

Clusters

Formation of Nanoparticles in Mesoporous Materials Review of Recent Literature

Article Title	Reaction Considered	Reference
Synthesis of Nanosized Platinum Cluster in Cubic Mesoporous Material via a Direct Introduction Method	Chloroplatinic acid was incorporated into MCM-48 during its synthesis, as well as by subsequent incipient wetness impregnation and ion exchange; clusters were formed and the direct introduction method yielded higher activity for benzene/toluene hydrogenation.	Chatterjee, M.; Iwasaki, T.; Onodera, Y.; Nagase, T., <i>Catal. Letters</i> , 61 (1999) 199-202.
Ag Nanowire Formation within Mesoporous Silica	Nanowires with diameters of 5-6 nm were formed in SBA-15 by AgNO ₃ impregnation followed by thermal decomposition; in addition, 10-15 nm particles were also observed by EM.	Huang, M. H.; Choudrey, A.; Yang, P., <i>J. Chem. Soc., Chem. Commun.</i> , (2000) 1063-1064.
Metallic Nanoparticles from Heterometallic Co-Ru Carbonyl Clusters in Mesoporous Silica Xerogels and MCM-41-type Materials	Impregnation of mesoporous materials with THF saturated with [NEt ₄][Co ₃ Ru(CO) ₁₂]; in 2.7 nm MCM-41, heat-treatment in Ar at 350°C yielded 1.5 nm metal particles, while 500°C treatment yielded 8 nm particles of the pure metals; thermal treatment at 900°C also yielded bimetallic Co/Ru hexagonal alloy particles; larger particles were formed on the xerogel.	Schweyer, F.; Braunstein, P.; Estournès, C.; Guille, J.; Kessler, H.; Paillaud, J.-L.; Rosé, J., <i>J. Chem. Soc., Chem. Commun.</i> , (2000) 1271-1272.
Preparation of Noble Metal Nanowires using Hexagonal Mesoporous Silica SBA-15	SBA-15 was impregnated with aq. noble metal salts, evaporated to dryness, soaked with CH ₂ Cl ₂ that was then evaporated, dried under vacuum, and reduced in a H ₂ flow at elevated temp. to form 7 nm nanowires; some metal particles were also formed.	Han, Y.-J.; Kim, J. M.; Stucky, G. D., <i>Chem. Mater.</i> , 12 (2000) 2068-2069.
TEM Studies of Platinum Nanowires Fabricated in Mesoporous Silica MCM-41	Pt nanowires with 3.0 nm diameter were formed; unsupported Pt nanowires obtained by removing the silica framework with HF agglomerated at about 300°C and broke at temps. Above 400°C.	Liu, Z.; Sakamoto, Y.; Ohsuna, T.; Hiraga, K.; Terasaki, O.; Ko, C. H.; Shin H. J.; Ryoo, R., <i>Ang. Chem., Intern. Ed.</i> , 39 (2000) 3107-3110.
Superparamagnetic Ceramic Nanocomposites: Synthesis and Pyrolysis of Ring-Opened Poly(ferrocenylsilanes) inside Periodic Mesoporous Silica	Pyrolyzed MCM-41/ferrocenylsilane composites at 900°C in N ₂ to form Fe nanoparticles in the 3-4 nm channels; magnetization data indicated that the 5.0-6.4 nm Fe particles were coated with a thin 0.4-0.6 nm oxide layer.	MacLachlan, M. J.; Ginzburg, M.; Coombs, N.; Raju, N. P.; Greedan, J. E.; Ozin, G. A.; Manners, I., <i>J. Am.</i>

		<i>Chem. Soc.</i> , 122 (2000) 3878-3891.
Ship-in-bottle Synthesis and Catalytic Performance of Platinum Carbonyl Clusters, Nanowires, and Nanoparticles in Micro- and Mesoporous Materials	Reductive carbonylation of Pt ions impregnated on NaY zeolite or mesoporous FSM-16 yielded Pt carbonyl clusters, which formed 1.0-1.5 nm Pt nanoparticles upon decarbonylation; H ₂ reduction of H ₂ PtCl ₆ /FSM-16 gave 2.5 nm Pt particles in the 2.7 nm diameter mesoporous of FSM-16.	Fukuoka, A.; Higashimoto, N.; Sakamoto, Y.; Sasaki, M.; Sugimoto, N.; Inagaki, S.; Fukushima, Y.; Ichikawa, M., <i>Catal. Today</i> , 66 (2001) 23-31.
Preparation and Catalysis of Pt and Rh Nanowires and Particles in FSM-16	Impregnation of FSM-16 (2.7 nm pore size) with Pt, Rh, and Pt/Rh salts followed by UV irradiation in the presence of water and 2-propanol yielded nanowires; in contrast, H ₂ reduction at 400°C resulted in the formation of nanoparticles; Pt nanowire gave high activity for butane hydrogenation, while Pt-Rh nanowire gave high activity for butane isomerization to isobutene.	Fukuoka, A.; Higashimoto, N.; Sakamoto, Y.; Inagaki, S.; Fukushima, Y.; Ichikawa, M., <i>Microporous Mesoporous Mater.</i> , 48 (2001) 171-179.
The Formation of Dimensionally Ordered Silicon Nanowires within Mesoporous Silica	Si nanowires were formed by treating a mesoporous silica with 5 nm pores with diphenylsilane in hexane at 500°C under a pressure of 375 bar.	Coleman, N. R. B.; Morris, M. A.; Spalding, T. R.; Homes, J. D., <i>J. Am. Chem. Soc.</i> , 123 (2001) 187-188.
Synthesis of Platinum Networks with Nanoscopic Periodicity using Mesoporous Silica as Template	Non-derivatized SBA-15 and MCM-48 were repeatedly impregnated with aq. Pt salt solns and then reduced in flowing H ₂ at 300°C to yield 70 wt% Pt loadings; removal of the silica framework with 10% HF gave Pt sponges.	Shin, H. J.; Ko, C. H.; Ryoo, R., <i>J. Mater. Chem.</i> , 11 (2001) 260-261.
Solvent-free, Low-temperature, Selective Hydrogenation of Polyenes using a Bimetallic Nanoparticle Ru-Sn Catalyst	Loaded clusters of Ru ₆ C(CO) ₁₇ and of Ru ₆ C(CO) ₁₆ SnCl ₂ into MCM-41 by a slurry process; all carbonyl ligands were removed by heat-treatment at 200°C to yield nanoparticles.	Hermans, S.; Raja, R.; Thomas, J. M.; Johnson, B. F. G.; Sankar, G.; Gleeson, D., <i>Ang. Chem., Intern. Ed.</i> , 40 (2001) 1211-1215.
New Catalysts for Clean Technology	Bimetallic nanoparticles were prepared from Ru ₆ Pd ₆ and Ru ₆ CSn carbonyl clusters and were anchored along the interior walls of mesoporous silica MCM-41. Under investigation were solvent-free, low temperature, selective hydrogenation and superior performance of a chiral catalyst confined within mesoporous silica.	Johnson, B.; Raynor, S.; Brown, D.; Shephard, D.; Mashmeyer, T.; Thomas, J.M.; Hermans, S.; Raja, R.; Sankar, G.; <i>J. Mol. Catal. A: Chem.</i> 182-183 (2002) 89-97.
Synthesis and Characterization of	MCM-41-TiO ₂ was equilibrated with aq.	Zheng, S.; Gao, L.;

Pt, Au or Pd Clusters Deposited Titania-modified Mesoporous Silicate MCM-41	metal chlorides at low pH for 8 h under Ar and then the slurry was irradiated with UV light for 4 h to reduce the metal chloride clusters to the metal clusters than could not be detected by EM nor XRD.	<i>Mater. Chem. Phys.</i> , 78 (2002) 512-517.
Incorporation of CdS Nanoparticles Inside Ordered Mesoporous Silica SBA-15 via Ion Exchange	Some protonated surfactant remained in SBA after washing with ethanol and was replaced by ion exchange with Cd ²⁺ (in inner pores of silica). Also used inert functional phenyl groups on SBA-15. Sample then treated with H ₂ S and calcined. Average CdS particle size was 3 nm.	Wang, S.; Choi, D.-G.; Yang, S.-M.; <i>Adv. Mater.</i> , 14 (2002) 1311-1314.
Solid-State NMR Studies of MCM-41 Supported with a Highly Catalytically Active Cluster	[Pd ₆ Ru ₆ (CO) ₂₄][Net ₄] ₂ was prepared and anchored to MCM-41. The mixture was stirred, and the solid was filtered and washed. The presence of the carbonyl cluster was verified with Nujol Mull IR spectroscopy. The removal of CO was achieved by heating the sample at 563 K in vacuum for 2 h. The absence of CO stretching frequencies was verified by solid-state IR spectroscopy.	Jones, M.; Duer, M.; Hermans, S.; Khimyak, Y.; Johnson, B.; Thomas, J.; <i>Angew. Chem. Int. Ed.</i> 41 (2002) 4726-4729.
Synthesis and Luminescence Property of Rare Earth Complex Nanoparticles Dispersed Within Pores of Modified Mesoporous Silica	A rare earth complex, Eu(AA) ₃ Phen, was synthesized and then was mixed with different mesoporous silica materials in aqueous solution, resulting in successful introduction of the complex into the pores of the silica.	Bian, L.; Xi, H.; Quian, X.; Yin, J.; Zhu, Z.; Lu, Q.; <i>Mater. Res. Bull.</i> 37 (2002) 2293-2301.
Highly Dispersed Metal Nanoparticles in Functionalized SBA-15	TPTAC-functionalized SBA-15 was mixed with the ethanol solution of H ₂ PtCl ₆ or HAuCl ₄ for 10 minutes to ensure a fully ion-exchanged sample, and then reduced in hydrogen flow at 373-573 K. Detection of Pt and Au nanoparticles in SBA-15 possible by PXRD, XAS, and TEM.	Yang, C.; Liu, P.; Ho, Y.; Chiu, C.; Chao, K.; <i>Chem. Mater.</i> , 15 (2003) 275-280.
Gold Nanoparticles in SBA-15 Showing Catalytic Activity in CO Oxidation	The surface of SBA-15 was functionalized with positively charged groups and [AuCl ₄] ⁻ species were subsequently incorporated into the channel system via ion exchange. A reaction rate of 2.7 x 10 ⁻⁴ mmol g ⁻¹ s ⁻¹ in CO oxidation was found for this composite material. TEM images of Au/SBA-15 reveal that gold particles start sintering at temperatures higher than 100°C, resulting in a significant drop in catalytic activity.	Yang, C.; Kalwei, M.; Schüth, F.; Chao, K.; <i>Appl. Catal. A: Gen.</i> 254 (2003) 289-296.
Silver Nanoparticle Growth in 3D-Hexagonal Mesoporous Silica Films	3D-hexagonal mesoporous films are used as templates to grow uniform Ag nanoparticle. The grafting of hydrophobic groups at the pore surface significantly slows down the silver ion diffusion, anchoring small Ag	Besson, S.; Gacoin, T.; Ricolleau, C.; Boilot, J.-P.; <i>J. Chem. Soc., Chem. Commun.</i> , (2003)

	clusters in micropores, and leading to organized domains of Ag particles (≈ 4 nm) in mesopores with a narrow size distribution.	360-361.
Palladium Nanowires and Nanoparticles in Mesoporous Silica Templates	Mesoporous silicas FSM-16 and HMM-1 were impregnated with H_2PdCl_4 . UV-irradiation of the sample in the presence of water and methanol vapors and subsequent H_2 -reduction resulted in the formation of Pd nanowires. One-step H_2 -reduction gave Pd nanoparticles in the mesopores.	Fukuoka, A.; Araki, H.; Sakamoto, Y.; Inagaki, S.; Fukushima, Y.; Ichikawa, M.; <i>Inorg. Chim. Acta</i> 350 (2003) 371-378.
Dithiol-mediated Incorporation of CdS Nanoparticles from Reverse Micellar System into Zn-doped SBA-15 Mesoporous Silica and Their Photocatalytic Properties	Zn-doped SBA-15 was prepared by adding $\text{Zn}(\text{NO}_3)_2$ during synthesis of the SBA material itself. CdS nanoparticles were prepared in reverse micellar solution. The ZnSBA-15 was added to the micellar solution to give CdS-incorporated ZnSBA-15.	Hirai, T.; Nanba, M.; Komasaawa, I. <i>J. Coll. Inter. Sci.</i> 268 (2003) 394-399.
Confinement of Cd_3P_2 Nanoparticles Inside Ordered Pore Channel in Mesoporous Silica.	Nano-sized Cd_3P_2 Has been confined inside the pore channels of MCM-41 by a surface modification method. The nanoclusters were mostly confined and dispersed in the channels of the mesoporous hosts.	Zhao, X-G.; Shi, J-L.; Hu, B.; Zhang, L-X.; Hua, Z-L., <i>J. Mater. Chem.</i> 13 (2003) 399-403.
Indium and Indium-oxide Nanoparticle or Nanorod Formation within Functionalised Ordered Mesoporous Silica	Organized mesoporous silica materials containing phosphonate groups were used for controlling the growth of indium(0) nanoparticles or nanorods, which are converted to indium-oxide without modification of their size and shape.	Guiari, y.; Soulantica, K.; Philippot, K.; Thieuleux, C.; Mehdi, A.; Reyé. C.; Chaudret, B.; Corriu, R.J.P., <i>New J. Chem.</i> , 27 (2003) 1029-1031.
A New Method for the Synthesis of Highly Dispersive and Catalytically Active Platinum Nanoparticles Confined in Mesoporous Zirconia	Sulfuric acid and ethanol were used to remove the surfactant from as-synthesized mesophase zirconia. A sucrose solution containing H_2PtCl_6 was filled into the pore channels by ion exchange under vigorous agitation.	Chen, H-R.; Shi, J-L.; Li, Y-S.; Yan, J-N.; Hua, Z-L.; Chen, H-G.; Yan, D-S., <i>Adv. Mater.</i> 15 (2003) 1078-1081.
Synthetic Insertion of Gold Nanoparticles into Mesoporous Silica	Gold particles were introduced into the mesopores of MCM-41 and MCM-48 during the synthesis of the respective silicates. Three different particle sizes were used for both silicates.	Kónya, Z.; Puentes, V.F.; Kiricsi, I.; Zhu, J.; Ager III, J.W.; Ko, M.K.; Frei, H.; Alivisatos, P.; Somorjai, G.A., <i>Chem. Mater.</i> 15 (2003) 1242-1248.
Probing of Functionalized Mesoporous Silica Nanoparticles using Transition Metal Clusters	MCM-41 was treated with $\text{Ru}_6\text{C}(\text{CO})_{16}\text{SnCl}_2$ to give bimetallic Ru_6Sn nanoparticles immobilized by reaction with surface silanol groups to form Si-O-Sn bonds; after derivatizing the MCM-41 with thiol groups and treatment with $\text{Ru}_5\text{C}(\text{CO})_{15}$, color	Hermans, S.; Sadasivan, S.; Judkins, C. M. G.; Johnson, B. F. G.; Mann, S.; Khushalari, D., <i>Adv. Mater.</i> , 15

	change and analysis indicated that the thiol groups were accessible and mainly located within the channels of MCM-41.	(2003) 1853-1857.
In Situ Formation of Gold Nanoparticles within Thiol Functionalized HMS-C ₁₆ and SBA-15 Type Materials via an Organometallica Two-Step Approach	Gold nanoparticles were located exclusively within the pore channels of mesoporous silica using a two-step procedure consisting of anchoring an organogold precursor within the channels followed by chemical reduction.	Guari, Y.; Thieuleux, C.; Mehdi, A.; Reyé, C.; Corriu, R.J.P.; Gomez-Gallardo, S.; Philippot, K.; Chaudret, B., <i>Chem. Mater.</i> 15 (2003) 2017-2024.
Encapsulation of Metal (Au, Ag, Pt) Nanoparticles into the Mesoporous SBA-15 Structure	Mesoporous silica were synthesized using a metal nanoparticle-copolymer unit as a template. The method is based on growing the mesopores around previously formed metal nanoparticles to take advantage of the excellent size and shape control achievable in the synthesis of colloidal dispersions.	Zhu, J.; Kónya, Z.; Puentes, V.F.; Kiricsi, I.; Miao, C.X.; Ager, J.W.; Alivisatos, A.P.; Somorjai, G.A., <i>Langmuir</i> 19 (2003) 4396-4401.
Preparation, Characterization, and Condensation of Copper Tellurolate Clusters in the Pores of Periodic Mesoporous Silica MCM-41	[(Cu ₆ (TePh) ₆ (PPh ₂ Et) ₅] was loaded into MCM-41 by solid-state impregnation, i.e. at 110°C and 10 ⁻³ Torr static vacuum; thermal condensation yielded Cu ₂ Te nanoparticles not detectable by EM nor XRD; heat-treatment at 550°C yielded XRD pattern of Cu _{0.64} Te _{0.36} particles not detectable by EM.	Kowalchuk, C. M.; Schmid, G.; Meyer-Zaika, W.; Huang, Y.; Corrigan, J. F., <i>Inorg. Chem.</i> , 43 (2004) 173-180.
Template Synthesis of Nanoparticle Arrays of Gold, Platinum, and Palladium in Mesoporous Silica Films and Powders	Metal nanoparticles are formed by H ₂ - or photo-reduction of metal precursors impregnated on mesoporous silica films. The film is then dissolved in dilute HF solution, isolating the nanoparticles, which are then stabilized with ligands such as 1-dodecanethiol and triphenylphosphine.	Fukuoka, A.; Hidenobu, A.; Kimura, J.; Sakamoto, Y.; Takanori, H.; Sugimoto, N.; Inagaki, S.; Ichikawa, M., <i>J. Mater. Chem.</i> , 14 (2004) 752-756.
Selective Synthesis of Pd Nanoparticles in Complementary Micropores of SBA-15	Pd was introduced into SBA-15 by ion exchange from a Pd(CH ₃ COO) ₂ ammonia aqueous solution, followed by washing and air drying. This material was reduced by H ₂ and then oxidized in air to produce PdO nanoparticles.	Yuranov, I.; Kiwi-Minsker, L.; Buffat, P.; Renken, A., <i>Chem. Mater.</i> , 16 (2004) 760-761.
Post-synthesis Deposition of V-zeolitic Nanoparticles in SBA-15	V-silicalite-1 nanoparticles were deposited in the pores of SBA-15 by means of a dry impregnation of the acidified suspension on calcined SBA-15. Crystalline V-activated zeolitic plugs in the mesoporous channels of SBA-15 were formed.	Meynen, V.; Beyers, E.; Cool, P.; Vansant, E.F.; Mertens, M.; Weyten, H.; Lebedev, O.I.; Van Tendeloo, G., <i>Chem. Commun.</i> , (2004) 898-890.
Synthesis of Silver Nanowires Inside Mesoporous MCM-41 Host	Silver nanowires were prepared using template method inside the channels of MCM-41. This method provides good control over the shape and size of the	Adhyapak, P.V.; Karandikar, P.; Vijaymohanan, K.; Athawale, A.A.;

	nanowires. Silver nanowire formation is confirmed by TEM and XRD.	Chandwadkar, A.J., <i>Mater. Letters</i> , 58 (2004) 1168-1171.
In Situ Formation of Silver Nanoparticles Inside Pore Channels of Ordered Mesoporous Silica	Ag nanoparticles were confined inside the pore channels of MCM-41 by in situ reduction method. The growth of the nanoparticles was clearly restrained by the channels and by UV-vis absorption spectroscopy, the nanoparticle size was estimated at approximately 3 nm.	Zhao, X-G.; Shi, J-L.; Hu, B.; Zhang, L-X.; Hua, Z-L., <i>Mater. Letters</i> , 58 (2004) 2152-2156.