Highly dispersed platinum nanoparticles on mesoporous materials*

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Abstract: The high surface area and controlled pore size of mesoporous materials made them efficient support for the dispersion of nanoparticles. In particular, highly dispersed Pt-loaded mesoporous materials are interesting systems for nanotechnology and catalysis. The structural, textural, and surface properties of a mesoporous support play a critical role in nanoparticle synthesis. This article presents the development of dispersion of nanoparticles on mesoporous supported materials such as MCM-41, SBA-15, KIT-6, and CMK-3 and their properties. Future research trends toward new approaches to designing Pt nanoparticles for electrochemical applications are proposed.

Keywords: carbon; mesoporous materials; nanoparticles; platinum; silica.

INTRODUCTION

The developments of nanoscience and nanotechnology have brought a profound revolution in materials science research and human lives over the past few years [1–10]. Nanoscience with various branches helps one understand the concepts at the atomic or molecular level, which induces many new branches such as nanomaterials [11–13], nanoelectronics [14,15], nanomechanics [16,17], and so on. Materials in the range of 1–100 nm have attracted a great deal of attention to understand and create new materials, devices, and systems by working at the atomic, molecular, and supramolecular levels. Porous materials have recently created a lot of interest owing to the large internal surface area and pore volume and tunable and narrow pore diameter. They are expected to be efficient materials in the area of drug delivery, sensors, catalysis, adsorption, photonics, separation, nanodevices, and fuel cells.

The textural properties of some important mesoporous materials, including MCM-41, SBA-15, KIT-6, and CMK-3, are shown in Table 1. Highly ordered mesoporous materials with superior textural properties are suitable to be used as a support material for dispersion of nanoparticles. In particular, Pt nanoparticles with smaller diameters are important for size-dependent catalytic reactions, nonlinear optics, magnetic materials, and fuel cells. Since the properties of nanoparticles are dependent upon the dimension and size, it is very important to control the size and shape of metal nanoparticles uniformly. In this connection, mesoporous materials are ideal candidates for dispersion of nanoparticles. There are several methods concerning the preparation of nanoparticles: (i) ion exchange of noble metals into silicate followed by reduction to form metal nanoparticles with mesostructure [18]; (ii) chemical vapor deposition of volatile metal compounds followed by decomposition in a porous structure [19]; and (iii)

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incipient wetness and impregnation [20,21]. Moreover, direct synthesis methods involving surfactant stabilization have been reported by several researchers to control the size and shape of metal nanoparticles [22–25]. From such a viewpoint, this article discusses transmission electron microscopic (TEM) study and developments of the technique for dispersing Pt nanoparticles over some of the important mesoporous materials, such as MCM-41, SBA-15, KIT-6, and CMK-3. At the end of the article, future research trends and further applications of Pt nanoparticles are proposed.

Table 1 Textural properties of some important mesoporous materials.

Material	Surface area, $A_{BET}/m^2\ g^{-1}$	Pore volume, Vp (cm^3/g)	Pore diameter, dp (nm)
MCM-41	1041	0.7	2.7
SBA-15	710	0.9	9.2
KIT-6	753	0.9	7.3
CMK-3	1366	1.1	3.5

HEXAGONAL MESOPOROUS SILICA MOLECULAR SIEVES

Hexagonal pore structured siliceous MCM-41 materials possess high surface area (~1000 m^2/g), large pore volume (~0.7 cm^3/g), and narrow pore size distribution, which are helpful for control and dispersion of nanoparticles [26–28]. Interestingly, the textural parameters of MCM-41 can be controlled by changing the synthesis composition and conditions such as surfactant chain length, silica source, incorporation of swelling agent, and aging time. High surface area materials are useful for forming very small Pt nanoparticles so that a lot of applications are found in the field of electronics and catalysis due to their unique electric, magnetic, and optical properties arising from their quantum size effect. Figure 1 shows TEM images of Pt nanoparticles (dark spots) dispersed on MCM-41 [41] with average particle size of 4.2 nm. No significant change in the surface area of Pt-MCM-41 sample is observed as compared to standard MCM-41. High surface area and large pore MCM-41 materials are effectively used as a support for Pt nanoparticles and applied for fuel cells, reduction of NO_x, CO preferential oxidation, methanol electro-oxidation, and other hydrogenation reactions [29–31]. Surface functionalization of MCM-41 also helps for quantitative and high dispersion of Pt nanoparticles. Up to now, siliceous MCM-41 [32], Ti-MCM-41 [33], Al-MCM-41 [29], Fe-MCM-41 [34], V-MCM-41 [35], other metal-loaded MCM-41 [36] and amine-functionalized MCM-41 materials [37] have been used as supported materials for high dispersion of Pt nanoparticles. Moreover, bimetallic nanoparticles supported on amine-functionalized MCM-41 and Al-MCM-41 were also used for isomerization and hydrocracking of *n*-decane [38,39].
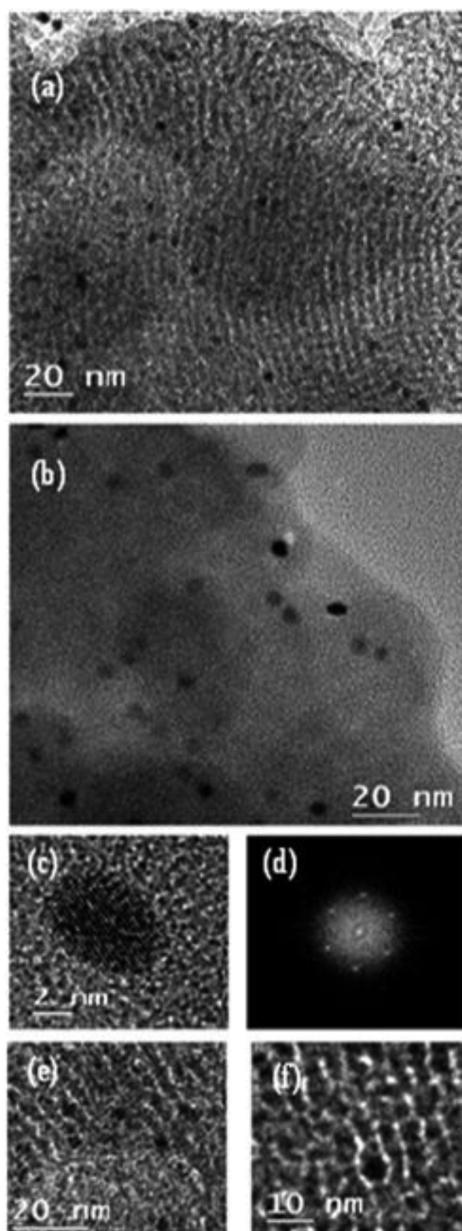
Fig. 1 TEM images of Pt-MCM-41 exposed to air after reduction (a), (b), (c), (d) Pt-MCM-41 reduced sample (e), (f) magnified images of selected area in (a). Reproduced from *Chem. Mater.* **18**, 2663 (2006). Copyright © 2006 American Chemical Society.

TWO-DIMENSIONAL HEXAGONAL MESOPOROUS SILCA

SBA-15 with ordered hexagonal arrangements of interconnected channels has higher hydrothermal stability compared with other mesoporous materials [42,43]. The properties of triblock copolymer are facile structure-directing ability, low-cost commercial availability, and biodegradability, which turned out to be a valuable supramolecular template for the synthesis of ordered mesoporous SBA-15 material.

The pores and pore wall of SBA-15 materials can be controlled either by changing the synthesis temperature or by addition of cosolvent during the synthesis. The surface area of siliceous SBA-15 is ~700 m^2/g, and pore volume ~0.9 cm^3/g. The pore diameter can be controlled from 4.6 to 30 nm by increasing the hydrophobic volume of the self-assembled aggregates [44]. As SBA-15 possesses superior textural properties with tunable pore diameter, metal nanoparticles can be highly dispersed without much agglomeration. In a typical synthesis of Pt, particles supported on SBA-15 with loading of 10 wt % are prepared using H$_2$PtCl$_6$·6H$_2$0 (Wako Chemicals) as a Pt source. SBA-15 and Pt particles are dispersed into ethanol followed by drying at room temperature in N$_2$ gas flow. The dried powder is reduced at 400 °C for 2 h in a H$_2$ gas flow.

High-resolution TEM images of Pt-loaded SBA-15 materials are shown in Figs. 2a,b. The images indicate that the Pt nanoparticles are encapsulated by ordered silica structures and the Pt particles are isolated and randomly distributed with average particle size of ca. 3–4 nm in the entire silica framework without severe agglomeration. Catalytic activity of the materials for crotonaldehyde hydrogenation shows that the activity and selectivity of crotyl alcohol is dependent on the size of Pt nanoparticles [45]. It is observed by powder X-ray diffraction (XRD) (Fig. 2c) that the structural order was well maintained
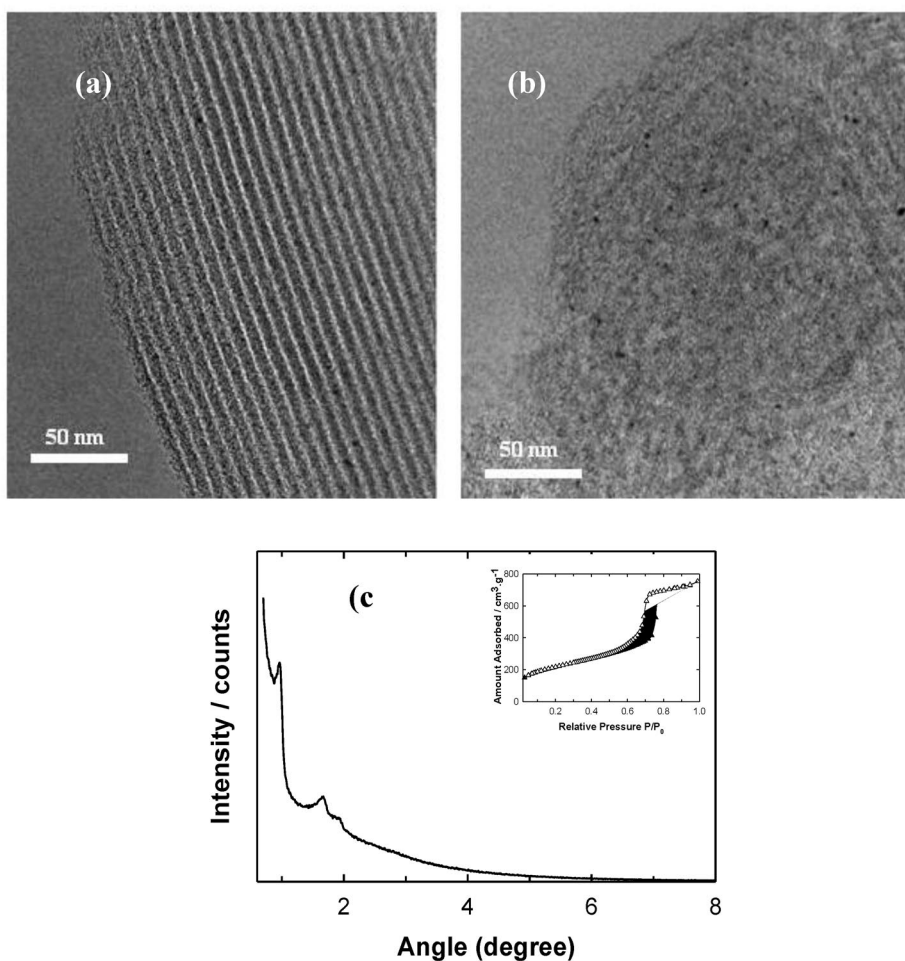

Fig. 2 Pt-loaded SBA-15 material after reduction (a), (b) TEM images, (c) powder XRD pattern; (inset) N$_2$ adsorption–desorption isotherm.

even after loading Pt nanoparticles in mesoporous materials. The nitrogen adsorption and desorption isotherm of Pt-loaded SBA-15 sample is shown in Fig. 2c (inset). The Brunauer–Emmett–Teller (BET) surface area of the sample is 740 m^2/g, which is close to the pure mesoporous silica SBA-15 sample. Han et al. reported unsupported Pt nanowires with uniform diameter of 7.0 nm using SBA-15 [46]. Pt-SBA-15 is also used as an active catalyst for hydrodesulfurization of 4,6-dimethyldibenzothiophone [47] and ethylene hydrogenation [48]. Selective catalytic reduction of nitric oxide was reported by Oh et al. using Pt-loaded Al-SBA-15 [49]. Other highly dispersed nanoparticles and catalytically active modified SBA-15 materials are used for hydroisomerization of *n*-dodecane [50], carbon monoxide oxidation and conversion [51], dehydrogenation of methylcyclohexane [52], and ethyl acetate combustion [53], etc.

BICONTINUOUS CUBIC MESOPOROUS SILICA

Bicontinuous cubic mesostructure, KIT-6 (*Ia*3*d* symmetry) is a fascinating material and is constructed with two helical chains [56]. It is very rare to get this kind of structure, and a few block copolymers can show bicontinuous structure with minimum surface charge. The use of block copolymers as templates allows tuning of the micelle structures by adjusting the solvent composition and molecular weight. After the first synthesis of promising materials, hexagonal SBA-15 using triblock copolymer, a similar strategy has been applied for mesoporous materials with different cubic structures with *Im*3*m*, *Pm*3*n*, and *Ia*3*d* symmetries. Moreover, these materials are expected to be superior to hexagonal structures for applications involving selectively tuned diffusion and immobilization of large molecules [54,55]. Cubic bicontinuous mesostructure KIT-6 was prepared using P123 as a surfactant and 1-butanol as cosolvent [56], which possesses surface area ~750 m^2/g with large pore volume 0.9 cm^3/g. Due to the order of bicontinuous structure and properties, KIT-6 mesoporous silica can be used as an efficient support for dispersion of Pt nanoparticles. The synthesis of Pt particles supported on KIT-6 with loading of 10 wt % was prepared similarly as the procedure of Pt-SBA-15 material except the support is KIT-6 instead of SBA-15. The structural order was maintained well after Pt loading in KIT-6 pore structure (Fig. 3c), and N$_2$ adsorption–desorption isotherm also confirms that mesoporosity is retained without any pore blockage as indicated by a sharp rise in the capillary condensation step (Fig. 3c, inset). TEM images of metal particles dispersed on KIT-6 indicate the Pt nanoparticles with an average particle size of 4–5 nm are uniformly distributed throughout the materials (Figs. 3a,b). Other cubic *Ia*3*d* mesoporous silica MCM-48 and Al-MCM-48 materials [57,58] are used effectively for dispersion of metal nanoparticles, which showed higher catalytic activity and selectivity of C$_7$-branched isomers in hydroisomerization of *n*-octane and hydrogenation of cinnamaldehyde under supercritical conditions as compared with other porous aluminosilicates.
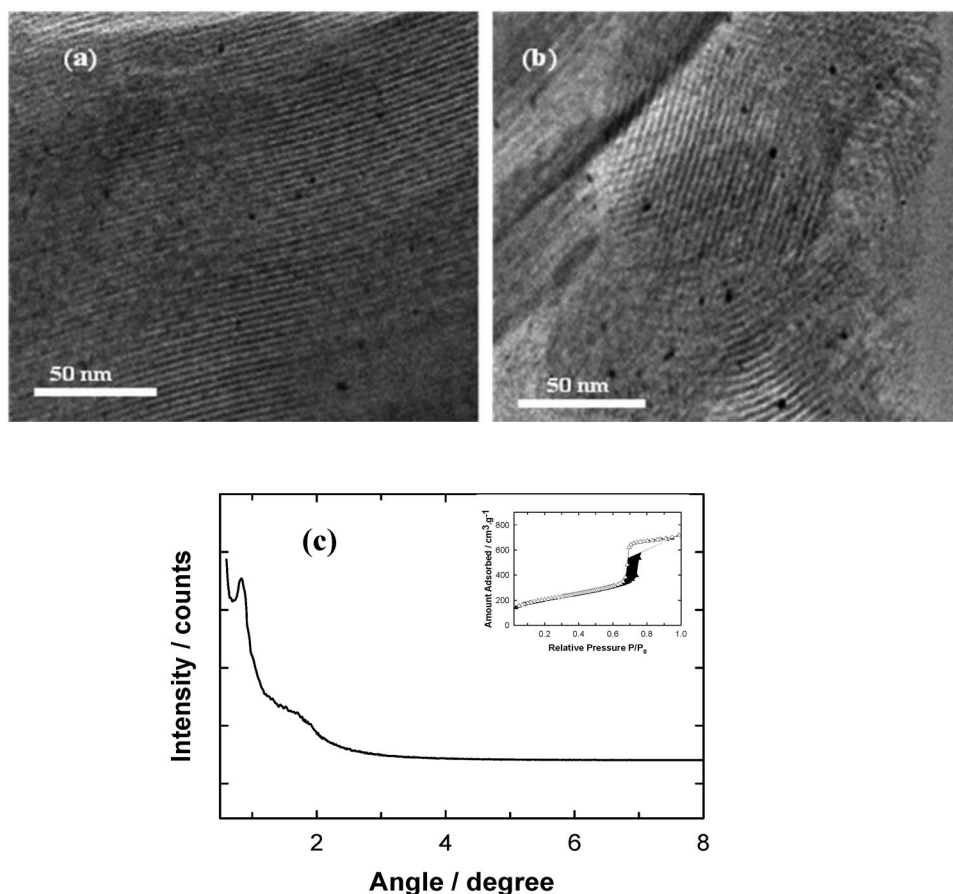
Fig. 3 Pt-loaded KIT-6 material after reduction (a), (b) TEM images, (c) powder XRD pattern; (inset) N_2 adsorption–desorption isotherm.

TWO-DIMENSIONAL MESOPOROUS CARBON

In recent years, porous carbons have attracted much attention due to their potential applications in catalysis, adsorption, storage of natural gas, separation process, and electrodes of electric double-layer capacitors [59–63]. Several different methods have been developed to synthesize mesoporous carbons. These include the carbonization of polymer aerogels such as resorcinol-formaldehyde resins [64], the catalytic activation of carbon precursors in the presence of metals and organometallic compounds [65,66], and carbonization of polymer blends with thermally unstable components [67,68]. These methods result in a mesoporous carbon with broad pore size distribution. Among them, the template synthesis method [63,69,70] has been extensively used for fabricating carbon materials possessing uniform and interconnected pores. The synthesis technique is known as "nanocasting". This synthetic technique involves infiltration of silica templates with an appropriate carbon source, carbonization of carbon precursor, and subsequent removal of silica. The resulting carbons are inverse replicas of ordered mesoporous silicas. Since the first successful synthesis of ordered mesoporous carbon (CMK-1) using MCM-48 [69], mesoporous carbons with various structures have been reported using different silica templates: e.g., CMK-2 [71], CMK-3 [72], CMK-4 [73] with cubic *Pm3n*, *Ia3d*, and hexagonal *p6mm* symmetries using sucrose [74], furfuryl alcohol [75,76], and acenaphthene [77] as carbon sources.

TEMs of Pt-loaded CMK-3 carbon sample are shown in Fig. 4 [78]. It is noted that Pt nanoparticles with average particle size of ca. 2–3 nm are uniformly dispersed on the carbon surface. Much attention has been paid to explore the use of Pt nanoparticles supported on mesoporous carbon for fuel cells. The performance of fuel cells mainly depends on electrocatalytic activity and long-term stability of the material. The electrocatalytic activity is closely related to dispersion of noble metal nanoparticles and overall performance of catalyst. The electrocatalytic stability for methanol oxidation indicates that the material has superior electrocatalytic property and stability, compared to commercial catalysts.
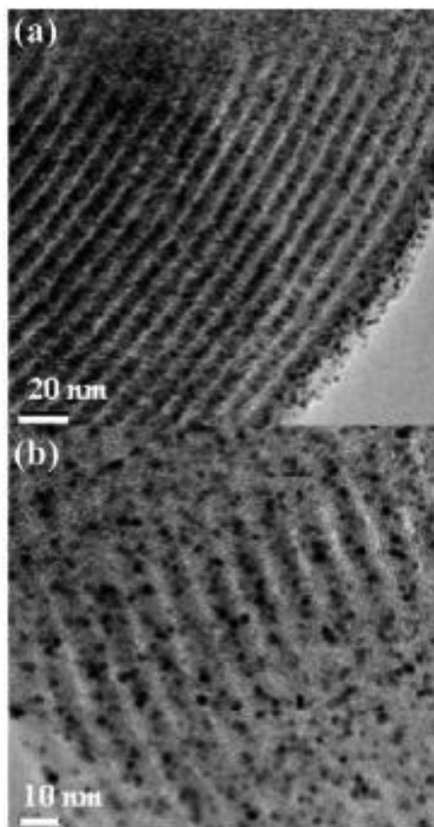

Fig. 4 (a), (b), TEM images of Pt-CMK-3 with average particle size of 2–3 nm. Reproduced from *Chem. Mater.* **20**, 1622 (2008). Copyright © 2008 American Chemical Society.

CONCLUSIONS AND OUTLOOK

Pt nanoparticles supported on mesoporous silica and carbon materials have proven to be superior catalysts for various reactions and electrocatalytically active for fuel cells. This article presented detailed research and TEM study on Pt nanoparticles supported on some important mesoporous materials and their applications. The above results showed that mesoporous silica and carbon can be used as efficient supports for dispersion of stable nanoparticles. The observed average metal nanoparticle size is ~4 and 2–3 nm over mesoporous silica and carbon supports, respectively. High surface area and electrocatalytically stable Pt/CMK-3 material showed superior performance for methanol oxidation as compared to other commercial catalysts. Despite rapid growth in the number of publications on preparation of Pt nanoparticles, cost-effective and highly efficient material for catalysis and fuel cells still remains a challenging task. Theoretical and experimental study demonstration of nanoparticles on porous struc-

tures with average particle size lower than 1 nm and experimental results for hydrogen production will reveal the physical and chemical properties of these materials in the near future.

ACKNOWLEDGMENTS

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