Chem. Mater. **1998,** *10,* 2950−2963

Inclusion Chemistry in Periodic Mesoporous Hosts

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Received April 3, 1998. Revised Manuscript Received July 7, 1998

This review provides an overview of different aspects of inclusion chemistry in ordered mesoporous host materials such as MCM-41 or MCM-48 (Mobil codes). A rich field of inclusion chemistry has been explored in this context, including sorption, ion exchange, imbibition followed by reduction, grafting of reactive metal alkoxides, halides etc., grafting of silane coupling agents (sometimes followed by subsequent reactions), grafting of reactive metal complexes, and polymerization in the channels. Finally, co-condensation of reactive species during the mesopore synthesis is a method to incorporate functionality into the walls of the channel system. Important applications of these modified and functionalized systems are heterogeneous catalysis and photocatalysis involving bulky grafted catalysts and/or the conversion of large substrates. Other potential applications include ion exchange and separations, removal of heavy metals, chromatography, stabilization of quantum wires, stabilization of dyes, and polymer composites.

1. Introduction

A new era in inclusion chemistry began with the discovery of periodic mesoporous materials by Beck et al. in 1992.[1] The narrow, controlled pore size distribution in the ordered hexagonal MCM-41 and cubic MCM-48 materials (Mobil codes) and the large pore openings have added a new dimension to intrapore chemistry that had previously focused on microporous zeolitic materials. This discovery has stimulated research in areas that include fundamental studies of sorption and phase transitions in confined spaces, ion exchange, the formation of intrachannel metal, metal oxide, and semiconductor clusters, and inclusion of various metal complexes and other guests. It is interesting to note that a process for the formation of “low-bulk density silica” had been patented by Chiola et al. in 1971.[2] In this process tetraethyl orthosilicate (TEOS) is hydrolyzed in the presence of cationic surfactants. Although the aforementioned patent does not describe the porosity or periodicity of the resulting materials, Di Renzo et al.[3] showed recently that the reaction products are similar to MCM-41. Another related family of mesoporous compounds has been explored by Kuroda et al.,[4] who showed that ion exchange of the layered polysilicate Na^+ kanemite with alkyltrimethylammonium ions, followed by calcination, gives a hexagonal mesoporous material.

The internal surface reactivity of the mesoporous hosts has been utilized by covalently anchoring a number of functional groups to the channel walls, including attachment of ligands that are used for the formation of bulky metal complexes. An alternative approach to grafting the mesoporous internal walls is beginning to develop; that is, co-condensation of framework precursors with metal sources that are covalently bound to a functional group. Finally, intrachannel reactions even include polymerization of preadsorbed monomers, thus leading to confined filaments of common polymers as well as conducting materials such as carbon.

Intriguing applications of these systems include catalysis with large substrate molecules, formation of novel nanocomposites, and separation.

2. Review of Inclusion Chemistry

An overview of inclusion chemistry in periodic mesoporous hosts, including literature until early 1998, will be provided in this review, according to the following subject headings: (1) sorption and phase transitions; (2) ion exchange and complexation; (3) metal and semiconductor clusters and wires; (4) oxide and sulfide clusters; (5) inclusion of metal complexes and other guests; (6) covalent grafting of ligands and functional groups; (7) hybrid materials obtained by in situ co-condensation; and (8) polymerization in mesoporous channels.

2.1. Sorption and Phase Transitions. With the invention of mesoporous MCM structures with defined, yet variable pore sizes it has become possible to study the physical properties of adsorbates in confined spaces as a function of pore size, including fundamental subjects such as the process of nucleation and crystallization of ice. Baker et al.[5] studied this process with porous silicas and ordered aluminosilicates in which the water crystallized in a hybrid form having cubic as well as hexagonal characteristics of ice. A behavior of “frustrated nucleation” was observed in the pores of MCM. Very gradual freezing was found by Morishige et al.[6] when studying the crystallization in MCMs with a pore size of 24 Å. However, MCM hosts with 42 Å pores gave rise to abrupt freezing and crystallization into cubic ice at the drastically reduced freezing point of 232 K.

The adsorption of the mono- and diatomic gases Ar, N_2, and O_2, as well as ethene and CO_2, was studied as

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10.1021/cm980243e CCC: $15.00

a function of temperature in MCM hosts with four different pore radii ranging between 12 and 21 Å. The capillary critical temperature was far below the bulk critical temperature, and depended on the ratio of the molecular diameter to the pore radius.[7] The capillary melting of methane in the channels of MCM-41, when studied with neutron inelastic scattering, showed similar deviations from bulk behavior. Here, the rotational melting is observed 10 degrees above the bulk value, whereas translational melting occurs 30 degrees below the bulk melting point.[8]

The hexagonal arrangement of the pore system in MCM-41 gives rise to an X-ray diffraction (XRD) pattern of at least five diffraction peaks in high quality samples. However, as demonstrated by Marler et al.,[9] the intensity of these peaks is not necessarily an indication of the order of the hexagonal arrangement in these materials. They reported on the inclusion of different sorbates such as bromoform into the channels of boron-containing B−MCM-41 to show that inclusion compounds with X-ray scattering power similar to that of the matrix may even result in complete extinction of XRD reflections. Peak intensity was nearly fully regained after removal of these sorbates.

2.2. Ion Exchange and Complexation. Large pore MCM supports are of great interest for numerous catalytic applications, some of which require the introduction of accessible ions into the pores. Ion exchange has long been studied for the microporous zeolite family and is now extended toward aluminum-containing and other MCM materials with charged walls.

Nickel. Nickel(II) ions have been intoduced by liquid ion exchange and via a solid-state reaction into MCM hosts by Kevan et al.[10] to generate Ni(I) species. The reduction of these ions to Ni(I) was afforded by thermal, hydrogen reduction, or by gamma irradiation in Al−MCM-41 when the ions were introduced from the liquid phase. Ni(II) was also introduced into the synthesis mixture, and the different Ni-containing mesoporous materials were compared in their activity to catalyze ethylene dimerization.[11] The activity decreased in the order Ni−MCM-41 (Ni in synthesis mixture) > Ni−AlMCM-41 > Ni−MCM-41 (both containing Ni from ion exchange), which was correlated with the concentration of catalytically active Ni(I) species.

Copper. Kevan and co-workers[12] further studied the copper-exchange capacity of different mesoporous materials. The ion-exchange capacity of aluminosilicate MCM-41 for copper(II) was highest when compared to zeolite Y, alumina, and MCM with extraframework aluminum and was found to be correlated with the concentration of tetrahedral aluminum in the framework.[12] In aluminosilicate MCM-41, the cupric ion remained coordinated to the framework upon adsorption and adduct formation with small ligands such as water, methanol, or ammonia. In contrast, large ligands, such as pyridine, did not coordinate with the copper, suggesting that it was located within the MCM walls.[13] In siliceous MCM-41, the ion-exchanged copper was removed from its ion-exchange sites upon adsorption of polar ligands such as methanol or pyridine that could form coordination complexes. In contrast, adsorbates such as ethylene and benzene only distorted the copper location upon adduct formation but did not remove the cations from their framework oxygen coordination.[14] Similarly, complex formation with Cu(II) was observed with water (with a distorted octahedral coordination) and ammonia in siliceous MCM-41, whereas in aluminosilicate-MCM, square-pyramidal coordination took place with the cation still attached to the MCM walls.[15]

Other Ions. Al−MCM-41 was ion exchanged with Na^+, K^+, Ca^{2+}, and Y^{3+}. Thermal treatment with water-saturated oxygen gas at different temperatures resulted in highly thermally stable materials that exceeded the stability of nonexchanged Al−MCM-41.[16]

Cesium in the form of CsCl and cesium acetate was introduced into Al−MCM-41 by ion exchange and studied in base-catalyzed Knoevenagel condensation and acid-catalyzed acetalization and aldol condensation.[17]

An alternative route to the commonly used ion exchange has been explored by "planting" cations into siliceous MCM-41. In this case, Mn(II) cations are introduced through partial ion exchange for the template ions into the as-synthesized MCM host. Subsequent calcination in air results in Mn^{2+}-containing MCM-41. This method allows one to vary the Mn^{2+} concentration over a wide range without loss of crystallinity.[18]

2.3. Metal and Semiconductor Clusters and Wires. High surface area inorganic supports have a long history of applications in heterogeneous catalysis. Crystalline zeolites have been widely used as stabilizing matrix for the preparation of highly dispersed metal particles. Their microporosity and molecular sieving behavior can provide selectivity in reactions involving small molecules. If reactions involving larger molecules or absence of shape selectivity are desired, large pore hosts are more appropriate supports. Thus, known pathways for the preparation of small metal clusters have been adapted for mesoporous supports.

Platinum. Conventional ion-exchange routes, including the exchange with $Pt(NH_3)_4^{2+}$ and subsequent activation in oxygen followed by reduction in hydrogen was described by Ryoo et al.,[19] who aimed to create small platinum particles supported in MCM-41. The resulting clusters showed a high catalytic activity for the hydrogenolysis of ethane. The authors grew platinum clusters and wires inside of the channels of MCM-41, MCM-48, and KIT-1 (a less ordered analog) through consecutive ion exchange, impregnation, and reduction of Pt^{2+} to image the internal morphology and dimensionality with transmission electron microscopy (TEM).[20,21] A variety of pathways, such as incipient wetness, ion exchange, or direct introduction of a Pt-salt in the synthesis mixture were used by Schüth et al.[22] for the introduction of platinum into MCM-41. These authors studied the catalytic activity of these catalysts in the low-temperature CO oxidation.[22]

Corma et al.[23] compared the catalytic activity of platinum supported on MCM-41 for the hydrogenation of aromatics with the activity of platinum on amorphous supports such as alumina and silica as well as in zeolite USY (ultrastable Y; faujasite structure). The highest dispersion, overall hydrogenation activity, and sulfur tolerance was found for Pt in MCM-41, but the highest turnover number was observed in USY, which also contains strong Bronsted sites.

Palladium. The catalytic activity of small palladium clusters supported on MCM materials was tested in several reactions. Schüth et al.[24] used a novel method to support monodispersed, preformed Pt clusters on MCM-41. The clusters were synthesized by reduction of Pd(II) acetate in the presence of stabilizing phenantroline ligands, and the clusters with seven and eight-shells of Pd, Pd7/8(phen), were isolated. These clusters were subsequently incorporated into the MCM-41 channels either directly during synthesis of the support or by incipient wetness impregnation into the calcined host from a water/pyridine mixture. The clusters introduced in situ were converted into PdO particles during template removal through calcination at 873 K. However, the clusters impregnated in the MCM host remained intact and were significantly more stable than on other supports. They showed a high activity in the oxidation of CO.

Siliceous MCM-41 was also used as support for the preparation of 20−25 Å sized palladium particles.[25] These particles were studied as catalysts for the hydrogenation of hexene and benzene. A high activity for hexene conversion at 298 K was found, but the catalyst was inactive for the selective hydrogenation of benzene.

Other researchers observed a substantial increase in activity with MCM-supported platinum and palladium particles in the complete hydrogenation of naphthalene when compared with catalysts with the same metals on amorphous alumina.[26]

Other Metals. Several other metal and metal-oxide clusters were introduced into mesoporous supports and used in catalysis. For example, the formation of small cobalt clusters was achieved in MCM-41 through the stabilizing effect of the alkylammonium bromide template.[27] The preparation was achieved by direct addition of $CoCl_2$ to the synthesis mixture. This approach did not result in the inclusion of cobalt into the MCM walls, but the presence of the template prevented unwanted sintering of the clusters during calcination or sulfidation. The structure of the MCM-41 host was retained.

Hydrogenation of hexene was tested with bimetallic ruthenium/silver clusters derived from the thermolytic decomposition of a new $[Ag_3Ru_{10}C_2(CO)_{28}Cl]^{2-}$ complex that was adsorbed intact to the MCM walls and characterized by extended X-ray absorption fine structure (EXAFS) spectroscopy and microscopy.[28]

Ruthenium clusters in the presence of alkali and alkaline earth promoters were studied for the synthesis of ammonia on zeolite X, magnesia, and MCM-41.[29] The ammonia synthesis is known to be structure sensitive. Attempts to synthesize Ru clusters with a similar size of 1 nm in all different supports were only successful in zeolite X and magnesia, but not in the mesoporous support where the dispersion was lower. These clusters and the promoters were supported on Si−MCM-41 and magnesia by impregnation with and subsequent decomposition of $Ru_3(CO)_{12}$ clusters. Ruthenium was introduced into zeolite X through ion exchange with the Ru(III)ammine complex salt and converted by reduction in hydrogen.

Metal-containing MCM supports were also claimed in a patent of Pelrine and co-workers[30] for the oligomerization of olefins with respect to the production of lubricants. The authors introduced group VIB metals such as Cr(III) acetate into the pores from aqueous solution. The preparation of the catalysts was completed by subsequent calcination and reduction in CO.[30]

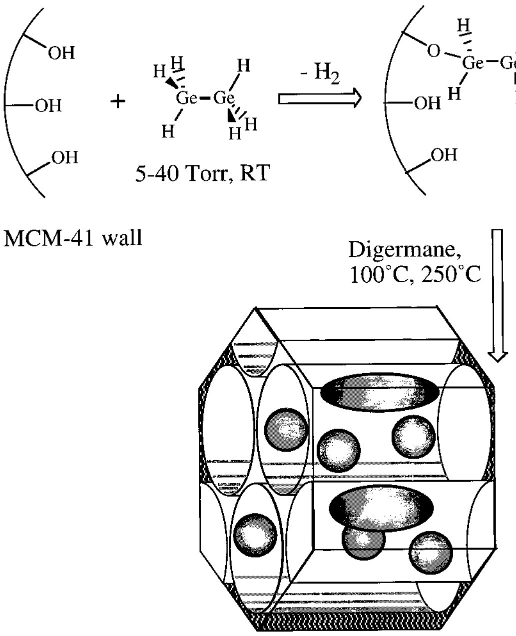

Figure 1. Vapor-phase adsorption of Ge_2H_6 and decomposition to germanium crystallites at elevated temperatures (see ref 31).

Semiconductor Clusters. Small semiconductor particles have attracted great interest due to their photochemical properties and possible applications in electronic and optical devices. To create semiconductor clusters that show variable band gaps as a function of cluster size it is necessary to find an arresting medium for controlled particle growth. Although this approach has been successfully demonstrated with glasses, polymers, and zeolites, mesoporous materials offer a range of accessible pore sizes and channel morphologies that should allow for effective packaging of the guest to form structures resembling semiconductor wires.

Leon et al.[31] have shown that vapor of digermane (Ge_2H_6) can be adsorbed into the MCM channels where it reacts with silanols and is subsequently converted to germanium quantum wires through thermal treatment (see Figure 1). The alignment of these quantum wires with the surrounding host was directly imaged with TEM and electron diffraction of the germanium crystallites. In a similar approach, indium phosphide was deposited in different dielectric hosts by MOCVD (metal-organic chemical vapor deposition). Quantum confinement effects were observed for all composites with hosts including chrysotile asbestos, MCM-41, and $ALPO_4$-5 (an aluminophosphate channel structure).[32]

2.4. Oxide and Sulfide Clusters. *Titanium and Vanadium Oxides.* The photocatalytic activity and electronic properties of small TiO_2 clusters of controlled size are of great interest. One approach to control particle size is to arrest the growth during synthesis in different media, e.g., through application of wet colloidal techniques with stabilizing agents, the growth in glassy matrixes or polymers, and in the cages of zeolites. In a recent investigation, Stein et al.[33] reacted $TiCl_4$ in hexanes with as-synthesized MCM-41, and used the

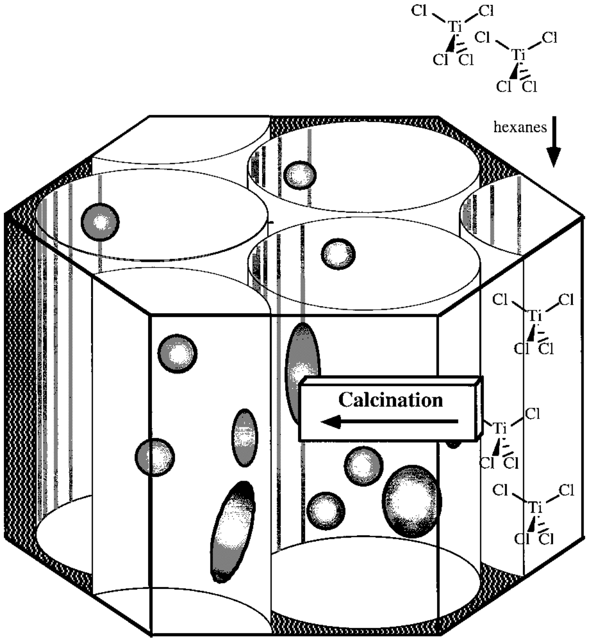

Figure 2. Schematic representation of the introduction of $TiCl_4$ into the as-synthesized MCM-41 and transformation into surface-attached TiO_2 clusters through calcination (see ref 33).

template necessary in the MCM-41 synthesis as stabilizing agent to produce well-dispersed, isolated particles of $(TiO_2)_{30-70}$ supported in the MCM host after calcination in oxygen (see Figure 2). The particles are mainly located within the MCM channels and are grafted to the walls via Si−O−Ti bonds. These grafted particles showed catalytic activity for photobleaching of rhodamine-6G.

The photocatalytic degradation of aqueous acetophenone was studied on TiO_2-loaded zeolites A, X, Y and on Al−MCM-41, and was found to be most effective at small titanium loadings in the mesoporous support. Maximum photoactivity was found with $<3\%$ TiO_2 in aluminum-rich MCM. Selective doping through incorporation of Fe, Mn, or V into the MCM framework suppressed the catalytic activity.[34]

Titanium (IV) grafted into MCM-41 and MCM-48 was studied in the peroxidative bromination reaction of phenol red in aqueous solution or in organic solvents. This report is the first of a functional biomimic of haloperoxidase enzymes that performs well under comparable reaction conditions.[35]

Titanium ions incorporated into the walls of MCM hosts were studied by Kevan et al.[36] as reactive centers for the attachment and stabilization of vanadium species. Vanadium imbibed from vanadyl sulfate solution into pure MCM-41 or Al−MCM-41 formed only mobile VO^{2+} ions. However, with Ti−MCM or Zr−MCM hosts, immobilized square-pyramidal VO^{2+} and tetrahedral V^{5+} species were observed at low loadings. These species were completely converted to tetrahedral V^{5+} upon calcination in air.[36] In a later Raman investigation, the structure of the V^{5+} species in siliceous MCM was determined to be isolated tetrahedral vanadate with three Si−O−V and one terminal V═O bond. In contrast, the terminal bond was not observed in the Ti-implanted MCM hosts at low loadings of vanadium. At higher loadings polymeric V−O−V species were observed.[37]

Manganese, Cobalt, and Molybdenum Oxides in Oxidation Catalysis. The reactivity of the numerous silanol groups lining the walls of siliceous MCM-41 was shown to be sufficient for anchoring the manganese carbonyl complex $Mn_2(CO)_{10}$.[38] Subsequent heat treatment in air converted this grafted complex to manganese-oxo species, which were used in the total oxidation of propene to CO_2. However, when the MCM silanol groups were passivated with Me_3SiCl prior to the adsorption of the manganese complex, the carbonyl complex did not react with the host.

The impregnation of MCM-41 with cobalt and molybdenum salts was performed to prepare catalysts for the oxidation of cyclooctene and aniline[39] as well as for hydrodesulfurization reactions.[40] The pores of a three-dimensional, less ordered analogue of MCM-41, KIT-1, could be coated homogeneously with a monolayer of MoO_3 or with small crystallites of NiO. These materials showed higher hydrodesulfurization activities than similarly treated MCM-41 or NaY zeolites.[41]

Iron Oxide. The preparation of small amounts of iron oxide semiconductor clusters in MCM-41 was reported; here the metal was introduced via incipient wetness with aqueous iron(III) nitrate into the calcined host.[42] Subsequent drying under reduced pressure resulted in small oxide particles that were indirectly imaged with TEM after being decorated with platinum via photodeposition from a $PtCl_6^{2-}$ solution. An increase in the band gap from 2.1 eV in bulk iron oxide to 4.1 eV in these Fe_2O_3 nanoparticles was measured.

The formation of semiconductor nanoparticles stabilized in MCM hosts was also achieved by in situ synthesis. In contrast to the postsynthesis modification already described, the precursors of the nanoclusters were introduced through the stabilizing effect of the template during MCM synthesis, thus incorporating tetraphenylporphine, ferrocene, or ultrafine gold particles.[43] Calcination of the ferrocene-containing host resulted in Fe_2O_3 nanoclusters with an excitonic absorption at 310 nm.

Cesium−Lanthanum Oxides. While acid catalysis represents a major application of zeolites, base catalysis has received much less attention. The introduction of basic functionalities into MCM hosts was achieved by Kloetstra et al.[44,45] through impregnation of aluminosilicate MCM-41 with cesium acetate alone or with additional lanthanum nitrate, and the resulting materials were studied in a number of catalytic reactions. Calcination following impregnation resulted in the formation of cesium oxide or cesium−lanthanum mixed oxide clusters. The isomerization of phenylalkanals to phenylalkyl ketones was studied with Al−MCM, MCM, and amorphous supports. Similarly, the Michael addition of ethyl cyanoacetate to ethyl acrylate and the Knoevenagel addition of enolates to benzaldehyde was described in detail with respect to the oxide composition in the MCM host and with respect to additional alkali metal−lanthanum oxides.[46]

2.5. Inclusion of Metal Complexes and Other Guests. *Chelate Complexes and Catalysis.* The large pore sizes of the MCM materials offer many opportunities for the inclusion of even large transition metal complexes. Although the intrapore surface is not as ordered as that of the classical crystalline zeolites, many

MCM materials present smooth silicate or other metal oxide surfaces with fairly well-defined hydroxyl group environments. The fact that much of the surface is protected from abrasion (and biodegradation) inside the pores as well as the enormous surface area make these materials very interesting candidates for solid catalyst supports. The following sections will discuss different strategies for the incorporation of complexes and other catalysts into the pore systems.

Copper pyridine complexes were introduced into MCM-41 by ion exchange.[47] Electron spin resonance (ESR) was used to elucidate the structure in the host, and isolated complexes as well as agglomerates of complexes were found. Impregnation was the method of choice to introduce the Jacobsen catalyst, a chiral manganese(III)salen complex, (*R*,*R*)-(−)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexane-diaminomanganese chloride into the channels of mesoporous silicates.[48] The catalyst is thought to be bound to the host through hydrogen bonding. The complex retained its catalytic activity and selectivity for olefin epoxidation after adsorption into the host, however, the study just mentioned did not exclude the possibility of leaching of much of the complex into solution under the aqueous reaction conditions.

Phthalocyanine (PC) complexes were included into MCM-type hosts directly during the synthesis by addition of PC to the synthesis gel of the mesoporous metal oxides V_2O_5, MoO_3, WO_3, and SiO_2.[49] A similar approach was used for the inclusion of zinc PC and rhodamine B in Ti−MCM-41.[50] In this case, the hexagonal structure of MCM was formed under inclusion of the PC complex in the surfactant micelles, but titanium was found to reside both tetrahedrally coordinated within the lattice and externally in the form of rutile particles. Although the Zn−PC is believed to reside in the form of monomers in the template micelles, rhodamine B is assumed to aggregate on the external surface (see Figure 3).

In extending the range of metal chelate complexes in MCM-41, iron(II)-phenanthroline[51] and iron(II)-8-quinolinol[52] were supported in the mesoporous host and were found to be active with respect to the hydroxylation of phenol using H_2O_2. As in the case of the supported Jacobsen catalyst already mentioned, leaching of the iron complexes cannot be excluded. Manganese bipyridine $[Mn(bpy)_2]^{2+}$ was immobilized on Al−MCM-41[53] where it showed a superior activity for styrene oxidation compared with homogeneous catalysis. Oxidation products in MCM included the epoxide, diol, and aldehyde. The immobilized catalyst showed no significant loss of activity when recycled, suggesting that leaching into solution was minimal.

A complexation method was used to introduce copper(II) ions into the channels of siliceous MCM-41. The surfactant macrobicyclic cage compound 5-dodecyl-12,17-dimethyl-1,5,9,12,17-pentaazobicyclo[7.5.5]nonadecane (C_{12}CESTO), which can complex the Cu(II) ions and can form micelles with the MCM template, was used as the shuttle.[54] The state of the ions was followed with electron paramagnetic resonance (EPR) in the gel, during calcination and dehydration. Adsorption studies with ammonia and deuterated water indicated that the cations behave in a manner similar to copper introduced uncomplexed during the synthesis and that they are located in the channels of MCM-41.

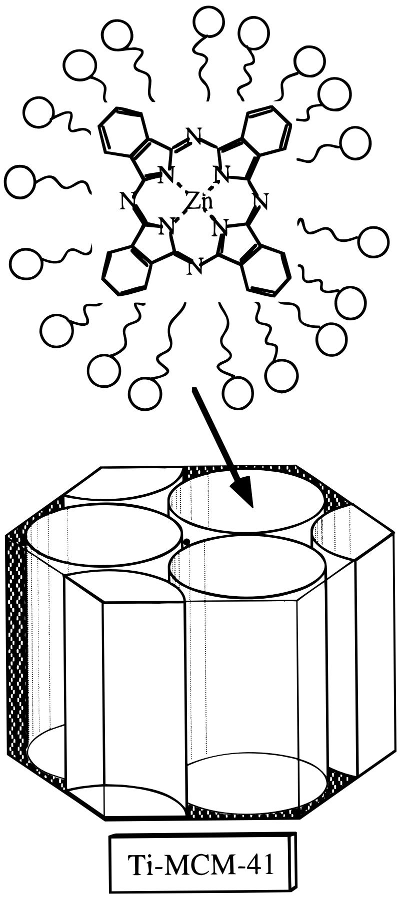

Figure 3. In situ micelle-assisted incorporation of Zn-phthalocyanine during MCM synthesis (as in ref 50).

Heteropolyacids. Soon after the invention of the mesoporous MCM materials, their large channels were recognized to be attractive spaces for the support of bulky catalyst species and for the conversion of large molecules. Kresge et al.[55] filed a patent describing the support of heteropoly acids (HPA), such as phosphotungstic acid, in MCM materials and their application in acid catalysis, such as the isomerization of paraffins and the alkylation of aromatics. In related work, van Bekkum et al.[56] described the preparation of the HPA $H_3PW_{12}O_{40}$ on siliceous MCM-41 with loadings of up to 50 wt %. The structure of the Keggin ion was retained during this process and the supported catalyst showed a higher activity for alkylation of butylphenol by isobutene and styrene than sulfuric acid or the bulk Keggin ion by itself. In a later publication, the impregnation of the same HPA was performed either from aqueous or methanolic solutions on amorphous or MCM supports.[57] Two phases were obtained from aqueous solution, the original Keggin ion as well as a larger W_{18} or W_{21} ion, whereas only the original W_{12} Keggin structure was obtained from alcoholic solutions. However, in the trans-de-*tert*-butylation of 2,6-di-*tert*-butyl-4-methylphenol, the larger ion was eight times more active than the supported original HPA.

Finally, $H_4SiW_{12}O_{40}$ was supported on siliceous and aluminosilicate MCM at loading levels of up to 50 wt %, without forming a bulk crystalline phase. Again,

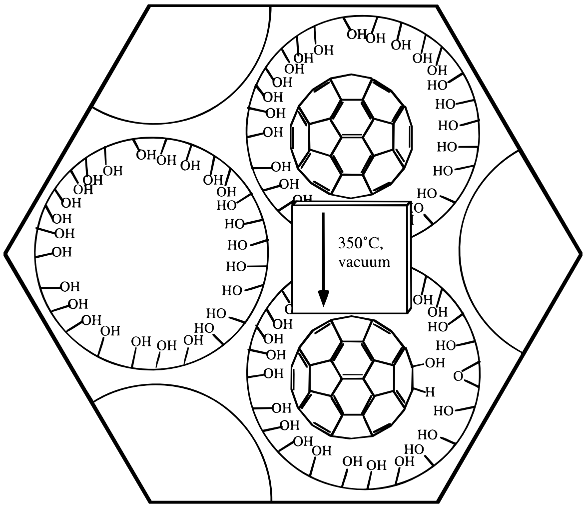

Figure 4. Schematics of fullerene inclusion and hydration at elevated temperature in the MCM channels (ref 61).

catalysts performed better than their parent bulk materials in the esterification of acetic acid by BuOH.[58]

Enzymes. The uniform hexagonal arrangement of the large channels in MCM-41 has stimulated the idea of applying these channels as ordering matrix for small proteins. Because the growth of suitable protein crystals for structural analysis with XRD is usually difficult, the prospects of aligning them into a crystalline array were discussed.[59]

Actual immobilization of different enzymes in MCM-41 was performed by Balkus et al.[60] The goal of the latter study was to enhance stability while exploiting the catalytic activity of these hybrids. Enzymes with increasing dimensions, from cytochrome C, to papain, to trypsin were adsorbed into siliceous MCM-41 with 40 Å channels. The authors observed a correlation between enzyme size and uptake, the loading efficiency being highest for cytochrome C. The larger peroxidase molecules were not retained by the MCM-41 support. Leaching of trypsin from the host was prevented by narrowing the pore size after adsorption through silanation. The entrapped enzyme still showed catalytic activity in the hydrolysis of *N*-α-benzoyl-DL-arginine-4-nitroanilide (BAPNA), although to a lesser extent than with other immobilization techniques.

Fullerene Guests. In several recent studies, the large pores of MCM hosts were used to house the bulky fullerene molecules. Possible interactions between this unique form of carbon and the MCM channel walls were of particular interest. The interaction of the C_{60} molecules with the surface hydroxyl groups of the MCM-41 host under heating was followed in an IR study.[61] It is believed that the fullerenes strip the hydroxyls from the silica surface to form C−OH and C−H groups (see Figure 4).

Changes in the optical properties of a C_{60}/MCM composite gave further indication of a strong interaction between host and guest.[62] Intense photoluminescence at 642 nm from confined C_{60} as well as an emission at 484 nm were observed; the latter was associated with passivation of the silica with C_{60}. MCM materials with different pores sizes (17 and 26 Å) were used as hosts for fullerene inclusion via sublimation.[63] The observed quantum size effects in the electronic and magnetic properties of these composites were associated with the spatial confinement.

Photochemical Processes and Radical Probes. The versatility of mesoporous MCM hosts and microporous zeolites for the presentation of confined reaction spaces has been demonstrated in numerous interesting photochemical studies. Furthermore, drastic variations in the acidic or basic properties of these hosts can be achieved through ion exchange or changes in lattice compositions, and the resulting hosts can then be used to stabilize radicals and transient species. Thus, Garcia et al.[64] used a series of alkali cation-exchanged zeolites as well as aluminosilicate MCM-41 for the adsorption of the methyl viologen cation MV^{2+}, and studied the influence of confinement and the charge balancing cation in the zeolites with a number of spectroscopic techniques. Flash photolysis resulted in long-lived radicals $MV^{\cdot+}$, which was taken as evidence that zeolites can behave as single electron donors.

On the other hand, acidic forms of zeolite MCM-22 and of MCM-41 were shown to react as electron acceptors when thianthrene (Th) was adsorbed into these hosts.[65] The radical cation $Th^{\cdot+}$ was formed, but only as long as Bronsted sites were available in the pores. Cation exchange with sodium led to a complete deactivation for radical formation.

The formation of radicals of *meso*-tetraphenylporphyrin (H2TPP) with MCM hosts of different acidity and pore size was studied by Kevan et al.[66] The photo yield for the porphyrin radical formation, induced by irradiation with visible light, increased with increasing pore size and the efficiency increased from Al−MCM-41 < MCM-41 < Ti−MCM-41. The latter sample produced long-lived radicals after 30 min of irradiation at room temperature that showed a decay of only 5% after 48 h.

Triphenylpyrylium (TPP^+) and dibenzotropylium (DT^+) cations were encapsulated in zeolite Y and MCM-41 and tested as photosensitizers in the dimerization of cyclohexadiene. The reaction was much faster in MCM-41 compared with zeolite Y, probably because of reduced diffusion limitations.[67] In another photochemical study in MCM-41, the rate constants for the luminescence quenching of fluoranthene by molecular oxygen were evaluated.[68]

The photosensitizer cation TPP^+ was either ion exchanged into MCM-41 or was synthesized within its channels from chalcone and acetophenone by Garcia et al.[69] The sensitizer was four times more effective in the *cis*-stilbene isomerization than its tetrafluoroborate salt in solution. The photophysics of TPP^+ and other tritylium ions was also studied in comparison with zeolite inclusions.[70] A strong enhancement of emission intensity was observed for TPP^+ in MCM-41 compared with the zeolite hosts. The stepwise synthesis of a series of different dye molecules, including tris(4-methoxyphenyl)methylium and malachite green in MCM-41 was reported.[71] These were derived from substituted triarylmethylium cations in zeolitic and in mesoporous hosts, using the corresponding benzaldehyde and *N*,*N*-dimethylaniline or anisole. The encapsulated dyes were active as photosensitizers for the dimerization of 1,3-cyclohexadiene.

In a novel approach, a spin probe technique was used to investigate the organization of the templating agent

Table 1. Overview of Surface Attachment Methods using Silane-Coupling Agents

author, year	coupling agent	*R′*; secondary reaction	reactivity
Pinnavaia, 1997[78]	$(RO)_3Si(CH_2)_3SH$		Hg
Liu, 1997[79]	$(RO)_3Si(CH_2)_3SH$		Hg
Brunel, 1997[80]	$(RO)_3Si(CH_2)_3{-}R'$	NH_2 Cl + piperidine	esterification of glycerol
Brunel, 1995[81]	$(RO)_3Si(CH_2)_3{-}R'$	Cl + Pyr $NH(CH_2)_2NH_2$ + Pyr NHC(O)N−Salpr	
Brunel, 1996[82]	$(RO)_3Si(CH_2)_3Cl$	+ Schiff base Salpr + Mn(II)	
Jacobs, 1997[84]	$(RO)_3Si(CH_2)_3{-}OCH_2CH(O)CH_2$	+ TACN + Mn(II)	olefin epoxidation
Jacobs, 1997[85]	$(RO)_3Si(CH_2)_3{-}OCH_2CH(O)CH_2$	+ TBD	base-catalyzed reactions
Balkus, 1997[86]	$(RO)_3Si(CH_2)_3R'$	ethylenediamine, diethylene triamine, ethylenediamine triacetic acid + Co(II)	+ Co−O adducts
Che, 1997[87]	$(RO)_3Si{-}(CH_2)_3NH_2$	+ [RuL(CO)-EtOH], L = porphyrin	alkene oxidation
O'Hare, 1997[88]	$[Fe\{(C_5H_4)_2SiMe_2\}]$		I_2

in the formation of MCM-41.[72] Thus, EPR studies were performed with the spin probe 4-(*N*,*N*-dimethyl-N-hexadecyl)ammonium-2,2,6,6-tetramethylpiperidinyloxy iodide, solvated in the surfactant domain during the formation of MCM-41, to elucidate the reaction progress from gel to final hexagonal array. The evidence showed that the micelles in the initial reaction mixture serve as precursors in the formation of MCM. After addition of TEOS (tetraethyl orthosilicate), the initial micelles transform into clusters of rodlike micelles surrounded by silicate ions that finally transform into the ordered hexagonal structures through condensation reactions. Hexagonal long-range order is already present after a few minutes following mixing, whereas silicate polymerization is much slower. No intermediate phase was observed upon MCM-41 formation, whereas the transformation to lamellar MCM-50 evolves through several stages.

2.6. Covalent Grafting of Ligands and Functional Groups. Large surface area materials, including amorphous metal oxides or crystalline alumosilicate zeolites, have a long and successful history as supports in catalysis and separations. In addition to acting as hosts for guest molecules through ion exchange or sorption, these materials present hydroxyl-covered surfaces that have been exposed to reactive silane coupling agents to tailor surface properties. These silanes may include functional groups or may be the intermediate for further attachments. Zeolites present some limitations in this regard due to their smaller pore sizes. Large pore MCM materials can now bridge the gap between crystalline microporous zeolites to the open amorphous supports. Thus, coupling agents with small or bulky functional sections can be grafted to MCM hosts, while still leaving enough pore volume for chemical reactions on their internal surface.

The versatility of the MCM materials for surface chemistry was recognized in two patents shortly after their invention. Thus, the silanol groups of the mesoporous supports were functionalized with main group and transition metal halides, hydrides, alkoxides, or acetates for applications in sorption and catalysis,[73] as well as for sensing through the addition of detecting components to the pore walls.[74]

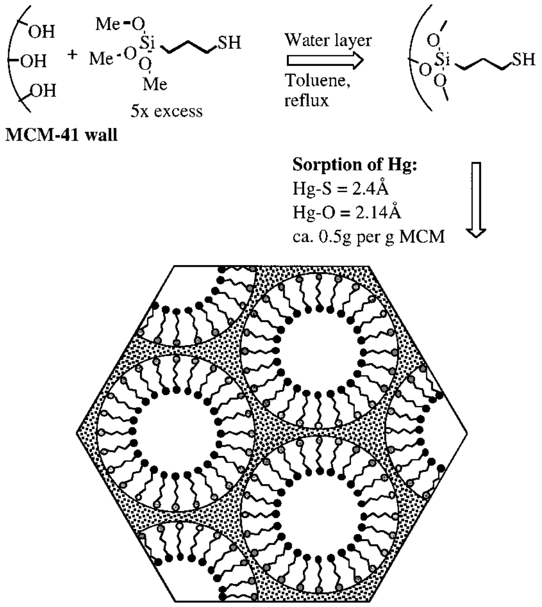

Figure 5. Grafting of a monolayer of thiol functionalities in MCM pores, prepared for the sorption of heavy metals (see ref 79). The coordination environment of adsorbed mercury is shown.

Coupling of Functional Silanes and Their Use in Complex Anchoring. Several detailed reports have recently been published in the open literature describing MCM surface modifications (see Table 1). A comprehensive study deals with the surface chemistry of siliceous MCM-41.[75] Three different types of surface silanols (e.g., single, hydrogen bonded, and geminal hydroxyls) were found, of which only the single and geminal hydroxyl groups were shown to be reactive toward chlorotrimethylsilane. The adsorption properties of trimethylsilylated MCM-41 for water and benzene were studied.[76] This reactivity toward surface silylation with trimethylsilyl groups was also shown with siliceous MCM-48, MCM-41, and Ti−MCM-41. The stability to moisture and compression was shown to increase for all three supports due to their improved hydrophobicity.[77]

The direct introduction of functionality into MCM-41 through the reaction with tris(methoxy)mercaptopropylsilane was achieved by two independent groups. The attachment of the thiol groups to the internal channels of the siliceous MCM-41 was deduced from the narrowing of the pore size from 36 to 27 Å.[78] In a large-pore Si−MCM-41 with 55 Å pore size, the concentration of thiol groups was varied and reached up to 76% of the full surface coverage (see Figure 5).[79] The SH-moieties were subsequently used in both studies for removing mercury from waste streams. The highly efficient materials were also stable after regeneration by washing with concentrated HCl.

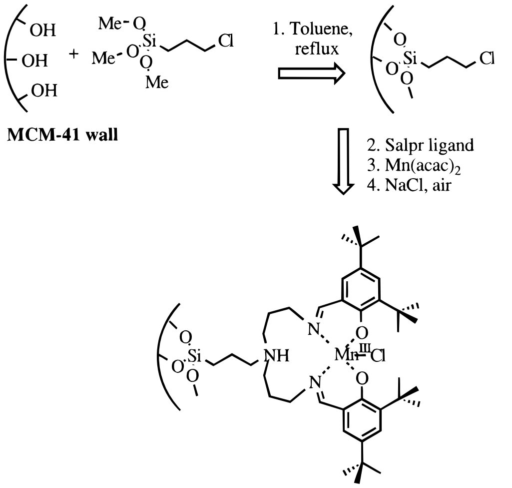

Figure 6. Multiple-step synthesis for the internal attachment of a manganese(III) Schiff-base complex in MCM-41 (see ref 82).

The surface-anchoring of catalytic functionalities into MCM supports by means of silane coupling agents was reported by Brunel and co-workers.[80] They used 3-amino- and 3-chloropropyl-triethoxysilane as intermediates for the grafting of primary and tertiary aminofunctions to MCM-41.[80] The dehydrated mesoporous support was refluxed in toluene containing the respective aminopropyl- or chloropropyl-silane coupling agent. Subsequent exposure of the chloropropyl sample to a solution of piperidine resulted in grafted piperidinopropyl functionalities. These new hybrid mesoporous catalysts showed high regioselectivity in the formation of α-monoglycerides in the epoxide ring-opening reaction of glycidol with fatty acids. The same research group grafted MCM-41 with other functional alkoxysilanes of which some were further reacted in a second step.[81] Thus, the MCM host was first modified with $(RO)_3Si(CH_2)_3X$, with X = Cl, $NH(CH_2)_2NH_2$, and NHC(O)N−Salpr (salpr = 3-[*N*,*N*′-bis-3-(3,5-di-*tert*-butylsalicylidenamino)propyl]amine). The first two functional groups were then further transformed into 2-$(NHCH_2)$Pyr and 4-$(NH(CH_2)_2NHCO)$Pyr.

A similar mechanism was used by Sutra and Brunel to prepare MCM-bonded manganese(III) Schiff-base complexes.[82] Here the MCM-coupled 3-chloropropyltriethoxysilane was used to anchor the pentadentate ligand 3-[*N*,*N*′-bis-3-(3,5-di-*tert*-butylsalicylidenamino)propyl]amine (salpr), which was finally converted into Mn(III)(salpr) complexes by ligand exchange (see Figure 6). An MCM-immobilized chiral amino-alcohol, ephedrine, was used as a catalyst for the enantioselective addition of diethylzinc to benzaldehyde.[83]

Another manganese complex was grafted to the MCM walls through a multiple-step synthesis. First, (3-glycidyloxypropyl)-trimethoxysilane was coupled to the support. The epoxy groups were further reacted with the amine functions of triazacyclononane (TACN) to result in the anchored 2-hydroxyalkyl-substituted TACN (see Figure 7).[84] Manganese complexes of the grafted ligands were shown to be active in the epoxidation of styrene and cyclohexene with hydrogen peroxide.

The epoxide-based grafting of a nitrogen-containing ring was also applied in the preparation of a novel heterogeneous base catalyst. Jacobs and co-workers[85] showed that (3-glycidyloxypropyl)-trimethoxysilane coupled to the MCM-41 support could bind a guanidine-type base such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), resulting in a strongly basic catalyst that was active for Michael additions, Knoevenagel condensations, and nucleophilic epoxidations, often at high selectivity.

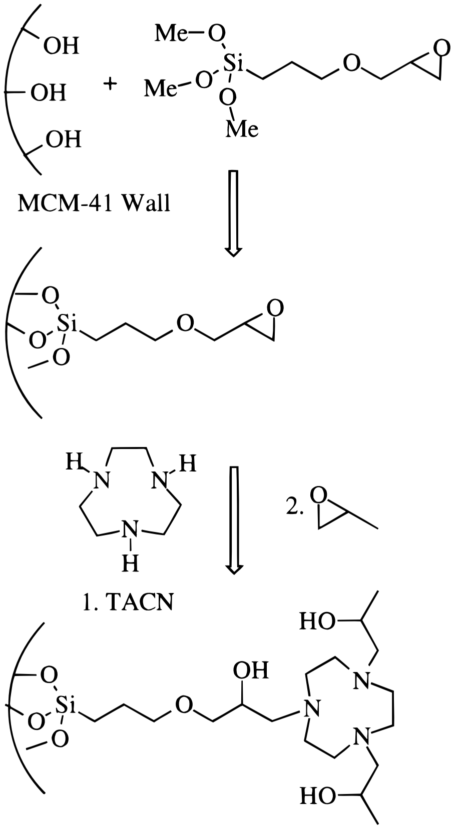

Figure 7. Anchoring of glycidyl functionalities and subsequent transformation into substituted triazacyclononane (TACN) ligands (as in ref 84).

The immobilization of cobalt chelate complexes was performed via methoxysilyl coupling agents functionalized with ethylenediamine (ED), diethylenetriamine (DET), and ethylenediaminetriacetic acid salt (EDT).[86] These complexes were subsequently reacted with Co(II), and the resulting materials showed some reactivity toward oxygen adduct formation with grafted ED and DET (see Figure 8). A similar approach was used by Che et al.[87] when they reacted 3-aminopropyl-triethoxysilane with the MCM to ultimately graft [Ru(II)*meso*-tetrakis(4-chlorophenyl)porphyrin]. Attachment of the porphyrin complex is attributed to the exchange of an ethanol ligand on the precursor porphyrin complex with the amino group on the coupling agent. The complex showed good catalytic activity for alkene oxidations with *tert*-butyl hydroxyperoxide.

Ferrocenyl groups were attached to the walls of MCM-41 by O'Hare and co-workers[88] in a one-step reaction via ring opening of (1,1′-ferrocenediyl)dimethylsilane. The grafted complex was readily accessible as indicated by immediate oxidation with iodine vapor. The samples were characterized by EXAFS and solid-state nuclear magnetic resonance spectroscopy (NMR).[88]

Grafting of Metal Complexes. The attachment of guests to the MCM wall can be performed without the

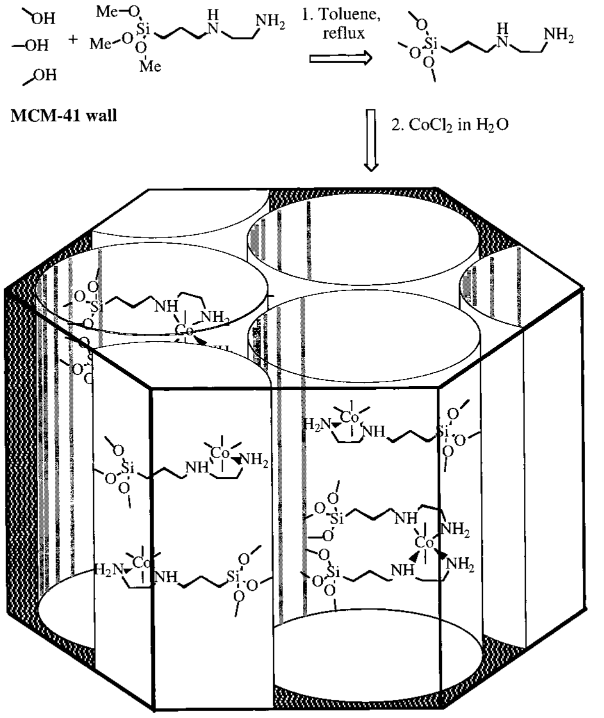

Figure 8. Reaction sequence for the anchoring of amino ligand-based Co(II) chelate complexes into MCM hosts (see ref 86).

use of intermediate silane coupling agents. This is achieved by the direct reaction of surface hydroxyl groups with reactive ligands of the species of interest (see Table 2).

The interaction of $Mo(CO)_6$ with different basic or acidic amorphous surfaces as well as with MCM-41 was studied using temperature-programmed decomposition.[89] It was proposed that the surface reaction is initiated by nucleophilic substitution of CO by surface oxide or hydroxyl groups. The MCM host showed no difference with respect to the desorption behavior when compared with silica.

An irreversible surface attachment of vanadium oxide species to MCM-48, the cubic member in the MCM-family, was achieved by Stucky et al.[90] The $OV(OiPr)_3$ was anchored to the pore walls from an anhydrous hexane solution and subsequently calcined in oxygen. Results of ^{51}V NMR and ultraviolet−visible (UV−vis) spectroscopy revealed that the vanadium oxo species were mainly coordinated to the MCM walls as $(Si-O)_3V=O$ entities.

The attachment of titanocene dichloride via the reactive chloride ligands to MCM-41 was used by Thomas et al.[91] The grafted complex was subsequently converted into Ti-oxo species through calcination in air. In situ EXAFS spectroscopy demonstrated the presence of surface-bound, four-coordinated titanium species that showed a high catalytic activity for the epoxidation of alkenes (see Figure 9). Pretreatment of the mesoporous MCM-41 silica surface with tetrabutylgermanium followed by calcination, prior to grafting with $TiCp_2Cl_2$, yields a mixture of TiOH groups supported on the different surface oxo species.[92] The resulting Ti-centers showed an increase in olefin epoxidation activity. Thomas et al.[93] also reported the surface anchoring of the cobalt complex $[Co_3(\mu_3\text{-}O)(OAc)_5(\mu_2\text{-}OH)(py)_3]PF_6$. The resulting hybrid catalyst was studied in the oxidation of cyclohexane to cyclohexanone and cyclohexanol, and its structure was elucidated with in situ EXAFS spectroscopy. Here, the hydroxyl group of the complex was expected to react with the surface silanols. However, the lifetime of this catalyst was improved when the MCM surface was previously functionalized with Me_2SiCl_2 and $Cl_3Si(CH_2)_3Br$, which was further reacted with glycine to immobilize the catalyst.

To introduce metal species into the channel walls of MCM hosts, ion exchange is not the only method. Thus, anchoring of $AlCl_3$, $SnCl_2$, $Zn(O_2CMe)_2$, or $Mn(O_2CMe)_2$ to the surface of siliceous MCM-41 and subsequent calcination led to metal-implanted mesoporous materials with ion-exchange capacity, high stability, and catalytic activity.[94] Several other researchers have exploited the reactivity of chloride ligands toward hydroxyl groups of the MCM-41 host, here for the heterogenization of the stereospecific catalyst ethylenebis(indenyl) zirconium dichloride (see Figure 10).[95] This catalyst was active for the production of isotactic polypropene when combined with methyl-aluminoxane (MAO). EXAFS studies showed retention of the Zr-indenyl framework, removal of chloride ligands, and methylation of the catalyst, similar to solution reactions. In an alternative approach, a heterogeneous aluminoxane derivative was prepared by in situ hydrolysis of trimethylaluminum in the mesoporous host.[96] Ethylenebis(1-indenyl)dimethylzirconium was reacted with this modified host, and catalytic activity for co-oligomerization of ethene and propene was demonstrated. It was found that the MCM pore size had an effect on the product molecular weight (longer chains were formed in narrow channels).

Anwander et al.[97] grafted lanthanide silylamide precursors via protolytic exchange reactions to the MCM support. In previous work, we introduced the bimetallic $Me_3SnMo(CO)_3Cp$ complex into the MCM-41 pores; this complex was anchored via the oxophilic trimethyl tin component to the mesoporous walls.[98] As demonstrated with EXAFS spectroscopy, small bimetallic clusters were formed upon heating under reduced pressure (see Figure 11).

7. Co-condensation Reactions for the Synthesis of Hybrid Materials. In the previous sections we have shown how MCM hosts have been used in a variety of reactions for the inclusion of catalytically and chemically active guests. Usually, the inclusion reactions are performed after MCM synthesis and template removal. However, it was recently recognized that the co-condensation of siloxane and organosiloxane precursors during MCM formation can result in truly new hybrid materials. This approach is an extension of the widely studied organically modified sol−gel derived materials. The condensation of the MCM walls can proceed already at room temperature, thus allowing even the co-condensation of organic moieties that could not survive the rigorous conditions of the 'classical' hydrothermal synthesis. The resulting hybrid materials offer functional groups that are directly incorporated into the walls of the host, in contrast to those grafted to the surface. Their connectivity can be anticipated as one with [Si]−C bonds reaching out of the walls instead of [Si]−O−Si−C when using grafting methods (where [Si]

Table 2. Overview of Surface Attachment Methods through Reactive Ligands

author, year	metal complex	reactivity
Stucky, 1996[90]	$OV(OiPr)_3$	water
Thomas, 1995[91]	$TiCp_2Cl_2$	epoxidation of alkenes
Oldroyd, 1998[92]	Bu_4Ge, Bu_4Sn; $TiCp_2Cl_2$	epoxidation of alkenes
Maschmeyer, 1997[93]	$[Co_3(\mu_3\text{-}O)(OAc)_5(\mu_2\text{-}OH)(py)_3]PF_6$	oxidation of cyclohexane
Woo, 1996[95a] O'Hare, 1997[95b] O'Hare, 1997[95c]	$Et(ind)_2ZrCl_2$	polymerization of propene
Van Looveren, 1998[96]	trimethylaluminum; $Et(ind)_2ZrMe_2$	co-oligomerization of ethene and propene
Anwander, 1997[97]	$[Nd\{N(SiMe_3)_2\}_3]$	
Bein, 1994[98]	$Me_3SnMo(CO)_3Cp$	
Ryoo, 1997[94]	$AlCl_3$, $SnCl_2$, $Zn(O_2CMe)_2$, or $Mn(O_2CMe)_2$	

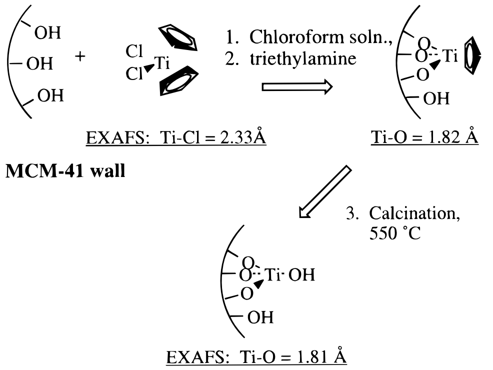

Figure 9. Reaction of titanocene dichloride with the surface silanols of MCM-41, and conversion into a heterogeneous catalyst by calcination (as in ref 91). EXAFS data show the coordination environment of the titanium species.

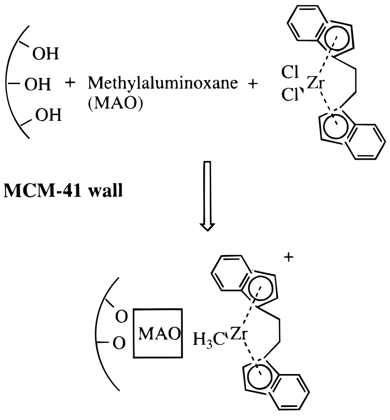

Figure 10. Reaction pathway to a heterogeneous propylene polymerization catalyst based on pretreatment with methylaluminoxane, followed by reaction with ethylenebis(indenyl) zirconium dichloride (as in ref 95).

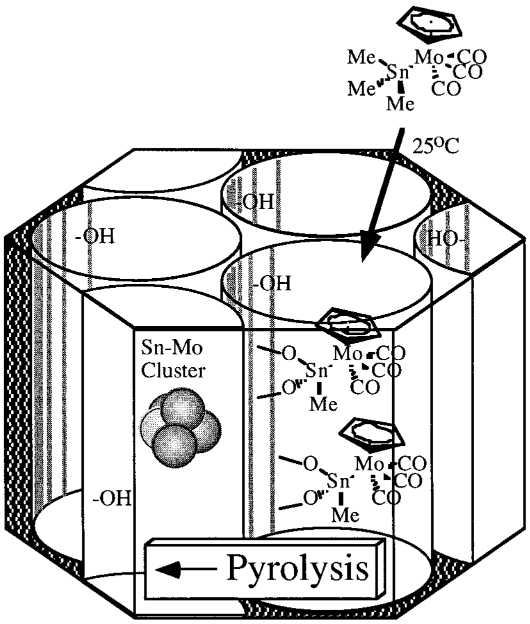

Figure 11. Proposed chemistry of a trimethylstannyl bimetallic complex in the pores of MCM-41. In this reaction, $Me_3SnMo(CO)_3Cp$ was anchored via the trimethyltin moiety to the mesoporous walls (see ref 98).

designates silicon atoms in the wall). This type of bonding should result in greater hydrolytic stability of the hybrid systems (see also Table 3).

Mann and co-workers[99] pioneered the co-condensation route. These workers reacted the silica precursor TEOS with phenyl- and octyl-triethoxysilane in the presence of hexadecyltrimethylammonium bromide template to produce hybrid mesoporous MCM-type systems. Subsequently, Mann et al.[100] extended this approach to a number of functional groups including thiol, amine, epoxide, imidazole, and alkyl-organosiloxanes. Co-condensation of all these groups except octyl-triethoxysilane gave high quality MCM-type materials. The original synthesis of MCM-type materials typically involves removal of the surfactant through calcination. However, the fragility of the organic moieties in the hybrid structures demands extraction of the template at more moderate conditions. Solvent extraction disrupted the structure of some of the hybrid materials, especially at high concentrations of the functional groups.[100] However, Mann's phenyl-, thiol-, and amino-functionalized MCM materials were stable to acid extraction procedures. In a related development, functionalized MCM hosts that are apparently stable to ethanol extraction of the template were prepared by Macquarrie et al.[101] They used neutral surfactant templates together with aminopropyl- and cyanoethyltrialkoxysilanes.

The co-condensation of functional groups showing chemical reactivity was reported by Stein et al.[102] Vinyl functions were incorporated into MCM-41 by co-condensation of TEOS with vinyltriethoxysilane and were shown to be stable to an acid extraction process (see Figure 12). The authors report the complete consumption of the vinyl functional groups, as followed by Fourier transform infrared (FTIR) and NMR spectroscopy, after up to 6 days in the presence of bromine. Stein[103] also reported on the co-condensation of TMOS and mercaptopropyl groups during MCM synthesis; the resulting materials showed significant uptake of mercury, similar to the thio-grafted MCM described by Liu et al.[79] The thiol groups were also oxidized to sulfonic

Table 3. Overview of Lattice Inclusion of Functional Groups in MCM-Type Materials Through Co-condensation

author, year	functional group	stability toward template extraction
Mann, 1996[99]	$\mathrm{(RO)_3Si{-}phenyl}$	yes
	$\mathrm{(RO)_3Si{-}}n\mathrm{{-}octyl}$	no
Slade, 1998[106]	$\mathrm{(RO)_3Si{-}phenyl}$	yes
Mann, 1997[100]	$\mathrm{(RO)_3Si{-}(CH_2)_3SH}$	yes
	$\mathrm{(RO)_3Si{-}(CH_2)_3NH_2}$	yes
	$\mathrm{(RO)_3Si{-}(CH_2)_3OCH_2CH(O)CH_2}$	
	$\mathrm{(RO)_3Si{-}(CH_2)_3imidazole}$	no
	$\mathrm{(RO)_3Si{-}CH_2CH{=}CH_2}$	no
Macquarrie, 1996[101]	$\mathrm{(RO)_3Si{-}(CH_2)_3NH_2}$	yes
Stein, 1997[102]	$\mathrm{(RO)_3Si{-}CH{=}CH_2}$	yes
Stein, 1998[103]	$\mathrm{(RO)_3Si{-}(CH_2)_3SH \rightarrow [Si]{-}(CH_2)_3SO_3H}$	yes
Van Rhijn, 1998[104]	$\mathrm{(RO)_3Si{-}(CH_2)_3SH \rightarrow [Si]{-}(CH_2)_3SO_3H}$	yes
Moller, 1998[107]	$\mathrm{(RO)_3Si{-}(CH_2)_3OC(O)C(CH_3){=}CH_2}$	yes

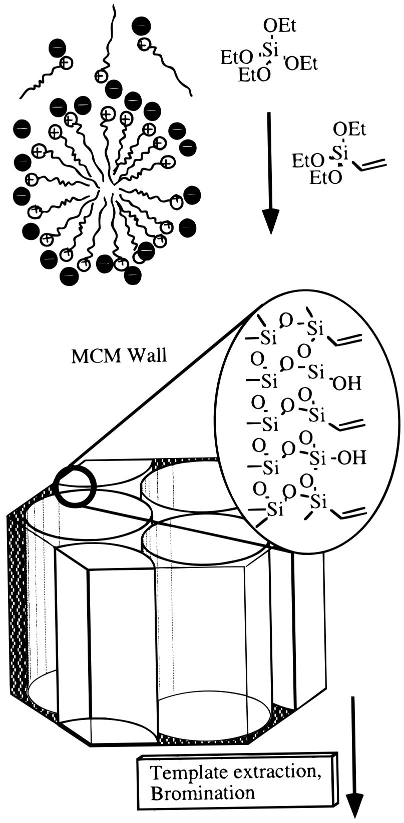

Figure 12. A strategy for introducing functionalities into the MCM wall through co-condensation of silicate precursor and silane coupling agents (see ref 102). In this case, vinyl functions were incorporated by co-condensation of TEOS with vinyltriethoxysilane.

acid groups, thus creating a solid acid with micropores of ~14 Å. This novel hybrid system was active in the conversion of 3,4-dihydro-2*H*-pyran to 2-ethoxytetrahydropyran. In related work, co-condensed thiol functionalities in MCM hosts were oxidized with hydrogen peroxide to give the anchored sulfonic acid groups, and promising activity for acid-catalyzed condensation and polyol esterification reactions was demonstrated.[104]

The co-condensation of phenyltriethoxysilane and/or tetraethyl orthosilicate with dodecylamine as a template at room temperature resulted in mesoporous materials that were reported to protect benzylic positions against radical bromination.[105] Similar co-condensation reactions (phenyltriethoxysilane, TEOS, and cetyltrimethylammonium surfactant) in combination with micelle swelling led to mesoporous phenyl-modified materials when mesitylene was used for swelling, but gave microporous materials when tetradecane or no swelling agent was employed.[106]

In a recent study, we performed the co-condensation of tetramethyl orthosilicate (TMOS) with 3(trimethoxysilyl)propyl methacrylate (TMSiPMA) in the presence of cetyltrimethylammonium chloride to produce a highly ordered functional mesoporous hybrid system.[107] The reactivity of the methacrylate functionality was demonstrated by facile addition of bromine and by copolymerization of methyl methacrylate monomers with the grafted groups.

Ying and co-workers[108] extended the concept of surfactant assembly in the synthesis of new mesoporous materials. Thus, a particular type of co-condensation involving the surfactant itself was presented. The reaction between $\mathrm{Nb(OEt)_5}$ and tetradecylamine gave a niobium complex that on treatment with water resulted in a hexagonal mesostructure similar to MCM-41. After calcination, mesoporous niobium oxide was obtained (see Figure 13).

2.8. Formation of Polymers in Mesoporous Channels. The regular system of large channels in MCM hosts offers unique opportunities for the preparation of new nanostructured composite materials. For example, in combining organic polymers with inorganic fillers, the mechanical strength of the polymers can be greatly enhanced.[109] Amorphous silica particles and to a smaller extent zeolites have been used in polymer composites, but few articles describe the utilization of MCM materials for the preparation of such nanocomposites. It is anticipated that a maximum in interconnectivity between both phases is achieved when using meso- or microporous instead of compact glassy fillers in a polymer matrix. This approach will channel the polymers through the pores and cross-link them around the filler particles.

The feasibility of forming polymer networks within the internal pore structure of porous materials was recently demonstrated. This was achieved through adsorption and subsequent polymerization of monomers in the host. Thus, Llewellyn et al.[110] adsorbed styrene, vinyl acetate, and methyl methacrylate (MMA) into MCM hosts with different pore sizes and studied the effect of confinement on polymer growth. An increase in chain length of PMMA with decreasing pore size of MCM-41 was associated with inhibited termination processes in the channels. In a recent study, we examined the polymerization of MMA in the mesoporous hosts MCM-41 and MCM-48 as well as in the mi-

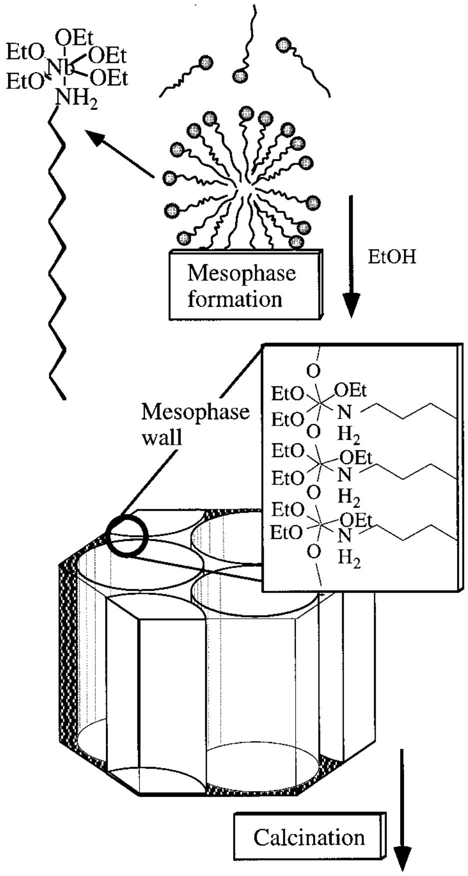

Figure 13. Ligand-assisted templating of a novel transition-metal-containing mesoprous structure: Formation of functionalized micelles and their condensation into a mesoporous niobium oxide molecular sieve (as in ref 108).

croporous channels of zeolites NaY/X and ZSM-5.[111] The monomers were introduced into the dehydrated and evacuated hosts from the vapor phase to avoid the formation of polymer layers on the external surface. Polymerization proceeded via radical initiation with high yield and resulted in nanocomposites with high polymer content. It is not surprising that the polymer dynamics change dramatically in the confinement of the host; on encapsulation, the glass transitions normally found in bulk polymers are suppressed. This result was observed in both the microporous as well as the mesoporous hosts.

In a related study, the adsorption of MMA in MCM-41 was also performed by Aida et al.[112] These authors observed that PMMA grown in the mesoporous channels of MCM-41 can exceed the bulk molecular weight by an order of magnitude; the chain length was controlled by the stoichiometry between the monomer and initiator.

A novel twist to the use of mesoporous hosts was introduced by Mallouk, Ozin, and co-workers.[113] These authors formed a polymer mold of the channel structure of MCM-41, followed by dissolution of the host in HF: Phenol-containing MCM-41 was treated with formaldehyde vapor and HCl gas at elevated temperatures to form a cross-linked phenolic resin. After extraction from the host, polymer mesofibers that can visualize the length of the mesoporous channels were recovered.

Polymers can also be used to carry metals such as iron into the MCM host to serve as ceramic precursors. The ring-opening polymerization of a preadsorbed [1]-silaferrocenophane inside the MCM channel structure led to poly(ferrocenylsilane)-loaded MCM-41 that could serve as precursor to magnetic nanostructures, including small particles of supported metallic iron.[114]

Nanoscale Carbon Wires Stabilized in the MCM-41 Host. As relentless efforts continue to reduce the size of electronic circuitry to reach higher storage density and faster data processing speeds, new concepts are being developed to build electronic circuits from *molecular* components. This strategy could be considered a “bottom up” approach in contrast to the conventional lithographic “top down” methods that are reaching diffraction limits in optical pattern transfer. Based on the presence of directional bonds in organic conducting polymers and their great structural variety, these materials have been prime candidates for the design of molecular electronics components. A review of the inclusion chemistry of conducting materials in inorganic hosts is available.[115]

Graphitic carbon is attractive as a candidate for conductive nanostructures because it is chemically stable and exhibits high conductivity. We have achieved the formation of carbon “wires” in the regular channels of MCM-41 using a precursor polymer.[116] The monomer acrylonitrile was introduced into the host through vapor or solution transfer, and polymerized in the channels by exposure to radical initiators from solution. It was found that long chains of polyacrylonitrile (PAN) had formed in the host (at the order of ~1000 monomers) and were long enough to extend through significant parts of the MCM-41 host.

Pyrolysis of the included polyacrylonitrile led to the formation of carbonized material in the channels of the host material (see Figure 14). The average graphite domain size in the pyrolized PAN−MCM samples was estimated with Raman spectroscopy. The carbon phase in the MCM-41 host is consistently more ordered than in bulk samples treated similarly, showing the important role of the host in structuring the growing graphitic carbon sheets. At pyrolysis temperatures of 1070 and 1270 K, the microwave conductivity of the PAN−MCM composite was ~10 times greater than that of bulk material treated in a similar process. This surprising result was associated with the greater order of the graphitic material in the MCM host.

The preparation of carbon nanotubes from chemical vapor deposition (CVD) reactions of hydrocarbon gas in mesoporous supports was recently described.[117] The phonon properties of the nanotubes were characterized with Raman spectroscopy.

Encapsulation of Polyaniline Filaments in MCM-41. The conducting polymer polyaniline was successfully stabilized in the channels of the aluminosilicate MCM-41.[118] Aniline vapor was diffused into the dehydrated channels of the host at room temperature, followed by immersion into a solution of oxidant. Polyaniline filaments (several hundred aniline units long) in the conducting emeraldine salt form were produced in the channels. The presence of encapsulated polyaniline was confirmed by a large drop in the MCM pore volume. Microwave measurements showed that the polyaniline filaments can still support mobile charge carriers when encapsulated in the nanometer channels.

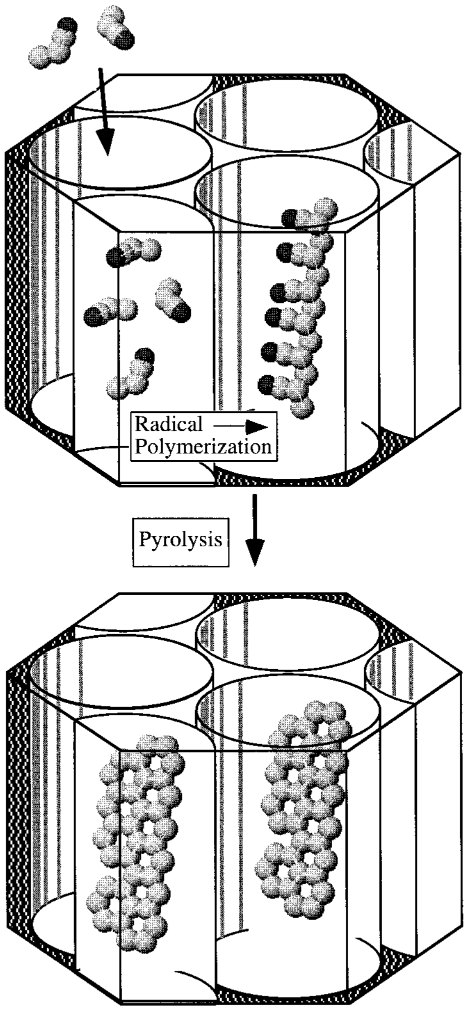

Figure 14. Encapsulation and polymerization of acrylonitrile in MCM hosts and the formation of conducting carbon filaments via pyrolysis (as in ref 116).

In related work, the stabilization of conducting polyaniline filaments in the channels of Cu(II)- or Fe(III)-containing aluminosilicate MCM-41 was demonstrated.[119] Adsorption of aniline vapor into the dehydrated, metal-containing host produced radical cations and/or short oligomers that were subsequently transformed into polyaniline by exposure to oxidant solution under exclusion of air.

3. Summary

This survey of inclusion chemistry in ordered mesoporous host materials gives an impression of the opportunities for creative chemistry in the interior of nanometer-size channels. The mesoporous hosts have been modified by various methods, ranging from adsorption over ion exchange to various grafting techniques using the intrachannel hydroxyls, and finally co-condensation with the walls during synthesis. Most work in this context has focused on the aluminosilicate or siliceous hexagonal MCM-41 materials but recently, additional systems, such as the cubic MCM-48 and transition-metal containing ordered mesoporous materials, have also been explored. A major motivation relates to potential applications in catalysis, including photocatalysis, where the large pores enable the heterogenization and stabilization of numerous catalytic species. The reactant molecules entering the channels can be quite large compared with those entering classical zeolites. Many other applications have been explored, including removal of heavy metals, stabilization of quantum wires and dyes, and polymer composites.

Acknowledgment. The authors gratefully acknowledge funding from the U.S. Department of Energy, Sprague Electric Company, and the German Ministry of Education and Research (BMBF).

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CM980243E