Brunauer–Emmett–Teller (BET) specific surface areas evaluated in P/P₀ from 0.05 to 0.25. Total pore volumes estimated based on the volume adsorbed at P/P₀ of 0.995. Pore sizes derived from the adsorption branches of the isotherms by using the BJH method.

Selective hydrogenation of nitroarenes is an environmentally benign and highly efficient process for producing anilines which are key intermediates for the manufacture of fine chemicals, pharmaceuticals and agrochemicals [34–37]. In the current study, the catalytic performances of Pd-loaded MSSs with different pore lengths were evaluated in the selective transformation of nitrobenzene to aniline. As shown in Figure 5a, the sample Pd/MSSs-40 presents a conversion of nearly 100% within 2 h. Whereas, the sample Pd/MSSs-75 and Pd/MSSs-120 with a longer channel length can only give a conversion of 57.6% and 38.4% under the same conditions, respectively. Pd/MSSs-75 needs 5 h to full convert the substrate, and Pd/MSSs-120 obtains a conversion of only 83.8% within 5 h. Moreover, using the conventional Pd/MCM-41 as the catalyst, a conversion of only 55.5% is obtained under...
the same conditions, which is much lower than those of the Pd/MSSs samples. This result indicates that
the morphology of mesoporous materials indeed has an important influence on the catalytic activity
of as-supported metal nanoparticles. In order to compare their catalytic activities more distinctly,
the turnover frequencies (TOFs) of the catalysts were calculated according to the conversion of nearly
30%. It can be clearly seen that the TOF of Pd/MSSs-40 is much higher than those of other catalysts
(Figure 5b), which is 2.18-fold, 3.53-fold and 6.0-fold higher than that of Pd/MSSs-75, Pd/MSSs-120 and
Pd/MCM-41, respectively.

Figure 4. Low-magnification TEM (a), high-magnification TEM (b), high-angle, annular dark-field
scanning transmission electron microscopy (HAADF-STEM) (c) and energy-dispersive X-ray
spectroscopy (EDX) element mapping (d–g) of the catalyst Pd/mesosilica nanosheet.

These results reveal that the channel length of mesoporous materials plays a critical role in
improving the catalytic activities of the as-supported metal nanoparticles. The shorter is the channel
length, the higher is the catalytic activity. Considering the similar BET surface area and pore volume
(Table 1), this is likely due to the fact that a short mesochannel can largely enhance the reactants and
products to diffuse into and out from the channel [38,39], thus presenting a higher accessibility towards
metal nanoparticles. In addition, it is interesting to observe that a significant activity enhancement is
realized once the channel length is decreased to below 50 nm (comparing the activity of Pd/MSSs-40
and Pd/MSSs-75). This suggests that a mesochannel with a length of ≤50 nm can promote the molecule
diffusion rate largely.
3.3. Loading Pd Nanoparticles in Mesoporous Silica Nanosheets with Tunable Thickness

Firstly, we prepared polystyrene microspheres via a previous publication. Typically, styrene (30%) was dissolved in a mixture containing water (8 mL) and ethanol (4 mL) was then added. After the polymerization was carried out at 70 °C for 24 h with a low stirring rate. The product was collected by filtration and washed with ethanol. Then, 0.96 g of polystyrene microspheres was dispersed in a bottle with a reflux condenser and a nitrogen gas inlet. The air in the flask was replaced by a stream of nitrogen, and the mixture was kept under nitrogen until the polymerization was finished. The resulting solid PS@mSiO₂ were collected by centrifugation and thereafter stirred at 25 °C for 6 h. After that, temperature was increased to 80 °C, and the mixture was stirred for 30 min, TEOS (0.3 mL) was quickly added. The obtained mixture was kept undisturbed overnight. The resulting solid PS@mSiO₂ were collected by centrifugation and then dissolved in a mixture containing water (8 mL) and ethanol (4 mL). After the mesosilica nanosheets were obtained by a simple grind. Generally, 20 min was essential to crushing the hollow microspheres. Adjusting the amount of TEOS led to the formation of mesosilica nanosheets with tunable thickness.

Turnover frequencies (TOFs) for different catalysts identified from a conversion of approximately 30%.

Table 2. Selective hydrogenation of different nitroarenes over the catalyst Pd/MSSs-40.

| Reaction conditions: nitroarene (0.5 mmol), 4.0 mL of ethanol, catalyst (Pd, 0.376 mol%), H₂ (1 atm), 80 °C. |
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Figure 5. (a) Kinetic plots of selective hydrogenation of nitrobenzene over different catalysts. (b) Turnover frequencies (TOFs) for different catalysts identified from a conversion of approximately 30%. (c) Recyclability test of Pd/MSSs-40 in selective hydrogenation of nitrobenzene. (d) TEM image of recovered catalyst Pd/MSSs-40 after five cycles. Reaction conditions: nitrobenzene (0.5 mmol), 4.0 mL of ethanol, catalyst (Pd, 0.376 mol%), H₂ (1 atm), 80 °C.
Considering the largely improved catalytic activity, the substrate scope and the catalytic stability were then examined. As shown in the Table 2, we can see that a conversion of nearly 99% can be always obtained in selectively hydrogenating nitrobenzene with different substituted groups including –CH₃, –C₂H₅, –OH, –OCH₃ and –NH₂ (1a, 1e–1h). Multi-groups substituted nitrobenzene can also be efficiently converted into corresponding aniline (1d). It is also found that the substituted position of nitroarenes has no influence on the catalytic activity (1a–1c). These results clearly reveal a high versatility of the catalyst Pd/MSSs-40. Moreover, we found that the catalyst Pd/MSSs-40 had a good reusability. After being used for five times continually, Pd/MSSs-40 still showed a conversion of ≥97% with an aniline selectivity of ≥98% (Figure 5c). We characterized the recovered catalysts after the fifth reaction and the TEM image indicates that there is no distinct aggregation in the metal nanoparticles (Figure 5d). This should be attributed to the anchoring effect of –NH₂ and the confinement effect of the mesochannels, resulting in the superior catalytic stability of Pd/MSSs-40.

3. Experimental Section

3.1. Chemicals

Tetraethylorthosilicate (TEOS, 98%), aqueous ammonia (NH₃·H₂O, 28%) and cetyltrimethylammonium bromide (CTAB, 99.0%) were purchased from Sinopharm Chemical Reagent (Shanghai, China). 3-aminopropyltriethoxysilane (APTES, 96%) was obtained from Meryer. Poly(vinyl pyrrolidone) (PVP, MW = 40,000) and 2,2-azobis(2-methylpropionitrile) (AIBN) were obtained from Beijing Solarbio Science and Technology Co., Ltd (Beijing, China). Sodium tetrachloropalladate (II) (Na₂PdCl₄, 98%) and all nitroaromatics were purchased from Aladdin(Shanghai, China). All chemicals were used as received without any further purification.

3.2. Synthesis of Mesoporous Silica Nanosheets with Tunable Thickness

Firstly, we prepared polystyrene microspheres via a previous publication. Typically, styrene (30 mL), PVP (2.25 g), AIBN (0.5 g), ethanol (95 mL), and water (3 mL) were added to a 250-mL single bottle with a reflux condenser and a nitrogen gas inlet. The air in the flask was replaced by a stream of nitrogen, and the mixture was kept under nitrogen until the polymerization was finished. The polymerization was carried out at 70 °C for 24 h with a low stirring rate. The product was collected by filtration and washed with ethanol. Then, 0.96 g of polystyrene microspheres was dispersed in a mixture of ethanol (60 mL), water (50 mL) and NH₃·H₂O (0.4 mL, 28 wt%). A solution of CTAB (0.48 g) dissolved in a mixture containing water (8 mL) and ethanol (4 mL) was then added. After the mixture was stirred for 30 min, TEOS (0.3 mL) was quickly added. The obtained mixture was thereafter stirred at 25 °C for 6 h. After that, temperature was increased to 80 °C, and the mixture was kept undisturbed overnight. The resulting solid PS@mSiO₂ were collected by centrifugation and washed with deionized water. The surfactant CTAB and polystyrene were subsequently removed via a simple calcination at 550 °C for 6 h, presenting mesoporous silica hollow microspheres. Finally, the mesosilica nanosheets were obtained by a simple grind. Generally, 20 min was essential to crushing the hollow microspheres. Adjusting the amount of TEOS led to the formation of mesosilica nanosheets with tunable thickness.

3.3. LoadingPd Nanoparticles in Mesoporous Silica Nanosheets with Tunable Thickness

Before loading Pd nanoparticles, the –NH₂ group was grafted on the mesopore surfaces of mesosilica nanosheets by a simple process of surface modification. Typically, 200 mg of mesosilica nanosheets were dispersed in 20 mL of toluene containing APTES (0.1 mL) and triethylamine (0.05 mL). The mixture was refluxed for 4 h at 120 °C. The solid was recovered by centrifugation and washed with ethanol and deionized water. Then the Pd nanoparticles were introduced into the mesochannels of the mesosilica nanosheet via a simple impregnation–reduction route. Specifically, 200 mg of NH₂-modified mesosilica nanosheets were dispersed in 50 mL of deionized water via sonication. After the fresh Na₂PdCl₄ aqueous solution (20 mm, 1.9 mL) was added dropwise, the mixture was
stirred for 4 h at 30 °C. Then 0.1 M fresh NaBH₄ solution (2.0 mL) was added dropwise, and the mixture was aged at the same temperature for 24 h. The solid was isolated by centrifugation and washed four times with ethanol. Finally, we obtained the catalyst after drying at 80 °C under vacuum for 6 h.

3.4. Catalytic Test

0.5 mmol of nitroarene, Pd catalysts (0.2 mol%), and 4.0 mL of ethanol were mixed in a 25 mL round-bottomed flask equipped with a reflux condenser. The solution was sealed and purged three times with hydrogen to remove the air at room temperature. The reaction was then performed at 80 °C in an oil bath under magnetic stirring. After the completion of the reaction, the solid catalyst was isolated by centrifugation. The obtained liquid phase was subsequently analyzed by Agilent 7890A gas chromatograph with a flame ionization detector (FID) (Beijing, China), and dodecane was used as the internal standard. For the recycling test, the catalyst was collected using centrifugation. The residual catalyst was washed with water and ethanol for several times and used directly for the next catalytic reaction. The loading amount of Pd was identified to be 2.0 wt% by inductively coupled plasma mass spectrometry (ICP).

3.5. Materials Characterization

Scanning electron microscopy (SEM) was performed on a JEOL JSM-6700F field-emission electron microscope (Tokyo, Japan). Transmission electron microscope (TEM) images were obtained on an FEI Tecnai G² F20s-twin D573 field emission transmission electron microscope with an accelerating voltage of 200kV. Powder X-ray diffractometry (XRD) patterns were obtained by using a Rigaku 2505 diffractometer (Tokyo, Japan) with Cu Ka radiation (λ = 1.5418 Å). N₂ adsorption–desorption isotherms were obtained at −196 °C on a Micromeritics ASAP 2010 sorptometer (Shanghai, China). Samples were degassed at 120 °C for a minimum of 12 h prior to analysis. Brunauer–Emmett–Teller (BET) surface areas were calculated from the linear part of the BET plot. Pore size distribution was estimated from the adsorption branch of the isotherm by the Barrett–Joyner–Halenda (BJH) method. The total pore volume was estimated from the adsorbed amount at P/P₀ = 0.995. Inductively coupled plasma mass spectrometry (ICP) analyses were carried out on a NexION 350 ICP-MS instrument (Shanghai, China).

4. Conclusions

In summary, we have prepared MSSs with perpendicular mesochannels and tunable channel lengths by crushing corresponding hollow microspheres and then studied the effect of channel lengths on the catalytic activities of as-loaded metal nanoparticles. In comparison to the conventional Pd/MCM-41, MSSs loaded Pd nanoparticles presented an up to 6-fold activity enhancement in the selective hydrogenation reaction of nitroarenes. Superior substrate applicability and good catalytic stability were also realized. Importantly, it was found that the catalytic activities were highly dependent on the channel length of mesoporous materials and the shorter was the channel length the higher was the catalytic activity.

It was proposed that a short mesochannel, particularly for a channel of less than 50 nm, can largely accelerate the molecule diffuse process and promote the accessibility of metal nanoparticles inside channels, thus presenting a much higher catalytic activity. We expect that the structure–performance relationship established in this work will provide some insights for designing and preparing advanced heterogeneous catalysts.

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