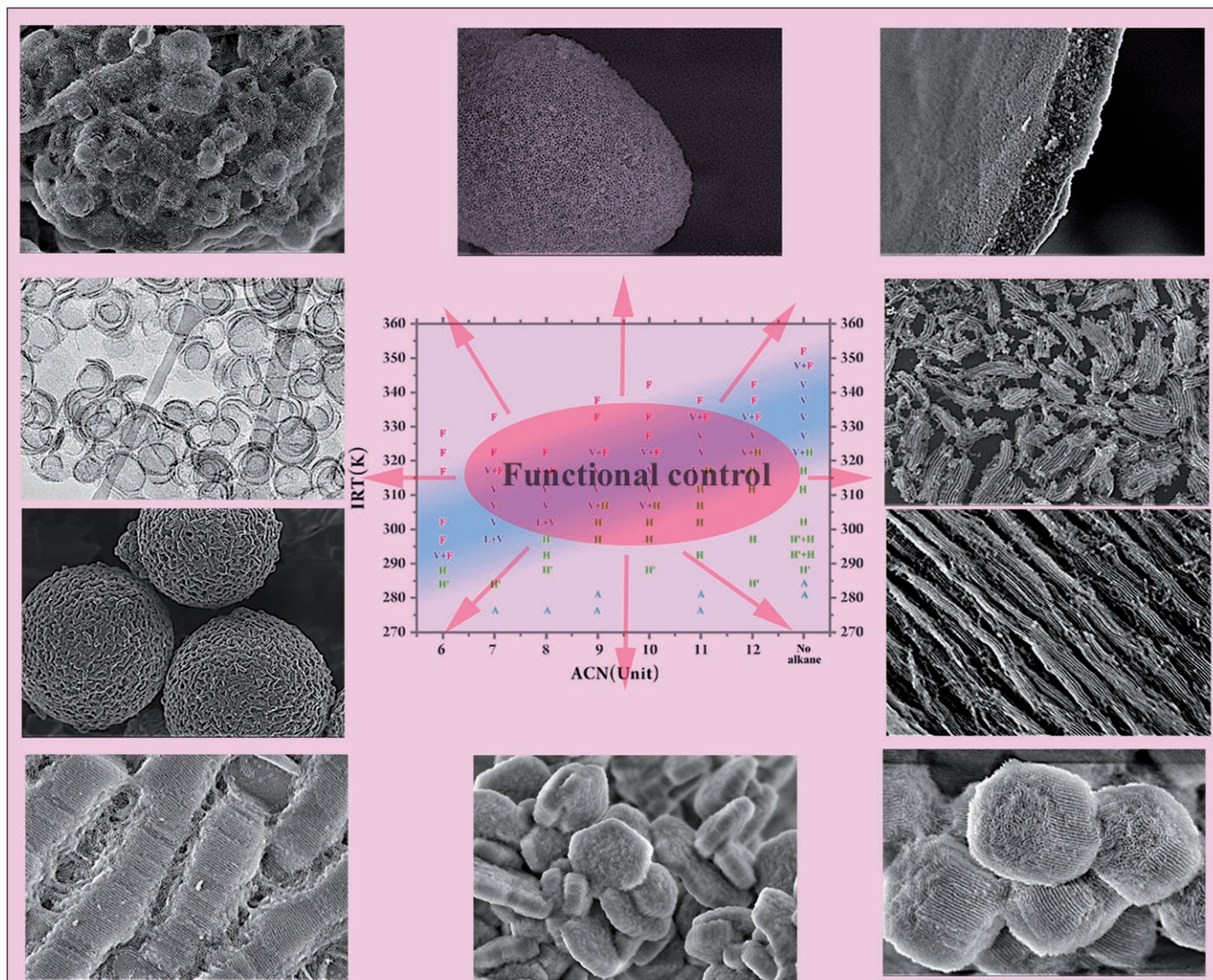
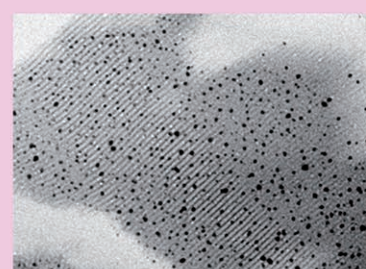
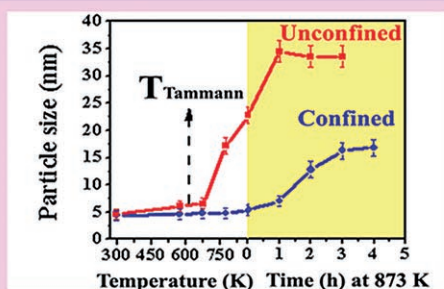
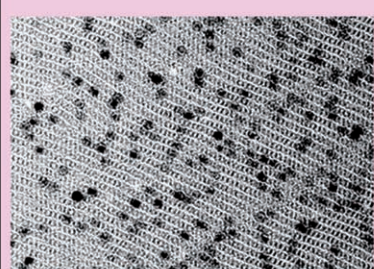


Textural Manipulation of Mesoporous Materials for Hosting of Metallic Nanocatalysts

Junming Sun and Xinhe Bao*^[a]



Confined metallic nanocatalysts



Abstract: The preparation and stabilization of nanoparticles are becoming very crucial issues in the field of so-called “nanocatalysis”. Recent developments in supramolecular self-assembled porous materials have opened a new way to get nanoparticles hosted in the channels of such materials. In this paper, a new approach towards monodisperse and thermally stable metal nanoparticles by confining them in ordered mesoporous materials is presented, and three aspects are illustrated. Firstly, the recent progress in the functional control of mesoporous materials will be briefly introduced, and the rational tuning of the textures, pore size, and pore length is demonstrated by controlling supramolecular self-assembly behavior. A novel synthesis of short-pore mesoporous materials is emphasized for their easy mass transfer in both biomolecule absorption and the facile assembly of metal nanocomposites within their pore channels. In the second part, the different routes for encapsulating monodisperse nanoparticles inside channels of porous materials are discussed, which mainly includes the ion-exchange/conventional incipient wetness impregnation, in situ encapsulation routes, organometallic methodologies, and surface functionalization schemes. A facile in situ autoreduction route is highlighted to get monodisperse metal nanoparticles with tunable sizes inside the channels of mesoporous silica. Finally, confinement of mesoporous materials is demonstrated to improve the thermal stability of monodisperse metal nanoparticles catalysts and a special emphasis will be focused on the stabilization of the metal nanoparticles with a low Tamman temperature. Several catalytic reactions concerning the catalysis of nanoparticles will be presented. These uniform nanochannels, which confine monodisperse and stable metal nanoparticles catalysts, are of great importance in the exploration of size-dependent catalytic chemistry and further understanding the nature of catalytic reactions.

Keywords: heterogeneous catalysis • mesoporous materials • metal nanoparticles • template synthesis

Introduction

Throughout the last decades, nanocatalysis has long been paid much attention due to its unique significance in

academia and considerable contributions to industry. Highly dispersed metal nanoparticles play a significant role in many catalytic reactions.^[1,2] To explore nanosize effect in catalysis,^[3] one has to be able to synthesize monodisperse metal nanoparticles with high thermal stabilities, which has been proved to be extremely difficult in practice.^[2,4] Although some feasible routes have been developed to synthesize soft-molecule-protected metal nanoparticles,^[5] it is difficult to prevent such particles from sintering during a high-temperature process.^[6] At high temperatures metal nanoparticles can be in a liquid form and surface/bulk atoms are highly mobile, leading to the interparticle diffusion and, hence, coalescence of metal particles.^[7–9] The low thermal stability of metal nanoparticles inevitably limits their applications. Inert inorganic supports with rigid frameworks and high surface areas could be used to get higher dispersion of metal-nanoparticle catalysts. However, non-uniform pore structure of the traditional supports (i.e., silica gel) often makes the preparation difficult and the obtained metal nanoparticles were often randomly distributed.^[2]

Recently, the discovery of supramolecular self-assembly of mesoporous materials has initiated intensive interest in various research areas.^[10] It also opened a new era for catalysis,^[11] such as biomolecule-based selective catalysis. It should be mentioned that the dimension of the channels of ordered mesoporous materials can be huge relative to most of smaller molecules involved catalytic reactions (from tens of angstroms to a few angstroms) and no predominant selectivity can be observed. However, due to their periodic, size-controllable pore channels and high surface areas, mesoporous materials can be regarded as “natural microreactors” to accommodate well-defined metals, metal oxide nanocomposites, semiconductors, carbon materials, and so forth.^[12]

In this concept paper, we mainly highlight the tuning/application of functional ordered mesoporous materials, towards the synthesis of monodisperse and thermal stable metal-nanoparticle catalysts by the confinement in their well-defined pore matrix. By finely controlling the self-assembly of surfactants, ordered mesoporous materials with tunable pore size, pore length and morph architectures have been obtained. These chemically significant mesoporous materials give a strong basis for the encapsulation of the monodisperse metal nanoparticles.

For the fabrication of monodisperse metal nanoparticles within the channels of mesoporous materials, conventional methodologies such as incipient wetness is evidently not a good choice, since metal nanoparticles with bimodal size distribution would be obtained on both internal and external surfaces of mesoporous channels. Strategies for selective encapsulation of monodisperse metal nanoparticles inside the channels of mesoporous silicas are in high demanded. On the other hand, the investigation on thermal stability of metal nanoparticles confined in nanochannels is even more important, since most catalytic reactions are high-temperature processes. In the final part, we are going to discuss the

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recent advances of metal nanoparticles confined in mesoporous materials concerning their applications in catalysis.

Functional Control of Mesoporous Materials by Tuning Supramolecular Self-Assembly Behavior

Mesostructure modification: Since the first report of ordered mesoporous MCM-41 silica in 1992,^[13] research on supramolecular self-assembly of mesoporous materials has exploded, indicated the thousands of reports to be found in the literature. In 1998, the discovery of that nonionic block copolymers (i.e., P123) could be used to direct the formation of ordered mesoporous silica, SBA-15,^[14] was paid more attentions due to its thicker pore walls and therefore higher hydrothermal stabilities, which is essential to their applications. The control of mesostructures by the nonionic block copolymers has also become one of the hottest issues in this newly developed research area.^[15–17]

Basically, from the geometry point of view, structures of mesoporous materials are closely related to the morphology of surfactant assemblies, which is determined by the packing parameters of the surfactant.^[18] However, it must be mentioned that when inorganic species are involved in the self-assembly of the surfactant,^[19] the synthetic parameters are much different from those of thermodynamically controlled, pure surfactant systems.^[20–21] The obtained inorganic product should be a transient phase that balances the thermodynamically favored phase and the quenched, condensed silicate phases.^[22] The detailed formation mechanism of self-assembled mesoporous materials is far more complicated than expected, and has been shown to be not only related to the synthetic parameters for soft templates, but also to the chemistry of inorganic species, inorganic–organic interactions, and so forth. There have been extensive reviews,^[23–25] concerning this particular field of research, which will not be discussed in detail in this paper. Herein, we just briefly introduce the recently developed *n*-alkanes (C₆–C₁₂)/P123/TEOS/NH₄F/H₃O⁺ complex emulsion system (TEOS = tetraethoxysilane). By finely controlling the initial reaction temperature and alkanes chain length, a synthetic phase diagram was obtained (Figure 1), from which various mesoporous materials with controllable structures such as hexagonal, lamellar, foams, and so forth have been obtained.^[22,26,27] Moreover, the solubilization of alkanes within the block copolymer micelle cores decreased

the CMT (critical micellization temperature). The formation of ordered mesoporous silicas was realized at the temperatures as low as 288 K, at which nonporous or disordered materials normally would be obtained in the absence of *n*-alkanes.^[22] This result is of great importance, since it opened a new way to prepare unprecedented large-pore 2D-ordered mesoporous silicas, which will be discussed in the following part.

Tuning the pore size: Engineering the pore size of ordered mesoporous materials is of great importance for their applications, especially in the field of host–guest chemistry (e.g., preparation of supported metal catalysts). Numerous synthetic routes have been reported to tune the pore size of mesoporous materials.^[17,28] The pore size of mesoporous materials, ignoring their mesostructure variations, can be tuned in a wide range from 2 nm to almost 30 nm. Among them, however, ordered 2D-mesoporous materials can only be modified from 2 nm to 12 nm with different surfactants and swelling agents.^[17] It is worth noting that we have developed a low-temperature route to tune the pore size of ordered 2D-mesoporous materials with the *n*-alkane (C₆–C₁₂)/P123/TEOS/NH₄F/H₃O⁺ complex emulsion system; it was found that by controlling the initial reaction temperature, ordered mesoporous silicas with tunable pore size were obtained by changing the alkane chain length (H region in Figure 1). Significantly, the pore size of highly ordered 2D-mesoporous silicas was unprecedentedly expanded to 15 nm, which has been confirmed by a combination of X-ray diffraction (Figure 2), transition electron microscopy, and nitrogen sorption techniques.^[29] Moreover, the solubilization ability of alkanes controlled the pore size of obtained mesoporous silica. The smaller the alkane chain length, the higher the

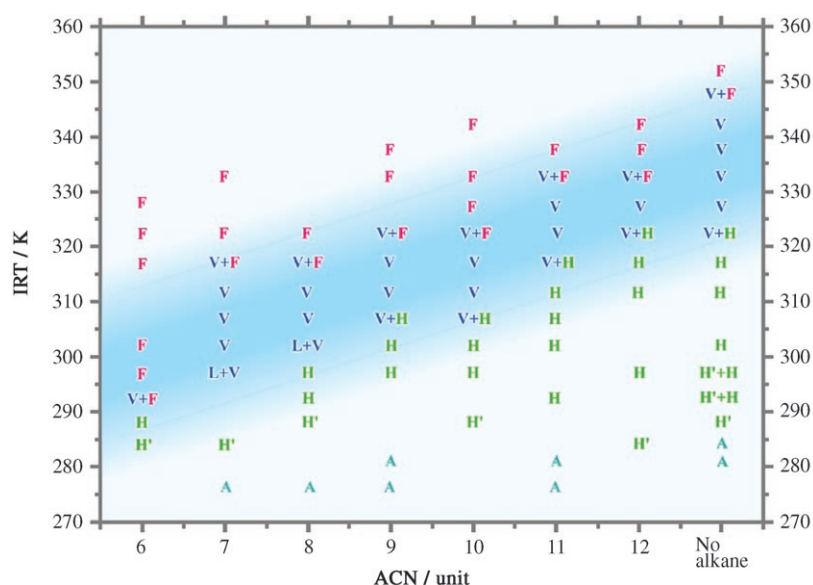


Figure 1. Synthesis phase diagram (ACN vs. reaction temperature) obtained in the alkane/P123/TEOS/NH₄F/H₃O⁺ emulsion system. (A = amorphous; H = hexagonal; H' = wormlike; H + H' = mixture of H and H'; L = lamellar; V = vesicles; F = foams). Reprinted with permission from *Langmuir* 2008, 24, 2372. Copyright 2008, American Chemical Society.

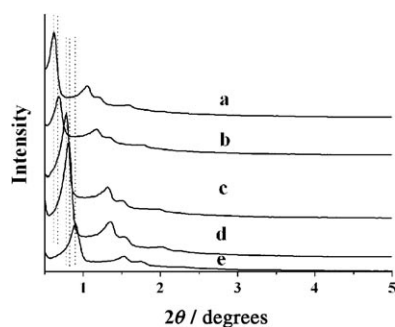
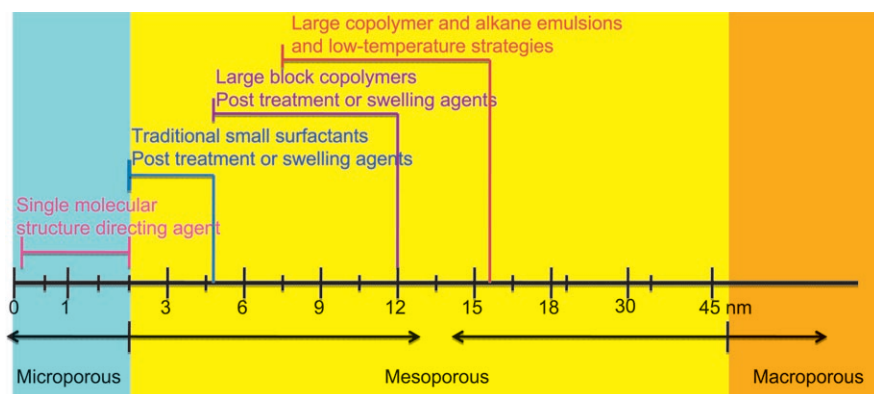


Figure 2. Small-angle X-ray diffraction patterns of the obtained SBA-15 synthesized by using *n*-alkanes with different alkaline length. a) hexane, b) octane, c) nonane, d) dodecane, e) no alkane. Reprinted with permission from *J. Phys. Chem. B* **2006**, *110*, 25908. Copyright 2006, American Chemical Society.

solubilization ability of the alkanes and the bigger the pore size of obtained mesoporous silica. The pore-size expansion trend with the alkanes chain length is in contrast to that of MCM-41, in which a molecular expansion mechanism was involved.^[30] With the same emulsion system, Kruk et al. found that the pore size could be further expanded when a higher hydrothermal temperature and longer time were employed.^[31] Scheme 1 gives an overview of the pore size of mesoporous materials obtained by using different methods. Currently, the maximum pore size for ordered 2D mesoporous materials is about 16 nm by using the low-temperature emulsion route.^[29,31]

Pore length control: Tuning the pore length, which is an important parameter of the mesoporous materials, is pivotal for their applications as catalysts.^[32] Actually, in the initial stage of self-assembled mesoporous materials, people were trying to get more accessible pores by means of decreasing the dimension of particles of the obtained mesoporous materials, and most of this research mainly concentrated on the ionic-surfactant-templated mesoporous materials, such as MCM-41. For instance, by using an evaporation-induced interfacial assembly process, Lu et al. synthesized spherical mesoporous nanoparticles on a special setup.^[33] During the



Scheme 1. Pore-size engineering of ordered 2D mesoporous materials by various strategies.

synthesis, the solvent evaporation resulted in an excess of surfactant at the liquid/gas interface of the small droplets, which induced the self-assembly of inorganic–organic composites into different mesophases. After the condensation of inorganic species, spherical mesoporous nanoparticles were successfully obtained. Cai et al. developed a facile diluted route,^[34] which has been followed by many research groups. With this method, MCM-41 nanoparticles ranging from tens to hundreds of nanometers have been obtained.^[35] Mann's group explored a quench method to stop the further growth of formed particles, which has been used to synthesize monodisperse MCM-41 nanospheres.^[36] Recently, Imai et al. found an efficient bi-surfactant route, in which one surfactant was used as a structure director, while another was employed to suppress the growth of formed mesoporous particles. Ultrafine MCM-41 spheres with diameters of 20–50 nm were successfully obtained.^[37]

For large-pore materials, such as SBA-15, typically, a rod-like morphology is observed with a uniform length of 1–2 μm . Driven by an unfavorable surface energy of the basal plane^[38] or shearing flow,^[39] these primary particles are further aligned end-to-end and side-by-side, forming larger fiberlike secondary morphologies, which was found to have very low mass transfer in the adsorption of biomolecules. While separated rodlike morphological SBA-15 was proven to be more suitable to biomolecular immobilization than those of collective morphology.^[32,40] The formation of fiberlike SBA-15 clusters depends mainly on the nature of non-ionic block copolymers, the assembly of inorganic species in strong acidic media, and shearing flow. To suppress alignment of rodlike primary particles to give secondary fiberlike SBA-15, Kosuge et al. tried to control the acidity and rate of stirring in the synthesis conditions. Monodisperse SBA-15 rods 0.5 \times 2 μm in size were obtained under static conditions.^[39] Yu et al. also found that using large amounts of inorganic KCl salts, monodisperse SBA-15 rods could be obtained successfully.^[41] Later, Sayari reported that the key role for the formation of rodlike SBA-15 is not inorganic salts, but the rate of stirring and the temperature.^[42] It can be seen that with these methodologies, separated SBA-15 rods were obtained. However, the pore length of the obtained mesoporous SBA-15 materials was still 1–2 μm . Recently, it was found that a rod-to-sphere transition phase^[43,44] could be captured in the $(\text{C}_6\text{--}\text{C}_{12})/\text{P123}/\text{TEOS}/\text{NH}_4\text{F}/\text{H}_3\text{O}^+$ complex emulsion system, as a result of which short-pore mesoporous silicas were achieved (Figure 3).^[45–47] Further studies indicated that the pore length of SBA-15 could be finely tuned in the range from 150 to 1000 nm by carefully tuning some of synthetic parameters, such as aliphatic alkane chain

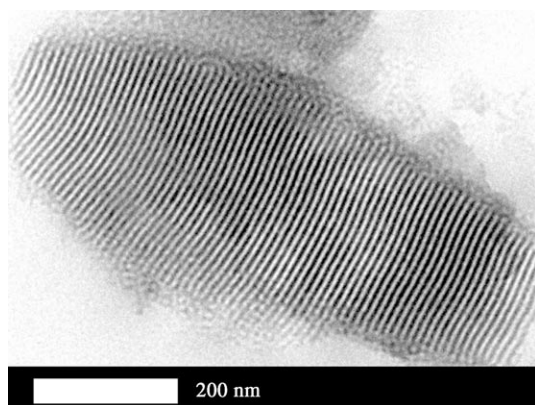


Figure 3. TEM image of cross-sectioned short-pore SBA-15 with parallel channels running along the short axis. Reprinted with permission from *J. Phys. Chem. B* 2006, 110, 25908. Copyright 2006, American Chemical Society.

length, initial temperature, inorganic concentration, and so forth (Figure 4). Mesoporous silicas with various chemically significant morphologies have been successfully ob-

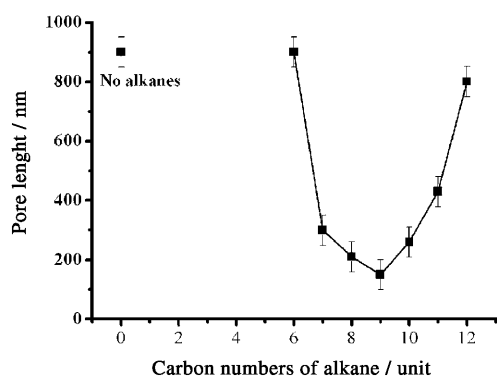


Figure 4. Effects of carbon number of alkanes used on pore length of the obtained mesoporous materials. Reprinted with permission from *J. Phys. Chem. B* 2006, 110, 25908. Copyright 2006, American Chemical Society.

tained.^[22,45–47] Significantly, the obtained short-pore mesoporous materials showed ultrafast biomolecule immobilization/separation ability.^[32,46] Han et al. also developed a double surfactant route to try to control the dimension of mesoporous silica. The particles size of ordered SBA-15 was decreased to 200 nm in width and 400 nm in length.^[48] Chen et al. explored a ternary surfactant system in which the block copolymer (i.e., P123) assembly could be confined within the CTAB-SDS bilayers (CTAB = cetyltrimethylammonium bromide; SDS = sodium dodecyl sulfate), forming platelike mesoporous silicas with short perpendicular ordered channels (smaller than 200 nm).^[49a] A very recent study demonstrated that irregular mesoporous particles from 50 to 300 nm have been obtained by controlling the amount of water or inorganic salts in the block copolymer (i.e., P123) system. However, the structure ordering of the obtained materials decreased a lot in most cases, especially for the small-

er colloid particles.^[49b] In other reports, ultralong SBA-15 fibers, microscale spheres, and large cubic mesoporous crystals have also obtained by using different routes, which have been discussed extensively.^[17]

Strategies in Encapsulation of Monodisperse Metal Nanoparticles within Mesoporous Materials

Since the discovery of mesoporous materials, people have tried to use them as hosts to occlude guest species, so-called inclusion chemistry.^[50] Herein, we just concentrate on the monodisperse metal nanocomposites encapsulated in the well-defined mesoporous materials, because of their potential applications in the fields of adsorption and catalysis. Currently, numerous strategies have been reported for the encapsulation of metal nanocomposites, which includes ion exchange,^[51–56] incipient wetness impregnation,^[57–61] in situ encapsulation,^[62–65] organometallic methodologies,^[66–70] and surface functionalization schemes.^[71–80]

Ion exchange/incipient wetness: Ion exchange or incipient wetness impregnation are usually first tried, since these methods are easy to manipulate and are generally used to prepare supported catalysts. However, early work indicated that they lack control of the nucleation and growth of metal nanoparticles with bimodal distribution or a mixture of metal nanoparticles and metal nanowires often resulted.^[55,57] This can be due to the highly mobility of metal ions through surface hydroxyl groups during the subsequent thermal treatment.^[56] Another key factor in the formation of monodisperse metal nanoparticles is to control the multinucleation of metals. Once the metallic nucleus is formed, the reduction potential on the nucleus will be decreased with respect to those metal ions in solution, so called self-reduction.^[81] The metallic nucleus continues to grow by the self-reduction of mobile metal ions during the following thermal treatment. However, there exists a competition between thermodynamics and dynamics during the formation of metal crystals. Thermodynamic control tends to lead to the formation of large metal crystals; while dynamic control leads to multinucleation and smaller metal particles. In this case, the temperature ramping rate plays the key role in controlling the competition. Confined bunches of metal nanowires have been synthesized within the ordered mesoporous materials by using a very slow temperature-ramping process. Increasing the ramping rate could lead to the multinucleation and the formation of metal nanoparticles within the channels of mesoporous silica.^[53] Therefore, it is critically important with the ion exchange/impregnation method to control the synthesis parameters to obtain the monodisperse metal nanoparticles within mesoporous materials.^[53] Interestingly, one study showed that, with the impregnation method, the morphology of guest species was also related to the pore structure of mesoporous materials; a 3D hexagonal pore structure lead to the facile formation of metal nanoparticles.^[58]

Actually, there are other routes to control the multination and diffusion of metal ions to prepare monodisperse metal nanoparticles. For instance, in solution synthesis, macromolecules with large amounts of functional groups (e.g., sucrose, dendrimers, etc.) could be used as protective agent or dispersive reagent to prepare monodisperse metal nanoclusters. Introduction of this synthesis system to the mesoporous materials by incipient wetness impregnation could also lead to the formation of monodisperse metal nanoparticles within the channels of mesoporous materials.^[59,61] Interestingly, by using an in situ carbonization of organic dispersive reagents and etching onto silica, Liu et al. obtained highly dispersed Pt nanoparticles embedded in the mesoporous carbon replicas (Figure 5).^[59a] Ichikawa's group

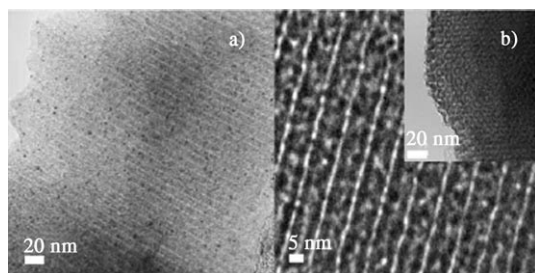


Figure 5. Highly dispersed Pt nanoparticles embedded within the framework of mesoporous carbon materials. Reprinted with permission from *Chem. Commun.* 2006, 3435. Copyright 2006, Royal Society of Chemistry.

employed the impregnation method followed by a mild UV-visible-irradiation-based reducing process, by which the diffusion of metal ions at higher temperatures process can be avoided. Highly dispersed metal nanoparticles (i.e., Pt or Au) arrays have been obtained within the mesoporous materials.^[58,60] The problem with these methods is that large particles always formed on the outer surface of mesoporous materials, especially powder samples, since the enrichment of the solution on the outside of particles is unavoidable for the incipient wetness routes.

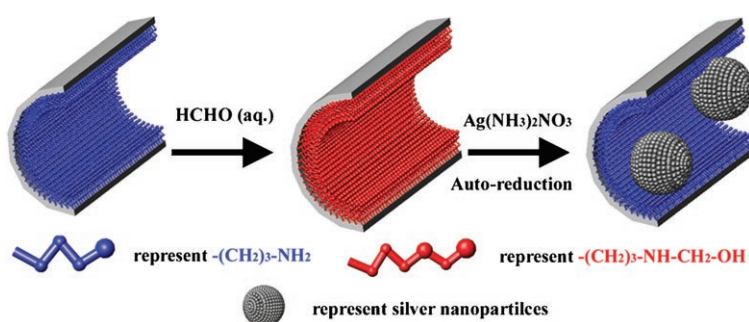
In situ encapsulation of metal nanoparticles/clusters: In situ encapsulation of monodisperse metal nanoparticles can be based on the preformed nanoparticles obtained by the solution synthesis method, which is more mature than the supported metal nanoparticles synthesis. It can also be based on the careful metal precursor selection and well-controlled synthesis conditions. With the former method, due to the relative higher stability of the preformed nanoparticles than molecular metal clusters, such nanoparticles can be dispersed in the synthesis mixtures of mesoporous materials (generally, strong acidic or basic). Upon solidification of the inorganic species, these metal nanoparticles are expected to be incorporated into the framework of mesoporous materials.^[62] With the latter method, available recent examples indicated that anionic metal precursor (i.e., H_2PtCl_6) can be incorporated in situ within the surfactant micelles with the

help of the cationic surfactant CTAB or other co-solvent during the mesoporous materials synthesis.^[63,64] Upon thermal treatment, Pt nanoparticles can be obtained while removing the surfactant. With these methods, one needs to carefully select the metal precursor and protecting ligand to match the surfactant assembly and to avoid destroying the ordered structure of the mesoporous materials.^[63–65] However, the loading amount of metal obtained by these methods is still limited.^[62]

Organometallic methodologies: Organometallic complexes or clusters are highly active towards silanols on silica-based inorganic supports. Uniform metal complex can be grafted on the surface of formed support by using a surface reaction under the anaerobic and anhydrous conditions.^[4] The amorphous nature of mesoporous materials endows them with large amounts of silanol groups on their inner pore walls. Highly reactive organometallic complex precursors can be introduced into the channels of mesoporous materials by evaporation/solvent mixing, which can further react with the silanols and be grafted on the walls by covalent bonding.^[66–69] By using a suitable thermolysis process, metal clusters or nanowires can be produced. In addition, preformed, well-defined, organometallic metal/bimetal clusters have also been introduced into nanochannels by a chemical grafting process, followed by a gentle thermolysis process under vacuo, and removal of the organic ligands. The metal clusters cores were still highly dispersed and confined within the channels of mesoporous silicas, although their structures underwent some changes.^[70] These mesoporous materials containing confined metal clusters are essential to the investigation of some basic catalytic properties, such as the size-dependent catalysis.^[4b] However, although these methods showed much improvement relative to the traditional impregnation ones, they still cannot control the selective encapsulation within nanochannels, and the metal nanoclusters/particles located on the outer surface still undergo aggregation during the higher temperature process.

Surface functionalization schemes: Due to the relatively weak interaction between the cationic metal (i.e., most of later transition metals) and silanols, in general, it is difficult to fabricate metal nanoparticles within the channels of mesoporous silica materials in a controlled fashion by simply impregnating or by ion exchange. However, functional groups such as thiol or amino groups, can be immobilized onto the inner walls by means of a grafting process with a silane coupling reagent. The fixed functional group can act as a strong ligand to pull and anchor the corresponding metal ions into the channels of mesoporous materials. For instance, thiol groups have been grafted onto the surface of mesoporous silica; cationic gold was then immobilized within the mesoporous silica by the strong metal–sulfur complexation, followed by a solution reducing process (using NaBH_4). In this way monodisperse gold nanoparticles were successfully obtained.^[71] Positively charged $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{N}(\text{CH}_3)_3\text{Cl}$ (TPTAC)-modified mesoporous silica ma-

materials have been also used to capture negatively charged metal precursors. For example, Pt, Au, and PtAu nanowires/nanoparticles have been fabricated by using a thermal decomposition process.^[72,73] Amino groups have been immobilized within channels of the mesoporous materials. The functional mesoporous materials were further used to anchor different metal ions, which was followed by a thermolysis to get metal/metal oxide nanoparticles within mesoporous silica materials. However, some of metal ions, such as Ag^+ , showed highly mobility, and most of them diffused easily out of mesopores, forming large particles during the thermal treatment process.^[74] Even within the channels, nanowires or a mixture of metal nanoparticles and metal wires were often obtained.^[79] It indicates that for various metals, due to the difference in chemical properties, the difficulty in controlled preparation varies. Especially, when a thermal treatment process is involved in the metal reduction, metal ions can easily diffuse out of the channels, forming large particles on the outer surface of mesoporous materials. In 2002, Shi's group developed a novel in situ reduction route for the selective encapsulation of metal nanocomposites within the mesoporous materials SBA-15.^[75,76] The silanols on outer surface of as-synthesized SBA-15 were first modified with methyl groups; this was then followed by a series of anhydrous organic reactions to give the reducing Si-H functional group. After introducing the metal precursors (e.g., H_2PtCl_6 or H_2PdCl_6), they can be reduced in situ to Pd nanoparticles or Pt nanowires within the channels of mesoporous SBA-15. Our group recently explored a facile autoreduction route to fabricate monodisperse silver nanoparticles on silica-based materials. When using mesoporous materials, the amino group can be selectively grafted within the channels of mesoporous silica, and formaldehyde can be used to react with the grafted amino group, forming a new, reusable, fixed, reducing functional group $-\text{NHCH}_2\text{OH}$ (Scheme 2). Upon introducing metal precursors (e.g., $\text{Ag}(\text{NH}_3)_2$), highly dispersed silver nanoparticles were successfully encapsulated within the channels of mesoporous materials (Figure 6).^[78,79] Actually, our following work indicated that other metals such as Pt, Pd, Au, and so forth can also be obtained in terms of high dispersion and homogeneity within mesoporous silica materials.^[80]



Scheme 2. Scheme representing a facile in situ autoreduction route to fabricate highly dispersed metal nanoparticles within the channels of mesoporous materials. Reprinted with permission from *J. Am. Chem. Soc.* **2006**, *128*, 15756. Copyright 2006, American Chemical Society.

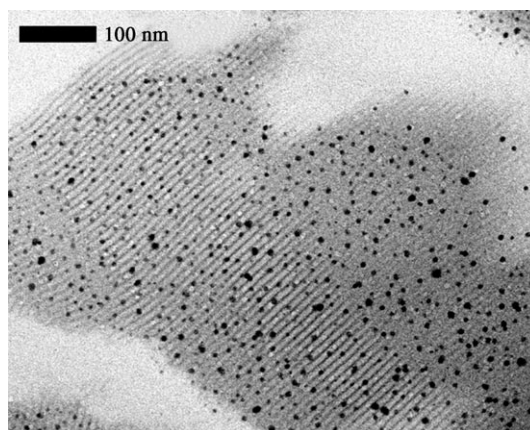


Figure 6. Highly dispersed silver nanoparticles within the channels of SBA-15. Reprinted with permission from *J. Am. Chem. Soc.* **2006**, *128*, 15756. Copyright 2006, American Chemical Society.

Thermal Stability of Metal Nanoparticles Confined in Mesoporous Materials

Catalysts deactivation could be from many reasons such as sintering, coking, poisoning, and so forth.^[7] Sintering was found to be a key factor in the deactivation of some industrial catalysts (e.g., ethylene epoxidation and methanol oxidation). Highly dispersed silver nanoparticles on the outer surface of $\alpha\text{-Al}_2\text{O}_3$ would diffuse and aggregate/sinter after a period higher temperature reaction.^[82] To understand the aggregation mechanism and prevent metal nanoparticles from sintering, surface scientists have done extensive investigations on the open, flat, metal/metal oxide surfaces in vacuum systems. 2D and 3D Ostwald ripening and particle diffusion were found to be the main reason for metal nanoparticle sintering.^[83–85]

The thermal stability of metal nanoparticles is closely related to their mobility on the support during the high-temperature process, while the mobility of metal nanoparticles is mainly determined by their Tammann and Hüttig temperatures ($T_{\text{Tammann}} = 0.5 T_{\text{F}}$, $T_{\text{Hüttig}} = 0.3 T_{\text{F}}$, T_{F} is the absolute melting temperature).^[7] When the treating temperature is higher than the Tammann temperature, atomic mobility increases dramatically. Driven by the tendency to minimize the surface energy, metal nanoparticles are apt to agglomerate during the high-temperature treatment, especially when the treating temperature is higher than its Tammann temperature. As a result, interparticle diffusion and subsequent agglomeration/sintering occur in most cases. Another significant aspect is that the melting point of metal nanoparticles decreases drastically with decreasing

particle size (Figure 7),^[8] which further explains the lower thermal stability of nanoscale metal particles.

Mesoporous materials such as SBA-15 have thick pore walls and higher thermal (hydrothermal) stabilities.^[14,86] The

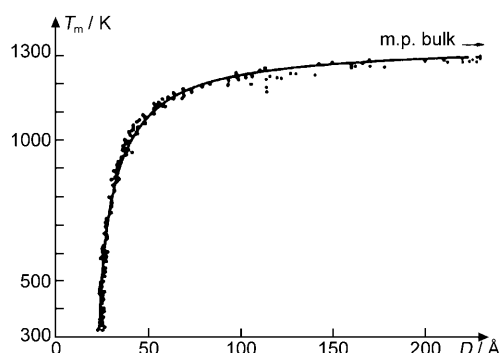


Figure 7. Melting-point temperatures of different sized gold nanoparticles. Reprinted with permission from *Phys. Rev. A* **1976**, *13*, 2287. Copyright 1976, American Physics Society.^[8]

periodic pore matrix, unlike the traditional inorganic support (e.g., silica gel), clearly demonstrate that they are ideal hosts for accommodating and confining uniform metal nanoparticles. Yang et al. found that highly dispersed Pt nanoparticles confined within the SBA-15 showed no observable mobility at 773 K.^[73] Dai et al. found that highly dispersed gold nanoparticles confined within channels of SBA-15 were highly resistant to sintering.^[87] Pd nanoparticles confined in the complementary micropores of SBA-15 were found to show higher stabilities.^[88] Metallic cobalt nanoparticles confined within the channels of SBA-15 were found to be air-stable and reusable.^[68] Fukuoka et al. reported that mesoporous materials containing confined Pt nanoparticles showed higher durability.^[89] Highly dispersed metal/bimetal clusters confined within the channels of MCM-41 were also demonstrated to be highly stable.^[70]

Although thermal stability of metal nanoparticles confined within mesoporous materials have been mentioned in some cases, there is seldom systematic investigation concerning the higher thermal stabilities of such confined nanoparticles. We have developed a facile route to encapsulate highly dispersed metal nanoparticles (e.g., silver) onto silica-based materials, especially within the mesoporous silicas. We further investigated the thermal stability of silver nanoparticles confined on SBA-15.^[79] We chose silver as it has a low Tammann temperature and we used it to compare and observe the confinement effect of mesoporous materials. Indeed, our systematic studies indicated that the confinement of metals in mesopores resulted in the unusual thermal stability of silver nanoparticles trapped inside the channels of SBA-15. It was observed that they could withstand a long-term high-temperature (e.g., 773 K, which is much higher than the Tammann temperature of bulk silver; i.e., 617 K) thermal treatment without any observable coarsening (Figure 8).^[79] This character is essential to the practical ap-

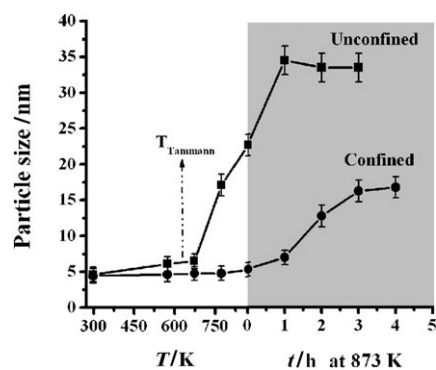


Figure 8. Mean silver particle size evolution versus temperature and time; the graph shows evident nano-confinement by the channels of mesoporous materials, especially, after the Tammann temperature. Reprinted with permission from *J. Am. Chem. Soc.* **2006**, *128*, 15756. Copyright 2006, American Chemical Society.

lications in the high-temperature catalytic reactions. In contrast, silver nanoparticles located on the external surface of SBA-15 or silica gels tended to aggregate by means of an attractive agglomeration route with the treating temperature close to its Tammann temperature. At higher temperatures (e.g., 873 K), although the coarsening process could be retarded by the confinement of mesoporous channels, silver particles would still aggregate through Ostwald ripening.^[79]

Metal Nanoparticles Confined in Mesoporous Materials as Catalysts

Due to the confinement of uniform pore structures, most of the trapped metal nanoparticles could keep their uniformity even after a relatively high-temperature process (e.g., high-temperature activation, pre-treatment, etc.). It definitely provided the prerequisite for keeping them highly dispersed and thus maintaining activity during catalysis, which is shown in the following reported cases. In the early studies, Schüth et al. found the very small Pt nanoparticles (ca. 2 nm) encapsulated within MCM-41 materials showed very high activity in the CO oxidation reactions, for which 50% conversion was reached at temperatures as low as 360 K.^[57] Corma et al. found that gold nanoparticles trapped in the mesoporous silica materials exhibited high catalytic activity for the solventless, aerobic oxidation of alcohols to carbonyl compounds in the absence of base (Figure 9). Under these conditions the solid can be recycled without losing catalytic activity and maintaining the mesoporous structure.^[62b] Metallic cobalt nanoparticles confined within the channels of SBA-15 materials were found to be highly active in many intramolecular cycloaddition reactions.^[68] Johnson et al. found that monodisperse metallic/bimetallic nanoclusters confined in MCM-41 materials showed a vastly improved enantioselectivity in the hydrogenation reactions compared with the homogeneous analogues.^[70] Recently, Dai et al. reported that, after removing the amine ligands (i.e., activation), the highly dispersed gold nanoparticles confined in mesoporous SBA-

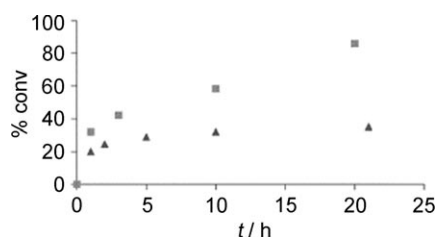


Figure 9. Conversion of 1-phenylethanol to acetophenone under solventless conditions over ■ mpAu-SiO₂ (gold nanoparticles confined within mesoporous materials) and ▲ Au/SBA-15. Reprinted with permission from *J. Mater. Chem.* **2005**, *15*, 4408. Copyright 2005, Royal Society of Chemistry.^[62b]

15 exhibited extremely high CO oxidation reactivity; 50% CO conversion was reached at temperatures as low as 253 K.^[87] Shi et al. reported that ultrafine Pd nanoparticles confined in mesoporous SBA-15 were more efficient than traditional Pd catalysts in Heck coupling reactions; only one fifth of the amount of catalyst was needed to reach the same conversion under the same reaction conditions.^[76] Fukuoka reported that highly dispersed Pt nanoparticles in meso-

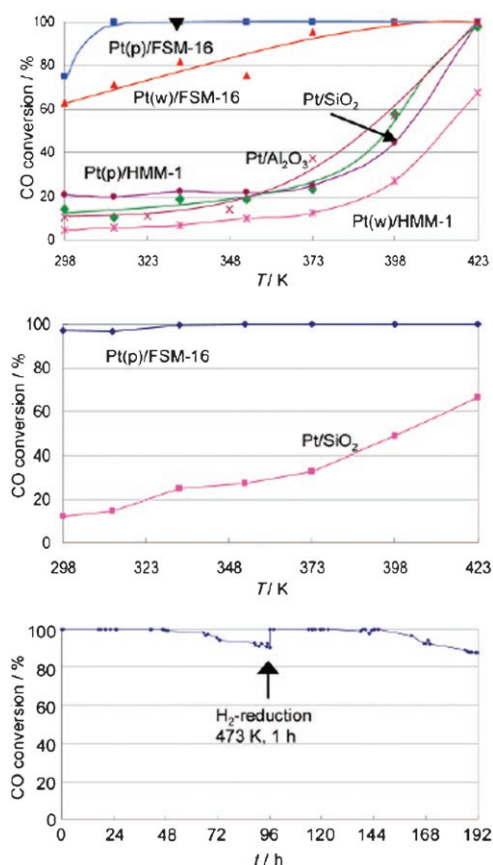


Figure 10. Preferential CO oxidation (PROX) reactions over supported Pt catalysts. Top: Under O₂/CO=1. Middle: Under stoichiometric O₂/CO=1/2. Bottom: Durability test of Pt (p)/FSM-16 at 353 K under O₂/CO=1. Conditions: CO 1%, O₂ 0.5–1%, N₂ 5%, H₂ balance, SV 12000 mL g⁻¹, 0.1 MPa. Reprinted with permission from *J. Am. Chem. Soc.* **2007**, *129*, 10120. Copyright 2007, American Chemical Society.^[89]

rous FMS-16 materials showed a 100% conversion of CO in hydrogen even at 313 K, which is much higher than traditional silica gel, alumina, and HMM-supported catalysts. Moreover, no decrease in the CO conversion was observed over Pt(p)/FSM-16 under the practical conditions of CO₂ (20%) and water vapor (2%) at 333 K (Figure 10).^[89] Mou et al. found that highly dispersed gold nanoparticles confined within the Al-SBA-15 exhibited higher activity toward CO oxidations at acidic conditions. However, the catalysts need a high temperature pre-treatment for activation, for which the higher dispersion as well as the high activity of the gold nanoparticles were still retained, because of the confinement of channels of mesoporous SBA-15.^[90] Highly dispersed copper metal nanoparticles confined within the channels of SBA-15 were also found to resist a higher temperature pre-treatment. These catalysts exhibited higher CO oxidation activities and complete CO oxidation took place at 463 K, which is lower than the temperature needed for bigger copper particles located on the outer surface of SBA-15.^[91] Zhao et al. recently reported that highly dispersed ruthenium incorporated in the mesoporous carbon materials showed very high activity and stability in the benzene hydrogenation reactions.^[59b] Very recently, our results indicated that inexpensive silver nanoparticles confined in meso-

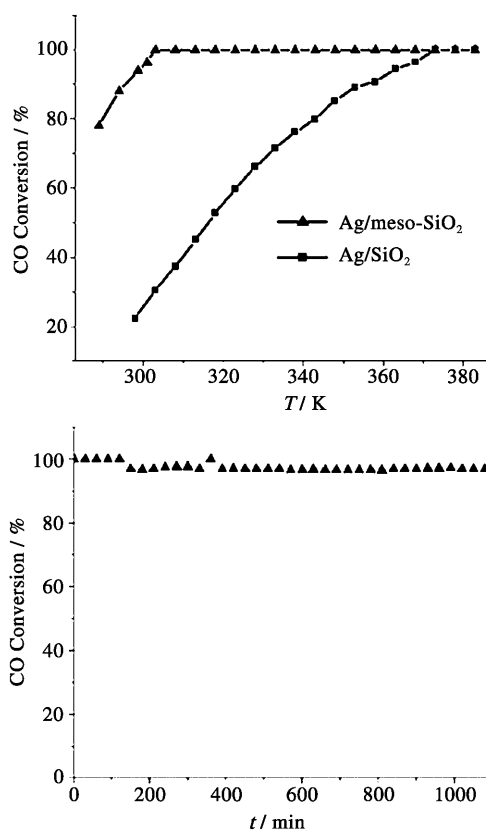


Figure 11. Top: Conversion of CO versus temperature over Ag/meso-SiO₂ and conventional Ag/SiO₂ catalysts. Bottom: Reaction performance of Ag/meso-SiO₂ catalyst with time on stream (303 K; 1 atm; flow rate = 50 mL min⁻¹). Reprinted with permission from *Chem. Commun.* **2008**, 2677. Copyright 2008, Royal Society of Chemistry.

structured silica materials also showed comparable CO oxidation activities with those noble metal nanoparticles (i.e., Pt, Au). At room temperature, a 100% conversion of CO has been realized (Figure 11).^[64b] In addition, we also found that by tuning the pore size of mesoporous silica, monodisperse silver nanoparticles with different particle size have also been obtained that showed size-dependent oxygen dissociation behavior and catalytic selectivities to formaldehyde in the methanol oxidation reactions.^[92]

Conclusion

In this paper, we brought forward the new concept toward higher thermal stable monodisperse metal nanoparticles confined by the channels of the mesoporous materials. Three successive parts have been briefly described. Rational control of structures of mesoporous materials by controlling self-assembly of surfactants was successful. Functional, ordered, mesoporous materials with tunable pore size and pore length have been obtained. Strategies in the successful encapsulation of monodisperse metal nanoparticles within the channels of functional mesoporous materials were also demonstrated. Metal nanoparticles confined in well-defined mesoporous materials showed unusual thermal stability, which is essential to their applications in the field of catalysis, especially for high-temperature catalytic reactions.

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