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Reviews

SOMC@PMS. Surface Organometallic Chemistry at Periodic Mesoporous Silica[†]

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Periodic mesoporous silicas (PMSs) give enormous stimulus to the field of nanostructured organic−inorganic composite materials, opening new horizons for selective organic transformations and material science. This article outlines advanced synthetic concepts of their intraporous surface organometallic chemistry involving alkyl, (silyl)amide, and alkoxide reagents. Conclusive methods of characterization, elaborating the importance of spectroscopic probe ligands and nitrogen physisorption, reinforce the excellent capacity of PMS materials as a model support of, for example, amorphous silica. Particular emphasis is placed on tailor-made hybrid materials, highlighting unexpected reaction behavior due to surface and pore confinement. Accordingly, surface silylation as an efficient method for designing the microenvironment is surveyed in detail.

1. Introduction

*S*urface *o*rgano*m*etallic *c*hemistry (SOMC), that is, postsynthetic derivatization of chemically and thermally robust condensed solid materials with molecularly well-defined organometallic compounds,[1−4] has given enormous impetus to the field of organic−inorganic composite materials. Such “supramolecular chemistry” represents a unique approach to generate novel hybrid materials of relevance for catalysis and material science. Prominent examples include organozirconium and organochromium-modified silica/alumina materials shown in Figure 1. The Union Carbide catalyst derived from Cp_2Cr and silica (**A**)[5,6] and silica-supported Ziegler−Natta systems such as $[(C_9H_7)_2C_2H_4]ZrCl_2$/MAO (**B**, MAO = methylalumoxane)[7,8] display industrially applied catalysts for the synthesis of HDPE (high-density polyethylene) and stereoregular polypropylene, respectively. Zirconium hydride surface species (Figure 1, **C**) initially reported by Y. I. Yermakov et al.[9] and J. Schwartz et al.[10] were shown to mediate olefin hydrogenation, isomerization, and polymerization. J.-M. Basset et al., who coined the term SOMC,[1e,11] further optimized the latter system and found novel, unexpected reaction pathways such as the depolymerization of polyolefins.[12]

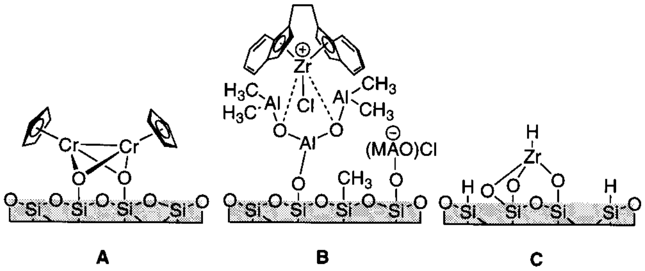

Figure 1. Highly reactive surface species obtained via SOMC on silica.

Organometallic chemistry in confined spaces adds a new dimension to SOMC as verified by highly efficient nanovessel reactors and quantum-confined materials.[3,4,13] Because of their intriguing structural and chemical features, semicrystalline periodic mesoporous silicas (PMSs) of the M41S[14] and SBA[15] families are discussed as one of the most attractive host materials. Their intrinsic zeolite-like pore architecture with tunable pore sizes and narrow pore size distributions provides a unique platform for studying the grafting of highly reactive organometallic compounds. Surface areas as high as 1500 $m^2\ g^{-1}$ and uniformly arranged mesopores (pore volumes as high as 3 $cm^3\ g^{-1}$) ensure both a higher guest loading and a more detailed characterization by means of nitrogen adsorption/desorption, PXRD (powder X-ray diffraction), and HRTEM (high-resolution transmission electron spectroscopy) compared to conventional silica support materials.[16,17] In 1994, T. Bein et al. initiated SOMC@PMS by grafting heterobimetallic complex $Me_3SnMo(CO)_3(\eta\text{-}C_5H_5)$ onto dehydrated MCM-41 to produce highly dispersed Sn_xMo_y clusters by thermal degradation (Scheme 1).[18] The anchoring via SiOSn linkages was proposed to limit the mobility of the molybdenum carbonyl fragment. Carbonyl species, particulary those

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[†] Dedicated to Professor R. Dieter Fischer on the occasion of his 65th birthday.

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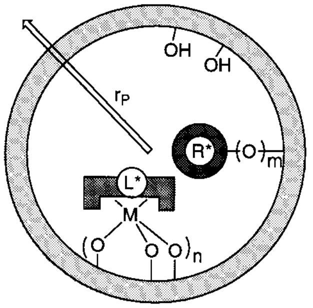
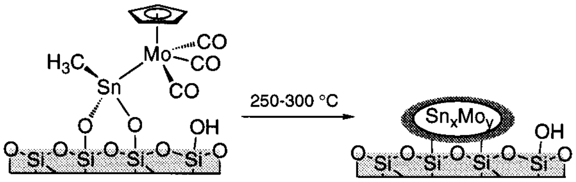


Figure 2. Schematic presentation of parameters determining the local, the microenvironment, and the mesoenvironment of metal-grafted porous materials ($2r_p$ = pore diameter d_p; $L^{(*)}$ = (chiral) ancillary ligand; $R^{(*)}$ = surface-attached group; for $n = 1$, the podality of the metal center M corresponds to Π^3; OH = residual surface silanol groups, affecting, e.g., the hydrophobicity of the material).

Scheme 1. Thermal Degradation of $Me_3SnMo(CO)_3(Cp)$@MCM-41



of the more noble metals, often tend to agglomerate and migrate out of the intracrystalline space to the outer surface.[4b]

Meanwhile, SOMC@PMS constitutes an integral part of organic−inorganic nanocomposite materials.[17] This review will give a comprehensive survey of SOMC@PMS covering the literature until the beginning of 2001. The synthesis of organometallic−inorganic composite materials will be discussed in detail. Special emphasis is put on peculiar material properties originating from the grafting process and pore architecture, while paying less attention to more routinely discussed beneficial effects of heterogenized homogeneous catalysts[19] such as ease of catalyst separation, recovery, and reuseability. Factors such as the podality Π^m of the grafted metal center, that is, the number of covalent M−O(support) bonds, the connectivity of the metal center, that is, the type of M−O−X(support) linkage, and the remaining (chiral) ligand environment $L^{(*)}$ are important factors for governing the reactivity of the hybrid material (Figure 2). The micro- and mesoenvironment imposed by surface-attached (chiral) groups $R^{(*)}$ and the pore diameter d_P are found to additionally tailor the reaction behavior. Group $R^{(*)}$ decorated pore walls modify the reactivity of the active metal site not only via various steric effects including metal spacing and stereochemical void space formation but also via hydrophobicity effects.

The intracrystalline space of PMS materials imposes a stabilizing environment that can be fine-tuned by variation of the pore diameter. Pore confinement is supposed to imply a stabilizing effect by better protecting the reactive site from deactivation and leaching effects (encapsulation phenomenon).[20] Moreover, implications of pore confinement for structure−reactivity relationships can be anticipated. For microporous zeolitic materials, the parallels to natural metalloenzymes have been investigated for almost 20 years and have been compellingly presented by N. Herron in his article "Toward Si-based life: Zeolites as enzyme mimics".[21] While ship-in-the-bottle synthesis is an attractive strategy for the synthesis of such zeozymes,[22] SOMC appears to be a prolific method for the development of biomimetic catalysts based on mesoporous host materials ("mesozymes"). The application of SOMC@PMS to emulate the incredible cooperativity between metal site, protein tertiary structure, and substrate molecule in natural enzymes is certainly challenging.

2. PMS as a Support Material

Porous oxidic materials featuring rigidity, thermal stability, and regular, adjustable, nanosized cage and pore structures are commonly classified as promising support materials, particularly for applications in the fields of catalysis, adsorption, and material science.[23] The intrinsic structural and morphological properties of semicrystalline PMS materials have been summarized in several review articles.[16] Although SOMC in the intracrystalline space of traditional microporous materials such as zeolites,[3,24] zeotypes,[25] and pillared clays[26,27] gives access to intriguing composite materials, this intrapore chemistry is restricted to smaller sized organometallic compounds. Even "small" compounds such as $AlMe_3$ (ca. 6.15 × 3.60 Å)[28] and $Fe(\eta^5\text{-}C_5Me_5)_2$ (ca. 5.73 × 7.19 Å)[29] are prone to pore blockage.[30] Table 1 gives an idea of the intracrystalline space available in nanoporous, that is, microporous and mesoporous, support materials of relevance for SOMC.[31−64] For example, zeolite Y, which is routinely employed for intraporous organometallic chemistry involving ship-in-the-bottle-synthesis,[65−67] possesses super cages (d_p of ≈13 Å), which are accessible by windows of 7.4 Å diameter only (Figure 3). Derivatization of extralarge microporous aluminophosphates via SOMC is hampered by their thermal instability (VPI-5)[41] and unfavorable pore morphology (Cloverite).[43,68]

PMS materials are unique insofar that they combine favorable properties of crystalline microporous materials, for example, structural variety,[69] with those of amorphous silica,[70] for example, high number of surface silanol groups. Because of their three-dimensional pore system and thermal stability, MCM-48, MCM-41, and SBA-15 silicas are discussed as the most promising candidates for SOMC. Uniform mesopores tunable in the range of 20−300 Å with narrow pore size distribution (Figure 3: BJH pore size distribution plot; fwhm = full width at half-maximum < 1 Å for pore sizes of ≈30 Å, within the limits of this model for the desorption branch) ensure an efficient intrapore chemistry comprising complex grafting, surface-mediated ligand exchange, and catalytic applications. As a rule, SOMC is performed under anaerobic conditions on dehydrated support materials to avoid deactivation and hydrolysis and hence agglomerization of the molecular precursor, for example, by the formation of metal hydroxide species. Dehydration is commonly performed under vacuum at temperatures between 200 and 300 °C, yielding silanol populations in the range of 1.5−2.5 $SiOH/nm^2$. Various types of silanol groups including isolated, vicinal, geminal, and hydrogen-bridged moieties were assigned by FT IR spectroscopy.[71] The surface coverage of the predominantly isolated silanol groups formed at elevated temperature not only depends on the

Table 1. Classification of Porous Materials of Relevance for SOMC

type	porous material[a]	largest pore[b] (d_p/nm)[c]	super cage (d_p/nm)[c]	ref(s)
microporous (large)	FAU (zeolite, cubic)	12 R (0.74 × 0.74)	1.2	31
	EMT (zeolite, hexagonal)	12 R (0.65 × 0.74)	1.3 × 1.4	32
	SAPO-37 (Si–AlPO$_4$)	12 R (0.7 × 0.75)	1.3	33
	DAF-1 (Mg–AlPO$_4$)	12 R (0.74 × 0.76)	1.63	34
	USCB-8 (Mg–AlPO$_4$)	12 R (0.75 × 0.77)	2.0 × 2.0 × 1.5	35
	UTD-1 (zeolite)	14 R (0.75 × 1.0)		36
	CIT-5 (zeolite)	14 R (0.99 × 1.00)		37
	AlPO$_4$–8	14 R (0.79 – 0.87)		38, 39
microporous (extra large)	ULM-5 (GaPO$_4$/F)	16 R (0.83 × 1.22)		40
	VPI-5 (AlPO$_4$)	18 R (1.2 × 1.3)		41
	Cloverit (GaPO$_4$)	20 R (0.60 × 1.32)	3.0	42
	JDF-20 (AlPO$_4$)	20 R (0.62 × 1.45)		43
mesoporous (>30 R)	MCM-41	– (2.0–10.0)		14, 44
	MCM-48	– (2.0–4.0)		45–49
	FSM-16	– (4.0)		50, 51
	KIT-1			52
	SBA-1	– (2.0–3.0)		53–55
	SBA-2	– (2.0–3.5)	ca. 4.0	53
	SBA-3	– (2.0–3.0)		53
	MSU-X	– (2.0–5.8)		56, 57
	SBA-15	– (5.0–30.0)		58
	SBA-8 (2D pore structure)	– (2.0)		59
	MCF-X (cellular foams)	– (<19)	24–86	60
	UOFMN-X/PMO/BSQMS	– (2.5–3.0)		61–63

[a] DAF, Davy Faraday Laboratory; UCSB, University of California at Santa Barbara; UTD, University of Texas at Dallas; CIT-5, California Institute of Technology Number Five; VPI, Virginia Polytechnic Institute; ULM, University of LeMans; JDF, Jilin–Davy–Faraday; MCM, Mobil composition of matter; FSM, folded sheet mesoporous materials; KIT, Korean Institute of Technology; MSU, Michigan State University; SBA, Santa Barbara; MCF-X, mesostructured cellular foams; UOFMN, unified organically functionalized mesoporous networks; PMO, periodic mesoporous organosilicas; BSQMS, poly(bridged silsesquioxane) mesophase. [b] Cage window (n R = n-membered ring of n TO$_4$-tetrahedrons, d_p = pore diameter). [c] For microporous materials from X-ray structure analysis, for mesoporous materials according to the BJH pore size distribution plot; note that although the BJH method is generally applied to determine the pore size distribution of PMSs, theoretical and geometrical calculations showed that the effective pore diameter is underestimated by ca. 1.0 nm.[64]

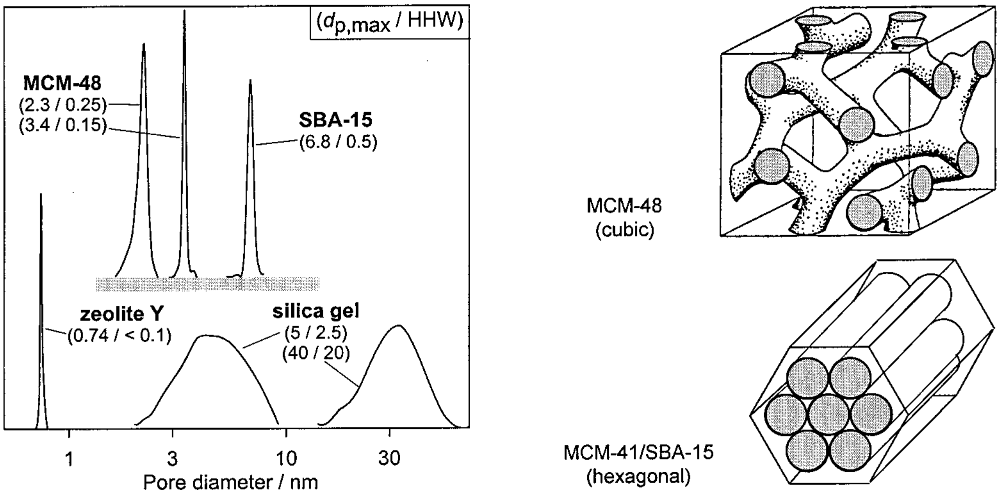


Figure 3. Pore size distribution of various porous materials and structural models of various PMS materials. Note that, in contrast to MCM-41, the hexagonally arranged mesopores of SBA-15 are interconnected by micropores.

pretreatment temperature but also on the synthesis procedure and type of PMS and pore diameter, that is, surface curvature. Like the commonly used amorphous silica and alumina supports,[1,2] PMS materials are capable of surface reactions via these silanol groups and strained siloxane bridges formed during the calcination and dehydration process at elevated temperature.[72] In particular, nitrogen physisorption measurements allow a unique picturing of the intraporous population, that is, of the steric bulk of the immobilized metal–ligand fragments, by representation of the surface area and the pore size distribution.[73] Hence, PMS materials seem also especially well-suited as *model* supports of the commonly used amorphous silica.[74]

3. Synthetic Aspects of SOMC@PMS

SOMC represents a highly efficient method to postsynthetically incorporate surface metal centers and is often superior to framework substitution methods, that is, isomorphous substitution via hydrothermal Si/M coprecipitation, because of better accessibility of the active centers. SOMC produces predominantly surface centers the distribution of which is easily controllable over a wide range. In addition to SOMC@PMS of real organometallics, that is, of alkyl, cyclopentadienyl, and carbonyl derivatives, this article includes also reference to other highly reactive metal–organic compounds. Such *pseudo*-organometallics, containing no direct metal–

Scheme 2. The pK_a Criterion as a Measure for Surface Reactivity

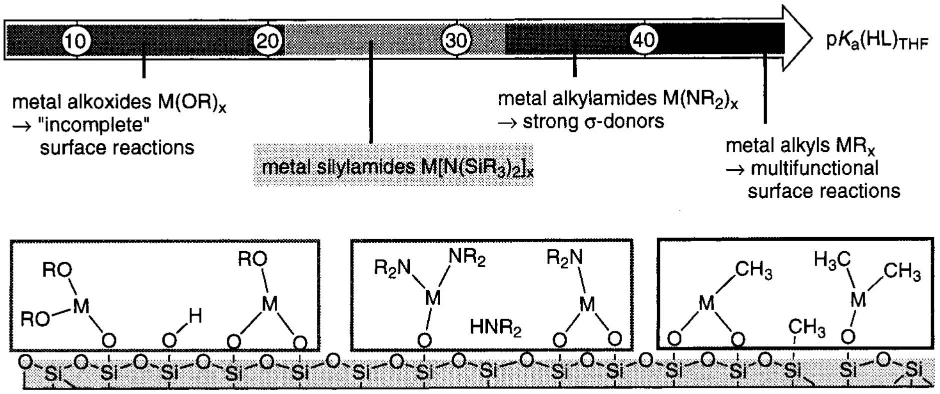


Table 2. Alkoxide-Based SOMC@PMS[a]

organometallic precursor	PMS	applications	ref
$Al(OiPr)_3$	MCM-41	hydrothermal stability	77
$Al(OiPr)_3$	MCM-41	MPV reduction of *tert*-butylcyclohexanone	78
$Al(OiPr)_3$	MCM-41	cumene cracking	79
$Nd(OCtBu_3)_3$	MCM-41	MPV reduction of *tert*-butylcyclohexanone	80
$Ti(OiPr)_4$	MCM-41	hydrothermal stability	77
$Ti(OiPr)_4$	MCM-48, SBA-15	dispersion of TiO_2 surface species	81
$Ti(OEt)_4$	Al−MCM-41	oxidation of cyclohexene with H_2O_2 or TBHP	82
$Ti(OnBu)_4$, $TiO(acac)_2$	MCM-41	anchoring of Zn(Pc)	83
$Ti(OnBu)_4$	MCM-41	photocatalytic oxidation of phenol to CO_2	84
$Zr(OnPr)_4$	MCM-48	peroxide activation	85
$Zr(OnPr)_4$	MCM-41	MTBE synthesis, *n*-pentane isomerization	86
$Zr(OiPr)_4$, Cp_2ZrCl_2	MCM-41	oxidation of cholesterol with TBHP	87
$VO(acac)_2$	MCM-48	VO_x surface species	88
$VO(acac)_2$	$HOSiMe_2$−MCM-48	VO_x surface species	89
$VO(OiPr)_3$	MCM-48	reactivity toward water; peroxide activation	90
$Cr(acac)_3$	AlMCM-41	ethylene polymerization	91
$Mo_2(OEt)_{10}$	MCM-48	peroxide activation	92
$W(OEt)_5$	MCM-48	peroxide activation	92
$Cu(TePh)_6(PPh_2Et)_5$	MCM-41	semiconducting nanowires	93

[a] acac = acetyl acetonate, pK_a (Hacac) = 9. MPV = Meerwein Ponndorf Verley. TBHP = *tert*-butylhydroperoxide. Pc = phthalocyanine. MTBE = methyl *tert*-butyl ether.

carbon linkage, feature otherwise readily hydrolyzable metal−X bonds as represented by amide and alkoxide ligands of enhanced basicity.[75] The basicity of the metal-bonded ligand, that is, the pK_a value of the protonated ligand, gives a reasonable measure of the reactivity of a metal−X(ligand) bond toward a dehydrated silica surface assuming a pK_a value of $\approx 5-7$ similar to silica gel (Scheme 2).[76]

Tables 2-4 classify the diversity of SOMC@PMS according to the molecular precursor, the mesoporous support, and aspects of characterization and application. Metal alkoxide complexes (Table 2),[77−93] particularly homoleptic derivatives $M(OR)_x$, have been widely used to postsynthetically modify silica surfaces. Depending on their substituents R, the pK_a value of alcohols HOR can range from 5 to 20. Mobil researchers initially employed metal alkoxide complexes of silicon, aluminum, and titanium as lining agents to improve the hydrothermal stability of MCM-41.[77] In the following, alkoxide complexes derived from oxophilic metal centers were often used to tailor PMS materials for catalytic applications, particularly oxidation catalysis. Although being the most inexpensive precursor for SOMC, metal alkoxide complexes reveal several disadvantages, including incomplete surface silanol consumption (Scheme 2),[80,85] release of strongly surface-coordinating alcohols, agglomerization of alkoxide surface species,[94] and limited secondary ligand exchange. It has been shown that highly fluorinated alcohols such as $HOC(CF_3)_3$ (pK_a 5.7) readily "degraft" rare earth metal centers from a MCM-41 surface.[95] Calcination of the metal alkoxide grafted materials is a popular approach for the synthesis of metal oxo overlayers.[80,90]

Table 3 lists SOMC@PMS based on molecular compounds containing a direct metal carbon bond.[96−127] Metal alkyls MR_x of groups 11, 12, 13, and early transition metals belong to the most reactive organometallic compounds. They are quite expensive and their handling requires rigorous exclusion of air and moisture (**Caution!** These organometallics and the grafted derivatives are hazardous materials that react violently and often ignite instantaneously upon air exposure). Because of their enhanced reactivity, all of the reactive surface silanol sites are consumed and even strained siloxane bridges (Scheme 2) formed at elevated temperature are disrupted.[96,97] Although this nucleophilic attack on the silicon atoms partially destroys the wall structure as shown for $AlMe_3$ and MeMgI, it can increase the hydrophobicity and the hydrothermal stability of the support material.[97] For their application in oxidation catalysis, group 4 metallocene complexes were directly anchored onto the surface by halide ligand displacement in the presence of a base (vide infra).[106] Solvent-dependent protonation and detachment of the cyclopentadienyl and indenyl ancillary ligand has been observed for the reaction of complexes $[(C_5H_4)_2SiMe_2]$-

Table 3. Alkyl- and Carbonyl-Based SOMC@PMS[a]

organometallic precursor	PMS	applications	ref(s)
MeMgI	BuO−MCM-41	hydrophobicity, hydrothermal stability	96
$AlMe_3$	MCM-41	Lewis acidic support	97
$AlMe_3$/*rac*-$[Me_2Si(2\text{-}Me\text{-}C_9H_5)_2]Y[N(SiHMe_2)_2]$	MCM-41	olefin polymerization	98
MAO/Cp_2ZrMe_2	MCM-41	MAO separation/ethylene polymerization	99
MAO/[*rac*-$C_2H_4(Ind)_2]ZrCl_2$	MCM-41	propylene polymerization	100, 101
$AlMe_3/[C_2H_4(Ind)_2]ZrMe_2$	MCM-41	propylene polymerization	102
$GaMe_3$/As(*tert*-Bu)$_3$	MCM-41	III−V semiconductor	103
$InMe_3/PH_3$	MCM-41	III−V semiconductor	104
$SnMe_4$, $SnEt_4$, SnH(*n*-Bu)$_3$	MCM-41	modification, reactivity	25
$Me_3SnMn(CO)_5$	MCM-41	dispersed Sn_xMo_y clusters	18
Sn(*n*-Bu)$_4$//Cp_2TiCl_2	MCM-41	oxidation of cyclohexene with TBHP	105
Ge(*n*-Bu)$_4$//Cp_2TiCl_2, $GeEt_3Cl//Cp_2TiCl_2$	MCM-41	oxidation of cyclohexene with TBHP	105
Cp_2TiCl_2	MCM-41	oxidation of cyclohexene with TBHP and H_2O_2(aq)	106
Cp_2TiCl_2	MCM-48	peroxidative halogenation	107
Cp_2MCl_2, M = Ti, Zr, V, Mo	MCM-48	oxidation of 2,6-DTBP with H_2O_2(aq)	108
{(*c*-$C_6H_{11})_7Si_7O_{12}$}TiCp	(Al−)MCM-41	oxidation of cyclooctene with TBHP	109
$[(C_5H_4)_2SiMe_2]TiCl_2$	MCM-41/48	oxidation of cyclooctene with TBHP	110
Cp_2TiCl_2/MAO	MSF	ethylene polymerization	111
Cp_2ZrCl_2/MAO,	(Al−)MCM-41	ethylene polymerization	112
$Cp^*{}_2ZrCl_2$/MAO $[C_2H_4(Ind)_2]ZrCl_2$/MAO	(Al−)MCM-41	ethylene polymerization	113
$Fe[(C_5H_4)_2SiMe_2]$	MCM-41/48	magnetic materials	114−116
$RuCp_2$	MCM-41	stereoselective hydrogenation	117
Pd(Cp)(η^3-C_3H_5)	Nb−MCM-41	Heck reaction	118
Me_2Au(acac)	MCM-41	oxidation of CO and H_2	119
$Mn_2(CO)_{10}$	MCM-41	oxidation of propene to CO_2	120
$Co_2(CO)_8$	MCM-41, SBA-15	Pauson-Kand reaction, thermal behavior	121, 122
$[Co_3Ru(CO)_{12}][NEt_4]$	MCM-41	magnetic nanoparticles	123
$[Ru_6C(CO)_{16}][N(PPh_3)_2]_2$, $[H_2Ru_{10}(CO)_{25}][N(PPh_3)_2]_2$	MCM-41	alkene hydrogenation by Ru nanoparticles	124
$[Ru_6Pd_6(CO)_{24}][NEt_4]_2$	MCM-41	alkene hydrogenation by RuPd nanoparticles	125
$[Ru_6C(CO)_{16}Cu_2Cl][N(PPh_3)_2]_2$	MCM-41	alkene hydrogenation by RuCu nanoparticles	126
$[Ru_{10}Ag_3C_2(CO)_{28}Cl][N(PPh_3)_2]_2$	MCM-41	alkene hydrogenation by RuAg nanoparticles	127

[a] MAO = methylalumoxane. Cp = C_5H_5 = cyclopentadienyl. Ind = C_9H_6 = indenyl. Cp* = $C_5(CH_3)_5$ = pentamethylcyclopentadienyl. MSF = mesoporous silica film. TBHP = *tert*-butylhydroperoxide. 2,6-DTBP = 2,6-di-*tert*-butylphenol. acac = acetyl acetonate.

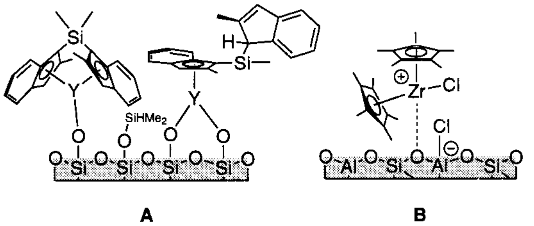
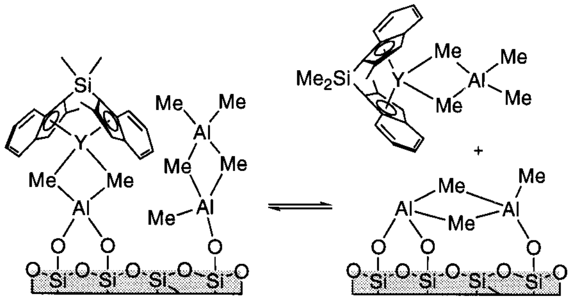


Figure 4. Proposed surface species obtained via the reaction of *rac*-$[Me_2Si(2\text{-}Me\text{-}C_9H_5)_2]Y[N(SiHMe_2)_2]$ with dehydrated MCM-41[98] and by direct grafting of $Cp^*{}_2ZrCl_2$ onto dehydrated Al−MCM-41.[113]

$TiCl_2$[110] and *rac*-$[Me_2Si(2\text{-}Me\text{-}C_9H_5)_2]Y[N(SiHMe_2)_2]$[98] (Figure 4/**A**) with dehydrated PMS, respectively. Heterogeneous single-site olefin polymerization catalysts were obtained via immobilizing the metallocene complex on MAO[99−101] or trimethylaluminum-modified[98] PMS surfaces, a method which is meanwhile industrially applied on silica supports.[7] The ethylene polymerization activities of zirconocene catalysts, for example, $Cp^*{}_2ZrCl_2$, directly supported on dehydrated Al−MCM-41 silica were higher than those of the same precatalysts immobilized on MAO-treated Al−MCM-41 silica (Figure 4/**B**).[113] Significant leaching of alkylated species was found when *rac*-$[Me_2Si(2\text{-}Me\text{-}C_9H_5)_2]Y[N(SiHMe_2)_2]$ was reacted with $AlMe_3$@MCM-41 (Scheme 3).[98]

Scheme 3. Proposed Surface Species Obtained via the Reaction of *rac*-$[Me_2Si(2\text{-}Me\text{-}C_9H_5)]Y[N(SiHMe_2)_2]$ with $AlMe_3$@MCM-41



Metal carbonyl complexes react with the surface silanol groups at elevated temperature, for example, by sublimative anchoring or by decomposition of a refluxing toluene solution.[120−127] Continuous adsorption of $Co_2(CO)_8$ onto MCM-41 from the gas-phase resulted in a maximum Co deposition of 20 wt %, corresponding to a monolayer with 2 Co/nm^2.[122c] The CO sheath prevents agglomerization during solution impregnation, while the PMS silanol groups facilitate the uptake of the carbonyl complex by hydrogen bonding via the carbonyl group.[127] Upon thermal treatment (ca. 200 °C/10^{-4} Torr), surface-dispersed bimetallic carbonyl clusters such as $[Ru_6C(CO)_{16}Cu_2Cl][N(PPh_3)_2]_2$ anchor via the more oxophilic metal.[126]

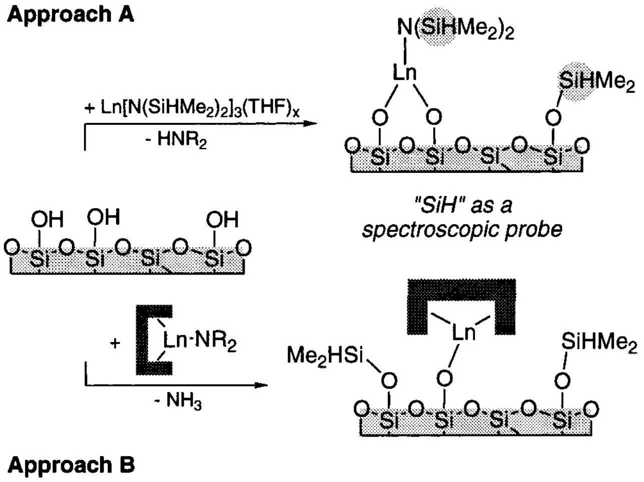
Until recently, there has been a dearth of data on SOMC of metal alkyl amide derivatives $M(NR_2)_x$ (Table 4).[94,128] Similar to metal alkoxides, their surface reaction generates strongly donating amines (Scheme 2) and

Table 4. Amide- and Silylamide-Based SOMC@PMS[a]

organometallic precursor	PMS	applications	ref(s)
$Al[N(SiHMe_2)_2]_3(THF)$	MCM-41	Diels–Alder cyclization (Scheme 14), MPV reduction of *tert*-butylcyclohexanone	74, 78
$Ti(NMe_2)_4$	MCM-48	oxidation of cyclohexene with TBHP	130
$Nd(N\textit{i}Pr_2)_3(THF)$	Al–MCM-41		95
$Nd[N(SiMe_3)_2]_3$	MCM-41	MPV reduction of *tert*-butylcyclohexanone, Nd oxide layer	80
$Nd[N(SiHMe_2)_2]_3(THF)_2$	MCM-41	MPV reduction of *tert*-butylcyclohexanone	
$Sc[N(SiHMe_2)_2]_3(THF)$	MCM-41	Diels–Alder cyclization (Scheme 14)	74
$Ln[N(SiHMe_2)_2]_3(THF)_2$, Ln = Y, La	MCM-41	Diels–Alder cyclization (Scheme 14)	74, 131, 132
$(L)Y[N(SiHMe_2)_2](THF)$	MCM-41	Diels–Alder cyclization (Scheme 14)	133
$Sm[N(SiHMe_2)_2]_2(THF)_x$	MCM-41/48	ketyl formation (Scheme 6)	134

[a] MPV = Meerwein Ponndorf Verley. TBHP = *tert*-butylhydroperoxide. H_2L = *N*,*N'*-Bis-(3,5-di-*tert*-butylsalicylidene)ethylenediamine, *trans*-1,2-Bis(2,4,6-triisopropylbenzenesulfonamidato)cyclohexane.

Scheme 4. Various Options of the "Heterogenized Silylamide Route"



siloxane cleavage reactions can be an issue.[129] Table 4 summarizes SOMC@PMS involving metal amide complexes.[130−134] In contrast to their alkyl, dialkylamide, and alkoxide derivatives, silylamide complexes of oxophilic and electrophilic metal centers display a favorable surface reaction[135] featuring (i) mild reaction conditions, (ii) formation of thermodynamically stable metal siloxide bonds, (iii) the production of a unique hydrophobic platform due to concomitant surface silylation, (iv) favorable atom economy, (v) suppression of extensive complex agglomerization due to the steric bulk of the silylamide ligands, (vi) release of weakly coordinating and hence easily separable silylamines, and (vii) the absence of any insoluble byproducts. Additionally, silylamide ligands provide a stabilizing environment (low coordination numbers, low metal oxidation states) for most of the main group and transition metals except for the noble metals.[136−138] Various conceptional approaches of this heterogeneously performed silylamine elimination have been initially reported for the lanthanide elements as outlined in Scheme 4.

Approach A is based on a two-step reaction sequence, comprising an initial grafting of silylamide complexes[131] and a subsequent surface-mediated secondary ligand exchange under fairly mild conditions.[74,80] Depending on the type of silylamide ligand (steric bulk) and the oxidation state of the metal center (number of ligands) ≈1−2.5 mmol of homoleptic silylamide complex can be grafted onto 1 g of dehydrated PMS material (surface area ≈1000 $m^2\ g^{-1}$). This corresponds to a relatively high surface coverage of 0.8−1.4 "Ln"/nm^2. For comparison, the multifunctional grafting of $AlMe_3$ gave a metal surface population of ≈2.7 Al/nm^2.[97] Approach B utilizes tailor-made heteroleptic molecular precursors exhibiting reactive docking positions (a silylamide moiety) and strongly chelating ancillary ligands such as SALEN and bissulfonamides, which disfavor protonolysis and counteract oligomerization reactions.[133] In addition to their favorable surface reaction silylamide ligands can be easily decorated with spectroscopic probe moieties as shown for the Si−H group of the dimethylsilylamide ligand $N(SiHMe_2)_2$. The IR spectra, representatively shown for the reaction of $Y[N(SiHMe_2)_2]_3(THF)_2$ with dehydrated MCM-41 (Figure 5, **C**), feature the complete consumption of the strong band at 3695 cm^{-1} due to the isolated OH groups (**A**) as well as the characteristic SiH stretch vibration modes for metal-bonded silylamide ligands (<2100 cm^{-1}, **B**) and for $\equiv SiOSiHMe_2$ surface sites (2145 cm^{-1}, **E**). The asymmetric and symmetric stretching vibrations of the "$YNSi_2$" fragment are also visible at 900 and 796 cm^{-1}.[74] The IR spectrum of a material obtained under analogous conditions from a dehydrated nonporous Aerosil AS200 (**D**) reinforces the importance of a high surface containing material and hence high immobilized complex/support ratios for an easy and quick characterization.

The profound importance of nitrogen physisorption for characterizing such intraporous SOMC is representatively shown for the grafting of $Sm[N(SiHMe_2)_2]_2(THF)_x$ onto dehydrated MCM-48 (Figure 6, **A** and **B**),[134] the subsequent reaction with fluorenone (Figure 6, **C**), and final acidic workup (Figure 6, **D**). The filling of the mesopores according to the approximate steric bulk of the immobilized species is impressively demonstrated and analysis of the Barret−Joyner−Halenda (BJH) pore size distribution suggests a regular distribution of the surface species accounting for reduced pore volumes and mean pore diameters. Note that use of pore-expanded PMS materials ensures the preservation of a mesoporous hybrid material after silylamide grafting, as indicated by the host-characteristic type-IV isotherm.[73]

Alternative synthetic strategies yielding porous organometallic−inorganic hybrid materials comprise complex immobilization via tethered ligands,[139] ship-in-the-bottle synthesis (physically entrapped complexes),[140] and self-immobilization through controlled thermolysis of labile organometallic complexes.[114,115]

4. Effect of Surface Confinement

Agglomeration, dispersion, and coordination phenomena are well-known to govern the catalytic activity of

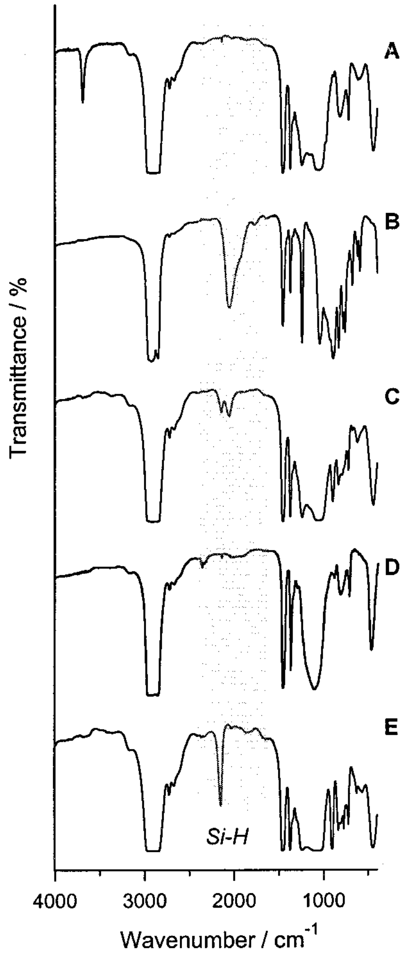


Figure 5. “Si–H” as a spectroscopic probe: The IR spectra (Nujol) of MCM-41$_{\text{dehydrat.}}$ (**A**, pretreatment temperature 250 °C, 3 h, 10^{-3} Torr), Y[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$ (**B**), [MCM-41]Y-[N(SiHMe$_2$)$_2$]$_x$(THF)$_y$ (**C**, pretreatment temperature 100 °C, 3 h, 10^{-3} Torr), [AS200]Y[N(SiHMe$_2$)$_2$]$_x$(THF)$_y$ (**D**, pretreatment temperature 100 °C, 3 h, 10^{-3} Torr), and [MCM-41]SiHMe$_2$ (**E**, pretreatment temperature 250 °C, 3 h, 10^{-3} Torr).[74]

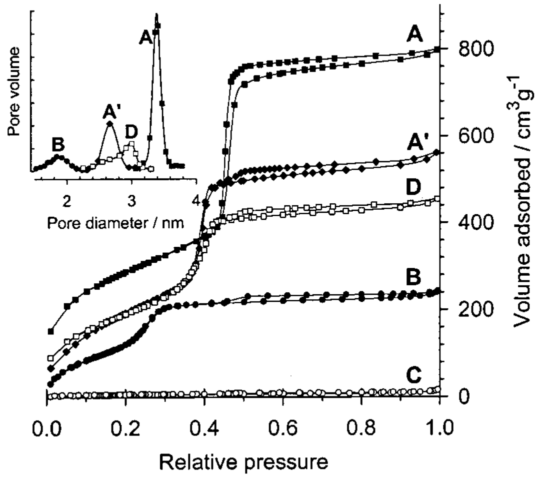


Figure 6. Nitrogen adsorption/desorption isotherms at 77.4 K and the corresponding BJH pore size distributions of the parent and modified MCM-48 materials **A** (–■–; 10^{-3} Torr, 4 h, 280 °C; $V_p = 1.21$ cm^3 g^{-1}/$d_p = 3.3$ nm), **A′** (–◆–; **A** + excess of HN(SiHMe$_2$)$_2$; 10^{-3} Torr, 3 h, 250 °C; 0.77/2.7), **B** (–●–; **A** + {Sm[N(SiHMe$_2$)$_2$]$_2$(THF)$_x$}; 10^{-3} Torr, >5 h, r.t.; 0.30/1.9), **C** (–○–; **B** + fluorenone; 10^{-3} Torr, >5 h, r.t.), and **D** (–□–; recovered material; 10^{-3} Torr, 3 h, 250 °C; 0.65/ 3.0). V_p = BJH desorption cumulative pore volume of pores between 1.5 and 6.5 nm in diameter. d_p = pore diameter according to the maximum of the BJH pore size distribution ($d_p < 2.0$ nm have to be viewed critically).[134]

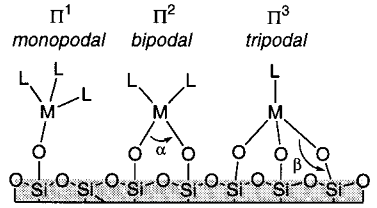


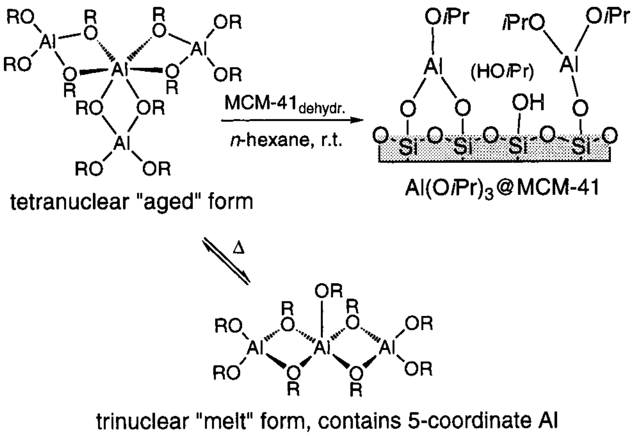
Figure 7. Classification of surface bonding by podality. Angles α and β determine the extent of surface confinement.

surface-deposited metal species.[1,2] In contrast to impregnation methods utilizing metal salts such as nitrates (“incipient wetness approach”), the grafting of oxophilic and Lewis acidic main group and early transition metal centers via SOMC produces highly reactive surface species without thermal post-treatment. SOMC at ordinary silica and alumina materials revealed that such surface species can exhibit unforeseen reactivity pattern.[12] Such enhanced reactivity can originate from sterically unsaturated metal centers featuring a highly distorted coordination environment and from a strongly electron-withdrawing effect of the support. Moreover, surface confinement implies a “small-ligand” chemistry of the metal centers. Numerically, the surface confinement of a metal center can be explained by its podality Π^m, that is, the number of covalent M–O(support) bonds, and the angles O–M–O and M–O–X(support) (Figure 7). While Π^m and the M–O(support) distances can be theoretically determined by quantification of the released protonated ligand and X-ray absorption spectroscopy (EXAFS, extended X-ray absorption fine structure; XANES, X-ray absorption near-edge structure), respectively, the two sets of angles remain unknown. Π^m depends on the silanol population, which can be controlled by thermal pretreatment, that is, dehydration, of the support material and its surface curvature. The intrinsic monodisperse pore structure of PMS materials facilitates the variation of the inner surface curvature, that is, the concavity of the pore walls, via the pore diameter. For example, formation of (≡Si–O)$_2$SnR$_2$ as the predominant surface species from the reaction of various alkyl tin complexes with MCM-41 was attributed to the enhanced inner surface curvature. In contrast, samples of microporous materials such as mordenite and cloverite, pretreated at the same temperature (200 °C), showed the formation of monopodal surface species.[141]

Grafting of Al(O*i*Pr)$_3$ onto MCM-41 in a nonaqueous environment according to Scheme 5, followed by calcination at 550 °C, produced a material (Si:Al = 5:1) that exhibited higher Brønsted acid content compared to Al–MCM-41 prepared by direct hydrothermal synthesis.[79] This was proven by a thermally programmed desorption of cyclohexylamine and by the catalytic cracking of cumene to benzene and propene.

Aluminum alkoxide-grafted MCM-41 also revealed a remarkably enhanced catalytic activity in the MPV reduction of cyclic ketones compared to the homogeneous system Al(O*i*Pr)$_3$.[78] A detailed ^{27}Al MAS NMR study revealed that the enhanced catalytic activity can

Scheme 5. Formation of Lower-Agglomerated Al-Isopropoxide Species upon Grafting or Thermal Treatment



be ascribed to the formation of low coordinated (4-, 5-), geometrically distorted aluminum species (Figure 8). It was proposed that surface confinement prevents the aluminum alkoxide moieties from agglomerization, while the silicate material simultaneously acts as an electron-withdrawing matrix. Note that the performance of MPV reductions depend on the Lewis acidity of the metal center and its ligand exchange ability.[142] The ^{27}Al MAS NMR spectrum of an Al(O*i*Pr)$_3$-grafted material (Figure 8, **B**), which did not change upon the catalytic reaction (Figure 8, **C**), exhibits besides the sharp resonance at 0 ppm, which is dominant in the spectrum of commercially available Al(O*i*Pr)$_3$ (Figure 8, **A**), an intense broad signal pattern in the range of 75 to −25 ppm, clearly indicating the formation of additional aluminum sites. Interestingly, a previous kinetic study showed that the "melt" form of Al(O*i*Pr)$_3$ (Scheme 5), which consists of the predominantly trimeric form with 4- and 5-coordinated aluminum centers, was found to be 10^3 times more reactive in MPV reductions than the tetrameric form containing 4- and 6-coordinated aluminum.[143] These findings could be corroborated by grafting 4-coordinate Al[N(SiHMe$_2$)$_2$]$_3$(THF) via the silylamide route, which produces lower coordinated aluminum surface species exclusively.[78] Subsequent silylamide/HO*i*Pr ligand exchange produced a material (Figure 8, **D**) that displayed similar catalytic activity.

A similar effect of surface confinement was detected for a special hetero-Diels−Alder reaction catalyzed by an Al-fod-grafted MCM-41 material (fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione).[74] The favorable catalytic activity of the hybrid material obtained via the silylamide route and subsequent silylamide/Hfod ligand exchange was attributed to the formation of aluminum surface centers with accessible coordination sites for dienophile activation via adduct formation. Note that the 6-coordinate molecular complex Al(fod)$_3$ is almost inactive. Coordinative distortions have also been observed for the interaction of Cr(acac)$_3$ with a dehydrated MCM-41 sample. EPR spectroscopy indicated Cr(III) centers in a strongly distorted octahedral coordination.[91]

Surface confinement seems to be also implicated in the reductive behavior of samarium(II) centers. The rate and selectivity of these one-electron reduction reactions, usually induced by the standard reagent *SmI$_2$*, are markedly affected by the type of solvents, additives such as strong Lewis bases, for example, HMPA, or metal salts,[144] and ancillary anionic ligands bonded to the Sm(II) center, for example, amide, alkoxide, or cyclopentadienyl ligands.[145] Sm(II) surface species obtained according to the heterogeneously performed silylamide route via reaction of bis(dimethylsilyl)amide Sm[N(SiHMe$_2$)$_2$]$_2$(THF)$_x$ with pore-expanded MCM-41 and MCM-48 (Scheme 6) form stable "storable" ketyl surface radicals and yield selectively the alcoholic product in the fluorenone/fluorenol transformation.[134] This contradicts the findings in homogeneous solutions where organosamarium(II) complexes treated with equimolar amounts of ketone hydrolyze to give the pinacol product exclusively.[145] The presence of sterically separated, surface-bound Sm(II) species seems to drastically modify the selectivity of this transformation. Further evidence for the formation of surface-confined and sterically unsaturated Sm(II) centers was obtained by FTIR spectroscopy: metal-bonded silylamide ligands featuring agostic Sm···SiH interactions were unequivocally indicated by a broad band of the SiH stretching vibration in the region from 2030 to 1920 cm^{-1}.[134]

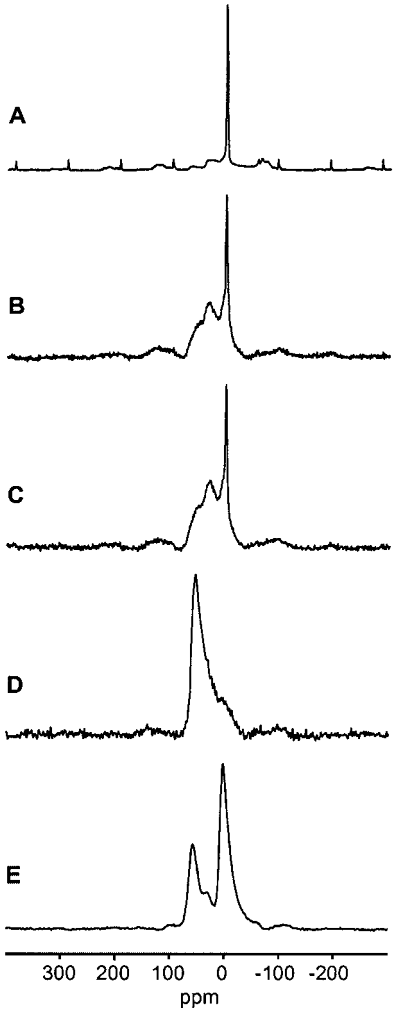
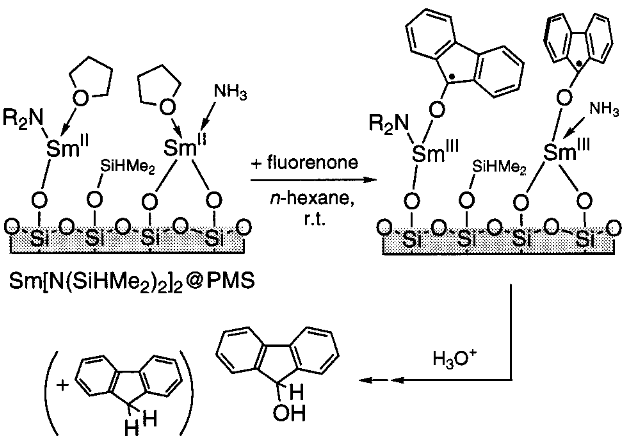
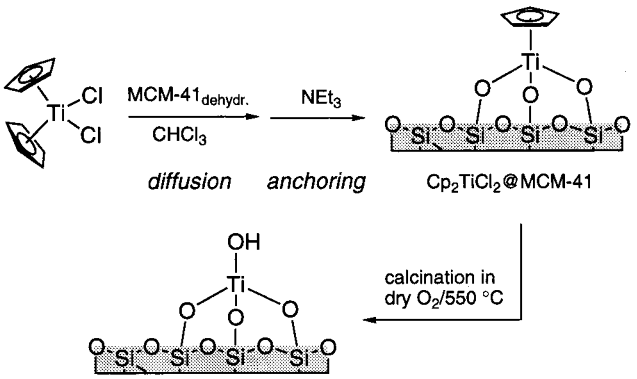


Figure 8. ^{27}Al NMR spectra: (**A**) Al(O*i*Pr)$_3$ as received from Aldrich; (**B**) Al(O*i*Pr)$_3$@MCM-41; (**C**) material **B** recovered from the first MPV catalytic run; (**D**) Al[N(SiHMe$_2$)$_2$]$_3$(THF)@MCM-41; (**E**) material **B** exposed to air for several days (completely hydrolyzed). All hybrid materials were evacuated for 5 h at 25 °C/10^{-2} Torr prior to measurement.[78]

Scheme 6. Formation of Surface-Confined Ketyl Radicals via Sm(II)@PMS

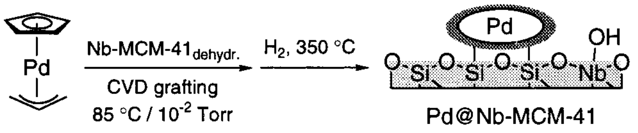


Scheme 7. Anchoring and Thermal Degradation of Cp_2TiCl_2 on MCM-41



EXAFS investigations revealed that grafting of Zr(O*n*Pr)$_4$ onto MCM-48 in *n*-hexane produced more isolated metal species relative to the incipient wetness approach as evidenced by the lowest number of Zr−O−Zr connectivities.[85] This was also confirmed for Ti(O*i*Pr)$_4$-grafted MCM-48 and SBA-15 materials by diffuse reflectance UV−visible, photoacoustic (PAS)-FTIR, and Raman spectroscopy.[81] Hydrolysis of such Zr-alkoxide surface species and subsequent treatment with 0.5 M H_2SO_4 and calcination at 600 °C produced a superacidic catalyst for MTBE synthesis and *n*-pentane isomerization.[86] The 2.5−3 times enhanced activity of this heterogeneous catalyst compared to that of commercial SO_4^{2-}/ZrO_2 was attributed to the increased number of highly exposed and easily accessible active sites. Utilization of organometallic precursors with bulky ligands even enhanced the formation of isolated, catalytically active surface sites. This was shown for the anchoring of titanocene complex Cp_2TiCl_2 featuring bulky cyclopentadienyl ligands (Scheme 7).[106] Surprisingly, according to EXAFS studies, this titanocene-grafting produced tripodal ($\equiv$Si−O)$_3$TiCp as the predominant surface sites. This structural information has been rationalized and amplified by a density functional theory (DFT) calculation.[146] The fact that the experimentally obtained short Ti−C(Cp) distances could not be reproduced by theory was attributed to the EXAFS measurements being representative of a species formed under kinetic control, that is, strained surface species due to geometry constraints and due to a high electronegativity of the surface. In the same study,[106] $TiCl_4$ or Ti(O*i*Pr)$_4$ precursor compounds were shown to exhibit a marked tendency for oligomeric titania-oxo species during the grafting sequence. The heterogeneous titanium hydroxy catalyst obtained according to Scheme 7 showed the highest turnover frequency for the catalytic epoxidation of alkenes (cyclohexene, pinene) with organic hydroperoxides catalyzed by Ti-containing mesoporous materials, for example, TOF = 37.3, for cyclohexene conversion with MPHP = 2-methyl-1-phenyl-2-propyl-hydroperoxide.[106] Again, Ti-grafted MCM-41 displayed a higher activity than framework Ti-substituted MCM-41.

Scheme 8. Anchoring and Reductive Thermal Degradation of Pd(Cp)(η^3-C_3H_5) on Nb−MCM-41



Ti-grafting experiments on dehydrated MCM-48 samples revealed that the ratio of monopodally and bipodally anchored species can be controlled by variation of the metal−organic precursor and by the distribution of surface silanol groups via the pore radii of the PMS samples.[130] It was found that Ti(NMe$_2$)$_4$ grafting of MCM-48 materials with pore diameters of 2.2, 2.6, and 3.4 nm (BJH pore size distribution, desorption branch) gave ≈20%, 30%, and 40% of bipodally anchored titanium, respectively. On the other hand, Ti(O*i*Pr)$_4$ grafting of the pore-expanded MCM-48 material afforded ≈60% of bipodal titanium species.

The excellent catalytic activity of a palladium-grafted MCM-41 material in the Heck carbon−carbon coupling reaction was ascribed to ultrahigh surface areas and highly dispersed catalyst species.[118] The heterogeneous catalyst was obtained by sublimation of Pd(Cp)(η^3-C_3H_5) through dehydrated Nb−MCM-41 under reduced pressure and subsequent reduction in hydrogen (Scheme 8). In comparison to impregnation methods, such vapor grafting afforded a markedly higher dispersion of metal centers, counteracting extensive cluster formation. Palladium metal surface areas and metal dispersions were determined by CO chemisorption as 140 m^2 g^{-1}/32% [vapor-grafted Pd(Cp)(η^3-C_3H_5)], 78 m^2 g^{-1}/17% [Pd(Cp)(η^3-C_3H_5)-impregnated], and 40 m^2 g^{-1}/9% [$PdCl_2$-impregnated]. The catalytic activity of these materials was investigated using activated and nonactivated aryl halides and styrene and *n*-butylacrylate as the vinylic substrate. For example, full conversion and a yield of 99% was obtained after only 1 h for the reaction of 4-bromoacetophenone *n*-butylacrylate (in air, 0.02 mol % catalyst, 120 °C, TON 5000). Surprisingly, the vapor-grafted material yielded a high conversion of nonactivated aryl substrates (67% for bromobenzene with *n*-butylacrylate: in air, 48 h, 0.1 mol % catalyst, 170 °C, TON 624), while the impregnated palladium materials gave only negligible conversion.

The presence of highly dispersed MnO$_x$ species, obtained by vapor grafting of $Mn_2(CO)_{10}$ onto MCM-41 and subsequent calcination in air at 300 °C, was ascribed to superior catalytic activity in the total oxidation of propene (maximum at ≈290 °C).[120] The onset temperature was ≈100 °C higher for a $Mn_2(CO)_{10}$-deposited ordinary silica material.

Table 5. Chlorosilane-Derived Surface Silylation[a]

chlorosilane	PMS	characterization, application	ref
$ClSiMe_3$	FSM-16	template extraction	156
$ClSiMe_3$	MCM-41	surface morphology	14
$ClSiMe_3$, $ClSiPh_3$	MCM-41	FTIR (different SiOH groups)	157
$ClSiMe_3$	MCM-41	pyridine, H_2O, and benzene adsorption, FTIR, ^{29}Si CP/MAS NMR	158
$ClSiMe_3$, $Me_3SiOSiMe_3$	MCM-41/48	stability (moisture, compression)	159
$ClSiMe_3$, $ClSiMe_2(n\text{-Bu})$, $ClSiMe_2(n\text{-Oct})$	MCM-41	surface morphology, N_2 adsorption	160
Cl_3SiMe ($SiCl_4$)	MCM-41	*n*-hexane diffusion, hydrophobicity	161
$ClSiEt_3$, $ClSiPr_3$, $ClSiBu_3$	FSM-16	N_2 adsorption, ^{13}C CP/MAS NMR, ^{29}Si CP/MAS NMR	162
$ClSiMe_3$, $ClSiMe_2(n\text{-Oct})$	MCM-41	template extraction	163
$ClSiMe_2(Vin)$	MCM-41	functionalization, + Br_2	164
Cl_2SiMe_2/H_2O	MCM-48	dispersion of $VO(acac)_2$	89
Cl_2SiPh_2, $(MeO)_3Si(CH_2)_3NH_2$	MCM-41	+ HBF_4 + $[Ru_6C(CO)_{14}C(\eta^6\text{-}C_6H_4C_{10}H_{20}O_6)]$, molecular recognition	165
Cl_2SiPh_2, $(MeO)_3Si(CH_2)_3NH_2$	MCM-41	+ HBF_4 + $KRuO_4$; alcohol oxidation with O_2	166
$Cl_3Si(CH_2)_3Br$	MCM-41	+ “Fe*” + $PdCl_2$, allylic amination	167

[a] acac = acetyl acetonate. “Fe*” = (*S*)-1-[(*R*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethyl-*N*,*N*′-dimethylethylenediamine (see Figure 11).

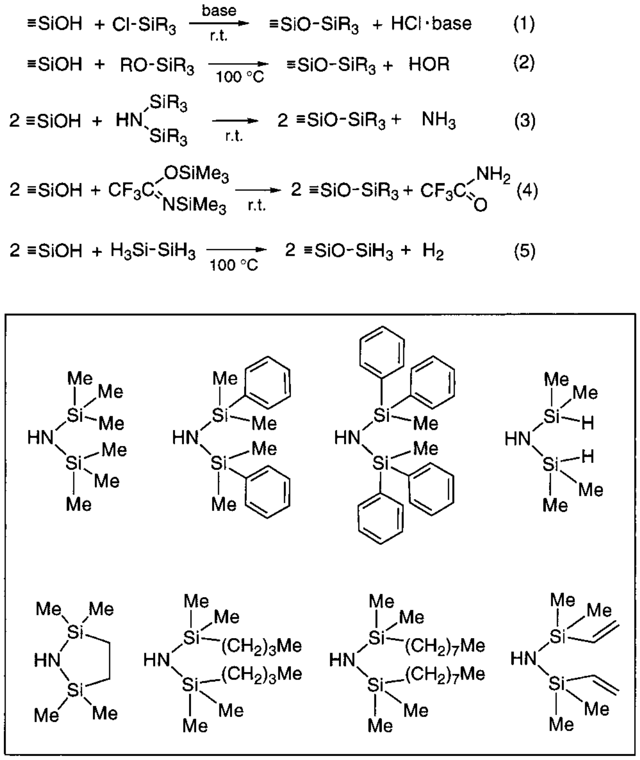
5. Effect of Local Environment, Microenvironment, and Mesoenvironment

Variation of the inner coordination sphere of the active metal site, that is, change of the local environment, is crucial for the design of homogeneous single-site catalysts[147] and, consequently, is examined for the development of more efficient and specialized catalysts of the category discussed in this article. Reports accumulate, revealing that the micro- and mesoenvironment implied by PMS materials can have important implications for both catalytic processes (“nanovessels” and “inclusion polymerization”)[148] and material science (“quantum confined materials”).[4,149] Particularly, surface morphology, surface polarity, and pore confinement are important factors for defining the micro- and mesoenvironment in PMS materials.

5.1. Surface Silylation. Silylation and alkylation reactions are of fundamental importance for the examination of the surface morphology and for the manipulation of siliceous support materials including zeolites.[150,151] Fine-tuning the catalytically active interface via adjustment of both the dispersion and accessibility of the catalytically active sites by steric and hydrophobicity effects is known to be crucial.[152] Silylating reagents such as chlorosilanes, alkoxysilanes, and silylamines have found widespread application in post-silylation experiments and their reaction with surface silanol functionalities has been reported in detail (Scheme 9).[70]

As a rule, chlorosilanes, $SiCl_xR_{(4-x)}$ (Scheme 9, (1)), and alkoxysilanes, $Si(OR)_xR_{(4-x)}$ (Scheme 9, (2)), require more drastic reaction conditions, that is, the reaction takes place at elevated temperature and in the presence of catalytic (e.g., H_2O) or stoichiometric amounts of additives (e.g., pyridine). In addition, these silylating reagents often display multifunctional surface reactions producing (undesired) byproducts such as alcohols and alkylammonium halides, which are difficult to separate. In contrast, silazane-based silylation reactions and SOMC seem to optimally complement each other. Silazane silylations are characterized by (i) mild reaction conditions, (ii) a relatively slow surface reaction, (iii) a monofunctional surface reaction, (iv) favorable atom economy, and (v) ease of thermal desorption of the excess silylamine released and the byproduct ammonia (Scheme 9, (3)).[153−155] Additionally, a rich pool of silylamine reagents is commercially available and new derivatives are readily synthesized.

Scheme 9



Although hexamethyldisilazane, $HN(SiMe_3)_2$, has been extensively studied as a silylating reagent of amorphous silica materials,[70] the inital silylation experiments on PMS materials focused on the application of chlorosilanes. Great efforts were made to physicochemically characterize the surface morphology of the mesoporous support materials (Table 5).[156−167] Analogous to previous investigations of amorphous silica materials, alkoxysilanes have been employed to tailor the PMS surface for applications in chromatography, adsorptive separation, and catalysis (Table 6).[168−191] Particularly, tethering of chiral homogeneous catalysts at the inner walls of PMS seems to be a popular approach to enter enantioselective catalysis.

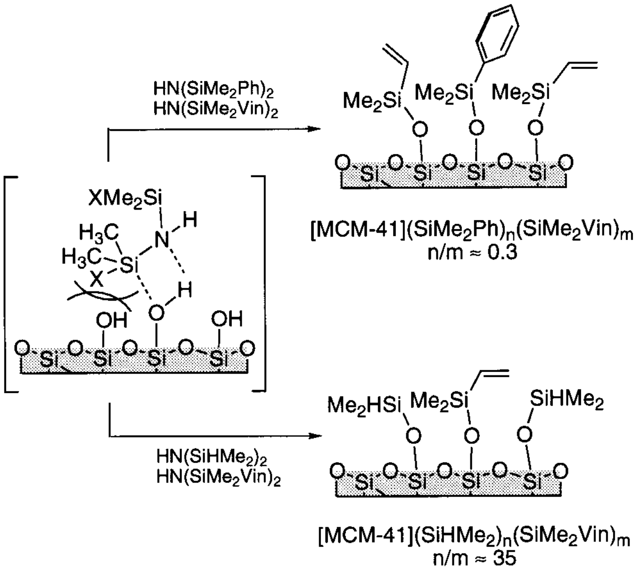
Table 6. Surface Functionalization via Alkoxysilanes[a]

alkoxysilane	PMS	application	ref(s)
$(EtO)_3Si(n\text{-Oct})$, $(EtO)_3Si(CH_2)_3NH_2$	MCM-41	N_2 adsorption	160
$(MeO)_3SiR$ (R = *n*-Pr, *n*-Dec, Ph)	MCM-41	bifunctionalization	168
$Si(OEt)_4$	MCM-41	pore size engineering	169
$(MeO)_3Si(CH_2)_3SH$	MCM-41	capillary gas chromatography	170
$(EtO)_3Si(CH_2)_3NH_2$	MCM-41/48	+ succinic acid + (*R*)-NEA; chiral HPLC	171
$(EtO)_3Si(CH_2)_xCH_3$ ($x = 7, 11$)	MCM-41	adsorption of nonyl phenol	172
$(MeO)_3Si(CH_2)_3SH$	MCM-41	adsorptive separation (Hg)	173
$(MeO)_3Si(CH_2)_3SH$	HMS	adsorptive separation (Hg)	174
$(MeO)_3Si(CH_2)_3R'$	MCM-41	+ Cu(II); CrO_4^{2-}, AsO_4^{3-} binding	175
$(RO)_3Si\text{-}X\text{-}Si(OR)_4$ R = Me, Et; X = C_2, CHCH, C_2H_4, 1,4-C_6H_4, 2,5-SC_4H_2, 2,2′−$S_2C_8H_4$, 1,1′-$Fe(C_5H_5)_2$	HMS	integral organic or organometallic functionality (cf. Table 1)	61−63
$(MeO)_3Si(CH_2)_3Cl$	MCM-41	+ TBD; transesterfication	176
$(MeO)_3SiR$ $R = (CH_2)_3OCH_2CH(O)CH_2$	MCM-41	+ TBD; Michael addition	177
$(MeO)_3Si(CH_2)_3SH$	MCM-41	+ H_2O_2; esterfication	178
$(MeO)_3Si(CH_2)_3NH_2$	MCM-41	+ HBF_4; local derivatization	165
$(MeO)_3Si(CH_2)_3NMe_3Cl$	MCM-41	+ NMe_3OH; Knoevenagel and aldol condensation, Michael addition	179
$(MeO)_3Si(CH_2)_3Cl$	MCM-41	+ (−)/(+)-ephedrine; addition of $ZnEt_2$ to benzaldehyde	180
$(MeO)_3Si(CH_2)_3NH_2$	MCM-41	+ Cr(III)-SALEN′; epoxidation	181
$(MeO)_3SiR$ $R = (CH_2)_3OCH_2CH(O)CH_2$	MCM-41	+ TACN + $MnSO_4$; epoxidation	182
$(MeO)_3Si(CH_2)_3Cl$	MCM-41	+ *t*-SALPRN + $Mn(acac)_2$	183
$(MeO)_3Si(CH_2)_3Cl$	MCM-41	+ 2*R*,3*R*-cyclohexane-1,4,7,10-tetra-azacyclodecane + propylene oxide + $MnCl_2$; epoxidation	184
$(MeO)_3Si(CH_2)_3R'$	MCM-41	+ salicylaldehyde + $Mn(OAc)_2\cdot 4H_2O$; epoxidation	185
$(EtO)_3Si(CH_2)_3PPh_2$	MCM-41	+ $Rh(PPh_3)_3Cl$; hydrogenation	186
$(EtO)_3Si(CH_2)_3NH_2$	MCM-41	+ Ru(Por)(CO)(EtOH); oxidation	187
$(MeO)_3Si(CH_2)_3R''$	MCM-41	+ $CoCl_2$; electrochemistry, + O_2	188
$(EtO)_3Si(CH_2)_3NH_2$	MCM-41	+ $Cl_2Pd(CNCH_2Ph)_2$; hydrogenation	189
$(MeO)_3Si(CH_2)_3NMeR'''$	MCM-41	+ $PdCl_2$; hydrogenation	190
$[Cu(apts)_x(Solv)_{6-x}]^{2+}$ $[Cu(appts)_2(Solv)_2]^{2+}$ $x = 3,5$; Solv = H_2O, MeOH	MCM-41	imprint coatings	191

[a] $R' = NH(CH_2)_2NH_2$. TBD = 1,5,7-triazabicyclo[4.4.0]dec-5-ene. Por = *meso*-tetrakis(4-chlorophenyl)porphyrine. TACN = 1,4,7-triazacyclononane. (*R*)-NEA = (*R*)-naphthylethylamine. $R'' = NH(CH_2)_2NH_2$, $NH(CH_2)_2NH(CH_2)_2NH_2$, $N(CH_2CO_2Na)(CH_2)_2N(CH_2CO_2Na)_2$. apts = $(MeO)_3Si(CH_2)_3NH_2$. appts = $(MeO)_3Si(CH_2)_3NH(CH_2)_2NH_2$. R''' = (*S*)-1-[(*R*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethyl-(see Figure 11). HMS, hexagonal mesoporous silica.

More recently, the various options of disilazane silylation have been reported in detail (Scheme 9).[192] Nitrogen physisorption and MAS NMR spectroscopy were applied to characterize the peculiarities of disilazane reactions including the effect of pore size engineering and the organic structure of the immobilized silyl groups. At ambient temperature, the silylation efficiency of disilazane compounds, $HN(SiR^1R^2{}_2)_2$, markedly depends on the size of the silyl group R^1 and R^2, respectively. For example, only 80% of the surface silanol groups of a MCM-41 sample, dehydrated at 280 °C/10^{-3} Torr, could be silylated by means of the standard silylation reagent $HN(SiMe_3)_2$ compared to the more efficient tetramethyldisilazane, $HN(SiHMe_2)_2$. The sterically even bulkier $HN(SiMePh_2)_2$ reacted with ≈40% of the silanol groups under the same conditions. This corresponds to a surface coverage of 1.5, 1.85, and 0.75 SiR_3/nm^2, respectively. Both *consecutive* and *competitive* silylation reactions revealed important details of the kinetics of this silylation reaction and support a controlled surface functionalization as shown for vinyl moieties (Scheme 10). These vinyl groups provide a unique platform for subsequent modification reactions as verified by the hydroboration reaction.

Scheme 10. *Competitive* Surface Silylation Utilizing Disilazane Reagents



N,*O*-Bis(trimethylsilyl)trifluoro acetamide, $[CF_3CO\text{-}SiMe_3]{=}NSiMe_3$, was described as a more efficient silylating reagent than trimethylsilyl chloride, $ClSiMe_3$, and hexamethyldisilazane, $HN(SiMe_3)_2$ (Scheme 9/(4)).[193] Treatment of as-synthesized hexagonal PMS materials with disilane, Si_2H_6, at 100 °C prior to template re-

Table 7. Surface Functionalization via One-Pot Hydrothermal Synthesis with Alkoxysilanes (Co-condensation Method)[a]

alkoxysilanes	PMS	characterization, application	ref(s)
$Si(OEt)_4$, $(EtO)_3Si(n\text{-Oct})$, $(EtO)_3Si(Ph)$	HMS	N_2 adsorption, TEM, $^{13}C/^{29}Si$ CP/MAS NMR, FTIR	196
$Si(OEt)_4$, $(EtO)_3Si(CH_2)_3NH_2$, $(EtO)_3Si(CH_2)_3CN$		N_2 adsorption, TG, DTA, FTIR	197
$Si(OEt)_4$, $(RO)_3SiR'$ (R = Me, Et) [R′ = allyl, Ph, $(CH_2)_3NH_2$, $(CH_2)_3SH$, $(CH_2)_3OCH_2CH(O)CH_2$, $(CH_2)_3ONCHNCH_2CH_2$, $(CH_2)_3OCH_2CH(O)CH_2$]	MCM-41	TEM, $^{13}C/^{29}Si$ CP/MAS NMR, bifunctionalization	198
$Si(OEt)_4$, $(EtO)_3SiPh$	MCM-48	TEM, ^{13}C CP/MAS NMR	199
$(EtO)_3SiMe$, $(EtO)_3Si(Vin)$	MCM-41	$^{13}C/^{29}Si$ CP/MAS NMR; stabilization	200
$Si(OEt)_4$, $(EtO)_3SiR$ (R = Me, Et, *n*-Oct, Vin, Ph)	SBA-3	$^{13}C/^{29}Si$ CP/MAS NMR, XRD, N_2 adsorption	201
$Si(OEt)_4$, $(MeO)_3Si(CH_2)_3NH_2$	MCM-41	N_2 adsorption; Knoevenagel condensation	202
$(MeO)_3Si(CH_2)_3SH$	HMS	adsorptive separation (Hg)	203
$Si(OEt)_4$, $(EtO)_3Si(Vin)$	MCM-41	XRD, TEM, N_2 adsorption; + Br_2	163, 204
$Si(OEt)_4$, $Si(OMe)_4$, $(EtO)_3Si(CH_2)_3SH$	MCM-41	TEM, ^{13}C CP/MAS NMR, XRD, TEM, N_2 adsorption; + HNO_3	205
$Si(OEt)_4$, $(MeO)_3Si(CH_2)_3SH$	MSU-X	SEM, ^{29}Si CP/MAS NMR, XRD, N_2 adsorption	206
$Si(OEt)_4$, $(MeO)_3Si(CH_2)_3SH$	MCM, HMS	+ H_2O_2, esterfication	177
$Si(OEt)_4$, $(MeO)_3Si(CH_2)_3R$ [R = 2,4-$(NO_2)_2C_6H_2NH_2$]	MCM-41	XRD, TEM, ^{29}Si CP/MAS NMR, UV; yellow mesoporous films	207
$(EtO)_3Si(CH_2)_2(CF_2)_5CF_3$	HMS	hydrophobicity, low-*k* dielectrics	208
$(MeO)_3SiR$ [R = $(CH_2)_3NH(NO_2)C_6H_3NO_2$]	HMS	chromophore; nonlinear optical material (χ^2)	208
$(MeO)_3Si(CH_2)_3NH$-dye	CMS	pH indicator	208
$Si(OEt)_4$, $(EtO)_3Si\text{-}X\text{-}Si(OEt)_4$ [X = CHCH, C_2H_4, $CH_2CH{=}CHCH_2$, 1,4-C_6H_4]	HMS/CMS	Raman, XRD, TEM, MAS NMR, integral organic or organometallic functionality (cf. Table 1)	63a, 208

[a] Dye = 5,6-carboxyfluorecein, succinimidyl ester. HMS, hexagonal mesoporous silica. CMS, cubic mesoporous silica.

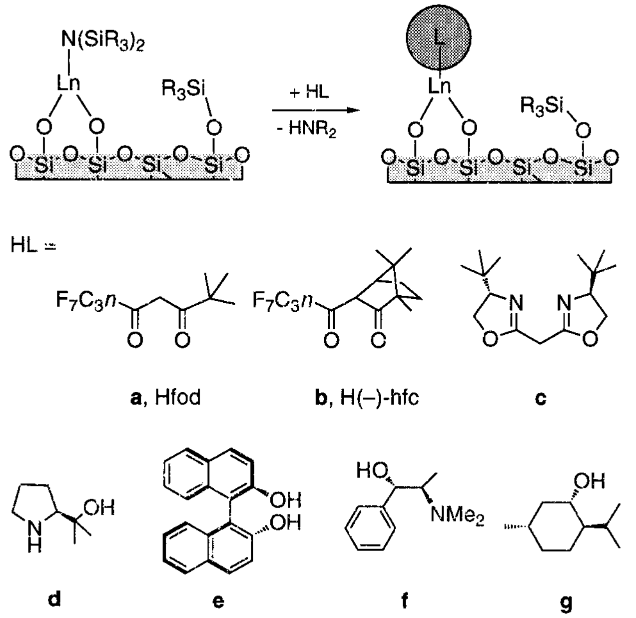
moveal was ascribed to a stabilizing effect (Scheme 9/(5)).[194]

Co-condensation "one-pot" reactions of differently functionalized alkoxysilanes[195] in the presence of a templating reagent represent an alternative route compared to the postsynthetic modification of structurally highly ordered PMS materials. Table 7 summarizes applications of this co-condensation approach toward organic/inorganic hybrid materials.[196−208] Although this method provides a uniform distribution of surface functionalities, the structural order of the resulting inorganic/organic hybrid materials is lower and markedly depends on reaction conditions (pH, temperature) and the molar ratios of the monomers employed.

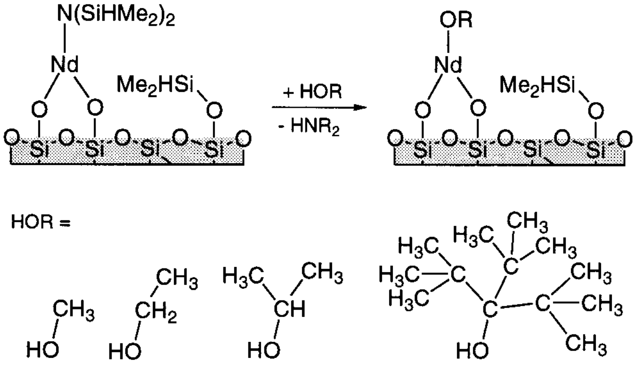
5.2. Implications for Organic Synthesis and Catalysis. Surface-mediated secondary ligand exchange seems particularly viable to change the local environment of surface-bound metal centers.[209] Silylamide grafting seems to be applicable for the high-throughput synthesis and screening of structurally defined rare earth metal catalysts on PMS materials.[132] Thus, by means of parallel synthesis any desired number of intraporous ligand exchange reactions can be conducted simultaneously under identical conditions, resulting in a large and structurally diverse array of promising substances. Scheme 11 tackles the screening of rare earth metal grafted MCM-41 silica for asymmetric catalysis.

Furthermore, surface-confined metal species give access to a "small ligand chemistry" of oxophilic and electrophilic metal centers, unknown in solution chemistry due to agglomerization phenomena. As a standard example, the class of lanthanide alkoxide complexes produces polymeric solid-state structures for OMe and OEt ligands, cluster compounds such as $Ln_5O(O\textit{i}Pr)_{13}$ for medium-sized ligands, and mononuclear complexes for the bulky ligand $OC\textit{t}Bu_3$ (Tritox).[210] Surface-mediated chemistry was shown to accomplish "mononuclear" Ln-alkoxide sites independent of the size of the ligand (Scheme 12). Such rare earth alkoxide surface complexes display subtly differentiated catalytic behavior in the MPV reduction of *tert*-butylcyclohexanone.[80]

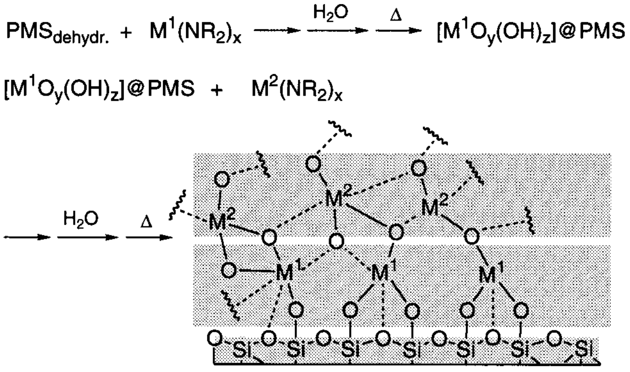
Scheme 11. "High-Throughput Synthesis" of Chiral Rare Earth Surface Species



Scheme 12. "Small-Ligand SOLnC" of Alkoxide Derivatives (SOLnC = *S*urface *O*rgano*lan*thanide *C*hemistry)



Scheme 13. Modular Design of a Multicomponent Catalyst via *Consecutive* Grafting

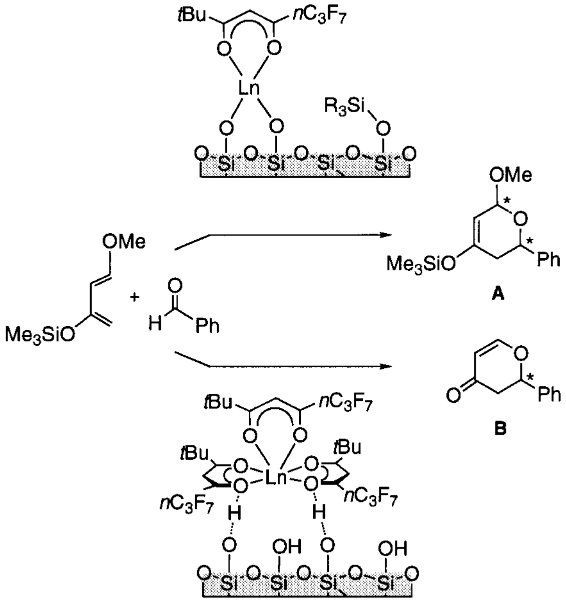


The PMS ligand not only affects the type of surface species formed during the grafting reaction but also atomically engineers the active metal site by acid/base and electronegativity effects through the M−O−X(support) linkage (connectivity). For example, surface sites of enhanced Lewis acidity, present in framework Al-substituted PMS, dramatically influence the immobilization of metallocene complexes (Figure 4) and, hence, the formation of catalytically active species.[112] Similarly, the chemisorption of homoleptic β-diketonato complexes on dehydrated PMS is directed by the presence of framework heteroatoms. It was shown for several transition metal derivatives[91,132] that ligand exchange occurred on Al-exchanged MCM-41 materials exhibiting a slightly higher degree of Brønsted acidity. The surface silanol groups of purely siliceous MCM-41 interact with the metal complexes via hydrogen bonding exclusively.

Consecutive grafting sequences according to Scheme 13 display a prominent route to tailor the reactivity of the surface for SOMC processes. The resulting heterobimetallic metal oxy/hydroxy layers can be employed to design nanostructured multifunctional heterogeneous catalysts.[211] Initial investigations of grafted titania epoxidation catalysts revealed that modifying a dehydrated MCM-41 sample with Ge(IV) via $GeBu_4$ or $GeEt_3Cl$ prior to titanocene grafting substantially alters the performance of the catalysts. This promoting effect was attributed to the partial displacement of Ti−O−Si≡ linkages by Ti−O−Ge≡ connectivities.

Modified PMS materials obtained according to the heterogeneously performed silylamide route provide a unique hydrophobic platform for the handling and isolation of sensitive substrate molecules and reaction intermediates. Such species show highly selective reaction behavior in the Danishefsky transformation, a special hetero-Diels−Alder reaction, to form product **A** exclusively, as shown in Scheme 14 (TOF = 70: Ln = Y, 50 °C).[74,132] This was ascribed to an in situ silylation due to the released silylamine, ensuring the complete "end-capping" of all of the Brønsted acidic surface silanol groups. Supportive of this was the catalytic behavior of a hybrid material which was obtained by contacting a dehydrated MCM-41 sample directly with $Y(fod)_3$. Although the latter material displayed an enhanced initiative catalytic activity comparable to molecular complexes, conversion of product **A** into **B** was observed from the beginning.

Scheme 14. The "Danishefsky Transformation" Mediated by [MCM-41]Ln(fod)$_x$



The beneficial effect of an organically modified hydrophobic microenvironment for the catalytic performance was also shown for framework titanium-substituted[212] and ligand-tethered PMS materials.[213]

Pore confinement of the catalytic center can have a favorable effect in some respects including (i) protection of the reactive site from deactivation processes, (ii) stabilization of labile reaction intermediates, and (iii) control of product selectivity (regioselectivity, enantioselectivty) and morphology. For example, the long-time stability of a confined catalyst was demonstrated for the above-mentioned Y(fod)$_x$-catalyzed Danishefsky transformation (Scheme 14).[74] The homogeneous catalyst $Y(fod)_3$ was more active at the beginning of the reaction; however, the conversion comes to an halt after ≈1 h (80%) and no further activity could be observed upon addition of another equivalent of the substrates. In contrast, although the initial activity of the PMS-confined catalyst was slightly decreased compared to its molecular congener due to diffusion limitation, almost 95% conversion is obtained after 50 h, and new subtrates are converted as quickly as the first time, revealing no marked decrease in activity toward the end of the reaction.

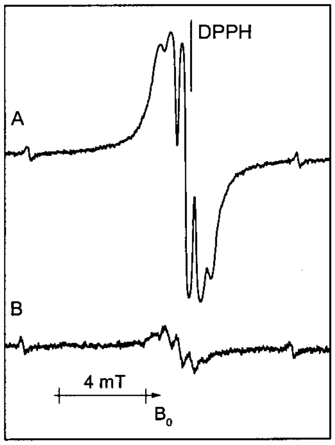


Figure 9. X-band EPR spectrum (T = 293 K) observed for $Sm[N(SiHMe_2)_2]_2(THF)_x$@MCM-41 (**A**) and $Sm[N(SiHMe_2)_2]_2(THF)_x$@AS200 (**B**) under an argon atmosphere (EPR settings: ν = 9.05 GHz, microwave power 2 mW, modulation frequency 100 kHz, modulation amplitude 0.05 mT; the two small satellites are due to the Mn^{2+} standard).[134]

Ketyl radicals display key intermediates in the reduction of carbonyl compounds and their stabilization markedly influences the product selectivities. The unequivocal formation of surface ketyl radicals for the Sm(II)-mediated fluorenone/fluorenol transformation (Scheme 6) was revealed by their X-band EPR spectra (Figure 9, **A**).[134] The rigid bonding of the radical to the surface was indicated by the absence of any qualitative changes in the spectra for recording temperatures between 130 and 323 K. In contrast, ketyl radicals produced on a dehydrated ordinary silica material (Aerosil-200, Degussa-Hüls, surface area 200 $m^2\ g^{-1}$) displayed a relatively weak EPR signal (Figure 9, **B**). Although nonporous Aerosil-200 gave similar Sm(II) surface species, showing qualitatively analogous reaction behavior, the ketyl radicals seem to be increasingly prone to hydrogen radical abstraction, as indicated by a significant amount of fluorenol in the supernatant solution. This ketyl destabilization was ascribed to the lack of the protective effect of the intrapore arrangement and the changed morphology of the Aerosil-200 silica material (presence of bulk silanol groups). The analysis of the BJH pore size distribution was in agreement with such a stabilization via pore confinement, indicating apparent total loss of pore volume and hence pore blocking (Figure 6).

Pore confinement of grafted homogeneous catalysts can be exploited for the nanofabrication of polymeric materials. A functionalized MSF material (*m*esoporous *s*ilica *f*ilm) prepared by coating a mica plate with a PMS layer ($P6_3/mmc$ structure with the c axis perpendicular to the film),[214] grafted with titanocene according to Scheme 7, and activated with methylalumoxane (MAO) was shown to act as a nanoextruder for crystalline nanofibers of linear polyethylene (PE) with a ultrahigh molecular weight (6 200 000) and a diameter of 30−50 nm.[111] It was proven by SAXS (*s*mall *a*ngle *X*-ray *s*cattering) and DSC (*d*ifferential *s*canning *c*alorimetry) that the mesoscopic pores in MSF serve as a template to produce extended-chain crystals of PE. Formation of the kinetically favored chain folding process, typical of ordinary HDPE, is suppressed because the pore diameter (≈30 Å) is almost 1 order of magnitude smaller than the lamellar thickness (270 Å) of the folded chain crystals of ordinary PE. Such extrusion polymerization mechanistically mimics the biosynthesis of cellulose. Identically grafted nonfibrous PMS such as MCM-41 produced crystalline PE containing a fibrous fraction, which displayed an ordinary powder XRD and DSC pattern, however. The same procedure was used to synthesize a novel molecularly hybridized PE/silica composite thin film (Figure 10). In contrast, use of glass instead of mica plates produced islanded PMS films and, as a consequence, islanded PE/silica composites.[215]

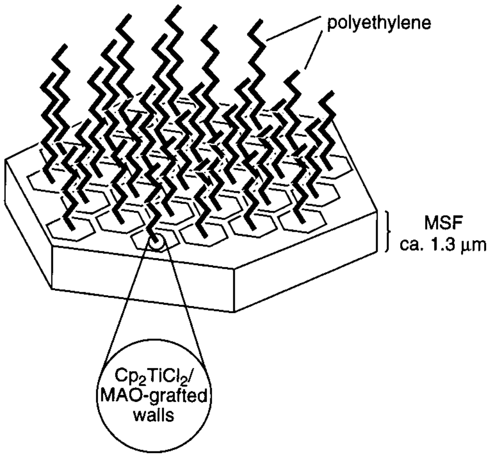
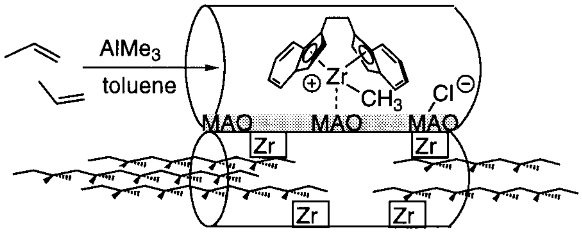


Figure 10. Schematic presentation of the polymerization of ethylene on a *m*esoporous *s*ilica *f*ilm (MSF).[214]

Scheme 15. Idealized Propylene Extrusion Polymerization from [*rac*-$C_2H_4(Ind)_2$]$ZrCl_2$//MAO@MCM-41



Heterogeneous single-site olefin polymerization catalysts obtained by subsequently reacting dehydrated MCM-41 with MAO and [*rac*-$C_2H_4(Ind)_2$]$ZrCl_2$ (Scheme 15) were also reported to affect the polymer morphology.[101] Propylene extrusion polymerization gave spherulite polypropylene (PP) particles of approximate diameter 10 μm, featuring a distinct core and shell arrangement. Although displaying a quarter of the activity (≈1400 kg of PP/(mol of Zr atm h)), these catalyts produced a 4-fold increase in the number-average molecular mass of PP (similar polydispersity 1.9) and a higher isotacticity PP (83%) relative to the homogeneous system (78%).[100] Better stereocontrol was associated with a lower monomer concentration at the active sites, disfavoring 1.3 insertion, and could be even enhanced by utilization of the extra large pore zeotype VPI-5 as a support material (Table 1).

Application of a different grafting procedure, involving formation of an in situ alumoxane-coated MCM-41 via reaction of hydrated MCM-41 with $AlMe_3$ solution, and addition of [$C_2H_4(Ind)_2$]$ZrMe_2$, produced a highly efficient catalyst for the copolymerization of ethylene and propylene (≈4000 kg of PP/(mol of Zr atm h)).[102] The

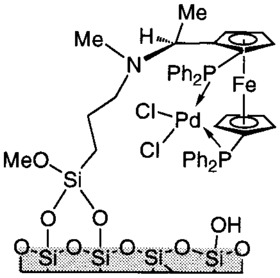


Figure 11. Chiral palladium complex tethered on MCM-41 via a silane-functionalized ferrocenyl ligand.[190]

catalytic activity of the heterogeneous catalyst, which was still active at Al/Zr ratios of 40, was significantly higher than that of the homogeneous system. Decreasing pore radii of the MCM-41 support were found to increase the molecular weight (M_n: $1.28 \times 10^{-3} \rightarrow 1.73 \times 10^{-3}$) and to change the physicochemical properties of the copolymer (liquid → wax). The large surface areas of the supported catalysts were proposed to suppress bimolecular deactivation processes.

Trimethylsilyl-pretreated MCM-41 materials of different average pore diameter were employed for the adsorptive separation of the structurally elusive MAO.[99] PMS materials prepared from a C_{16} surfactant were able to retain the most active fraction of co-catalyst MAO as shown for the Cp_2ZrCl_2-mediated (approximate molecular size 7.9 × 7.9 Å) polymerization of ethylene conducted independently with the "solution and solid fraction".

Chromium surface species generated by calcination of $Cr(acac)_3$-treated MCM-41 samples at 550−720 °C in oxygen were shown to be active in the gas-phase and slurry-phase polymerization of ethylene at 100 °C.[91] The catalytic performance of a Al−MCM-41-derived material was 14 kg of PE/(mol of Cr atm h), which is ca. a tenth of those of industrially applied Cr/SiO_2 catalysts (e.g., Union Carbide Catalyst, Figure 1/A), however, much better than those observed for Cr−Y zeolites. The same study revealed that purely siliceous MCM-41 and to a higher extent Al−MCM-41 display some catalytic activity in ethylene polymerization. The PE chains initially produced within the mesopores feature bundles of nanofibers of PE with a length of about 1 μm and a diameter of 50−100 nm. However, upon "prolonged" polymerization, the catalyst gradually fragments, producing crystalline and amorphous PE with a low bulk density and a high load melt flow index.

Tethering of a chiral catalyst derived from 1,1′-bis(diphenylphosphino)ferrocene and palladium(II) chloride to the inner walls of MCM-41 as shown in Figure 11 exerted a dramatic increase in regioselectivity and enantioselectivity in the allylic amination of cinnamyl acetate.[167] The anchored catalyst (50% preferred branched product/99% ee) was far superior to its homogeneous counterpart (2%/43%) and to a closely related nonporous carbosil-supported catalyst (<1%/racemate). A slightly modified catalyst displayed increased activity (TON 291) and enantioselectivity (17% ee) in the hydrogenation of ethyl nicotinate to ethyl nipecotinate relative to an analogous homogeneous silsesquioxane system (TON 98, racemate).[190] This catalytic behavior was ascribed to a chiral confinement of the catalytic center featuring a deliberately restricted spatial freedom in its vicinity. Apparently, *the design of highly stereoselective (enantiomeric) catalysts* is feasible...*when the active site is situated at the extremity of the tether, and is free to flutter in the molecular breeze during the process of the catalytic conversion*.[190]

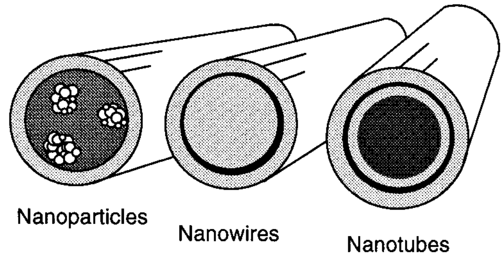
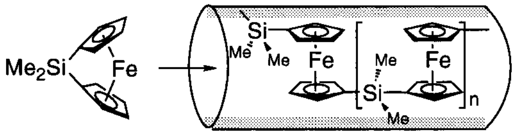


Figure 12. Nanostructures that can be templated inside cylindrical templates.[115]

Scheme 16. Ring-Opening Polymerization of a [1]Silaferrocenophane within the Channels of PMS

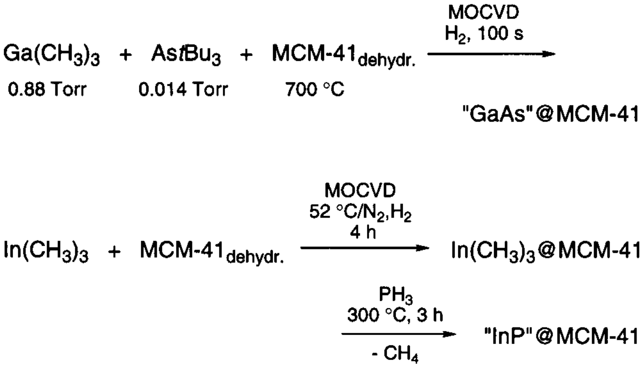


5.3. Implications for Material Science. The exploitation of PMSs as nanostructured host components is stimulated by the electronic systems technology and the search for devices with optoelectronic properties governed by low dimensionality.[4,149,216] PMS-based inorganic/inorganic and inorganic/organic composite materials can be designed as nanoparticles, nanowires, and nanotubes (Figure 12).[217] Inorganic and organic precursors were initially employed to construct nanowires inside the hexagonally arranged pores of MCM-41 with translational symmetry in two dimensions. Nanosized guest components introduced via salt impregnation and gas-phase deposition include GaN,[218] Si,[219] Ge,[220] Fe_2O_3,[221] Pt,[222] ZnO,[223] CdS,[224] Ag,[225] graphite-type carbon,[226] and polyaniline.[227] The application of organometallic precursors for the production of nanostructured materials with optoelectronic and magnetic functionality can fall back upon *m*etal *o*rganic *c*hemical *v*apor *d*eposition (MOCVD)[228] and sol−gel processes[229] established for the production of thin films of semiconductors and hard coatings.

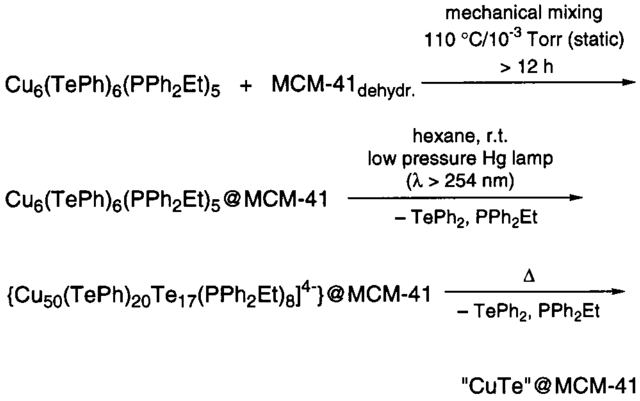
Solution and gas-phase impregnation techniques were applied to functionalize the dehydrated pore walls of MCM-41 with (1,1′-ferrocenediyl)dimethylsilane.[114−116] A multifunctional reaction originating from the susceptibility of [1]ferrocenophanes to nucleophilic attack by hydroxy groups and ring-opening polymerization under release of ring strain (Scheme 16)[230] was already detected at low loadings. Both ring-opened monomers and hyperbranched oligomers were asigned on the basis of MAS NMR spectroscopy.[114] At higher loadings additionally adsorbed monomer was converted into polymers between 75 and 200 °C accompanied by a color change from orange to yellow. Pyrolysis at 900 °C under nitrogen gave a black and magnetic ceramic without collapse of the ordered hexagonal structure.[115]

GaAs/MCM-41[103] and InP/MCM-41[104] heterostructures were synthesized by MOCVD techniques according to Scheme 17, employing common group 13 and group 15 sources. Quantum confinement effects[4,149]

Scheme 17. Generation of Quantum-Confined III−V Semiconductors inside MCM-41 by MOCVD



Scheme 18. Formation of a Telluride/Tellurolate Cluster inside MCM-41 [Cu$_{50}$(μ_3-TePh)$_{20}$Te$_{17}$(PPh$_2$Et)$_8$][PPh$_3$Et]$_4$ Was Observed in Solution[231]



brought about by the nanoparticle size regime of the semiconductor fillings were evidenced by blue shifting of the band gap dependent transition of the UV−visible absorption spectra and upfield shifting of the indium phosphorus resonance in the ^{31}P MAS NMR spectra. Although the interpretation of the photoluminescence spectra is hampered by the existence of large surface-deposited particles (e.g., 200-Å-thick GaAs layers), the photoluminescence maxima depend on the MCM-41 pore diameter supporting size-quantized semiconductor crystallites whose growth is restricted by the pore diameter of MCM-41. Application of HRTEM and PXRD corroborated these findings.

Impregnation of MCM-41 with heterobimetallic cluster [Co$_3$Ru(CO)$_{12}$][NEt$_4$] in THF, followed by thermal treatment under argon, produced highly dispersed magnetic nanoparticles with a narrow size distribution as evidenced by TEM; the dispersion was achieved under milder conditions compared to conventional metal salt precursors.[123] Dynamic and isothermal magnetic measurements revealed the formation of pore-confined magnetic metal particles as low as 250 °C.[231] Quantum-confined copper telluride nanoparticles were obtained through cluster condensation via thermal activation and photolysis of Cu$_6$(TePh)$_6$(PPh$_2$Et)$_5$ inside the pores of MCM-41.[94] Pore entrapment was suggested by UV−visible spectroscopy, PXRD, and nitrogen physisorption (Scheme 18).

Dimensionally ordered silicon nanowires were prepared by a novel supercritical fluid solution-phase technique.[232] The pores of PMS were rapidly filled by degrading diphenylsilane in a high-pressure reaction cell at 500 °C and a pressure of 375 bar for 15 min. Pore filling and structural order of the orange nanocomposite material were proven by nitrogen physisorption, PXRD, TEM, and MAS NMR spectroscopy. The blue-shifted absorption detected is likely associated with quantum confinement effects.

SOMC on mesoporous metal oxides further expands the fabrication of new materials with novel optoelectronic and magnetic properties. Particularly, transition metal oxide decorated pore walls allow distinct host−guest interactions. Their capacity for variable oxidation states, which is not shared by PMS analogues, can be exploited for, for example, the stabilization of mixed-oxidation state grains of type M^{n+}/M$^{(n+x)+}$. According to this strategy, (trimethylsilyl-silylated) mesoporous niobium oxide[233] was shown to act as an electron acceptor in a supermagnetic cobaltocene (Cp$_2$Co$^+$/Cp$_2$Co) composite,[234] for bis(arene) chromium ((C$_6$H$_6$)$_2$Cr$^+$/(C$_6$H$_6$)$_2$Cr) nanowires,[235] and for potassium fulleride (K$_3$C$_{60}$) nanowires.[236] The electronic properties of the niobium oxide host could be tuned by reduction with varying amounts of sodium naphthalene producing black, air-sensitive materials.[237]

6. Conclusions

Clearly, organometallic chemistry on periodic mesoporous silica, PMS, has to resemble that on amorphous and nonporous silica materials. However, changed surface morphologies and varying bulk effects afford subtle changes of surface attachment (e.g., podality Π^m) and electronic effects. In addition, the uniform composition and periodic structure of PMS materials produce well-defined nanoparticle replicas for the design of new chemicals and inorganic/organic composite materials. Nanosized cavities make these supramolecular systems ideal for use as precise reaction chambers accessible to an extended intraporous chemistry ("molecular factories"). Encapsulation and surface grafting yield confined nonagglomerated metal ligand species or nanoparticles, primarily by steric effects. Novel reaction pathways, arising from such sterically highly unsaturated metal centers surpass the phenomenology of contemporary molecular organometallic chemistry. An advanced concept of surface silylation will prove to be an efficient method for tailoring the meso- and microenvironment of nanostructured catalysts and to narrow the gap between nature and innovation. For example, extrusion polymerization of ethylene by metallocene-modified PMS mechanistically mimics the biosynthesis of cellulose[111] and metal alkoxide-grafted PMSs reveal analogies to vanadium bromoperoxidase in the catalytic peroxidative halogenation of large organic substrates at neutral pH.[92] A better understanding of the surface reactivity and attachment of the organometallic compounds/fragments and silylating reagents will be provided by the application of multivalent molecular model oxo surfaces (Figure 13).[238−240] Oligosilsesquioxane[238] and calix[*n*]arene[239] ligands seem to qualify as superior mimics despite considerable kinetic and thermodynamic limitations.

The promising liaison of PMS and (pseudo)organometallic chemistry is not restricted to the concept of postsynthetic surface derivatization through grafting.

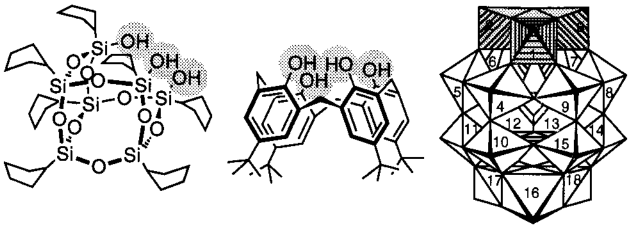


Figure 13. Molecular oxo surfaces for the modeling of SOMC@PMS.[238–240]

Ship-in-the-bottle techniques can be used to synthesize organometallic/inorganic composite materials as evidenced by the formation of $[Pt_{15}(CO)_{30}]^{2-}$ via impregnation of MCM-41 with H_2PtCl_6 and subsequent reductive carbonylation.[139] Metal alkoxide derivatives of, for example, aluminum, titanium, and niobium, are routinely employed to incorporate metal centers into the siliceous framework[241] and as a source for the synthesis of bulk mesoporous metal oxides according to a template-assisted sol–gel process.[242] Moreover, various organometallic reagents including CH_3ReO_3[243] and Cp_2TiCl_2[244] were used as dopants during hydrothermal synthesis. Finally, ferrocene-functionalized surfactant molecules[245] and silica precursor molecules[63,246] act as structure-directing reagents for the synthesis of mesostructured metal oxides.

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