

Design and Preparation of Organic–Inorganic Hybrid Catalysts

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I. Introduction

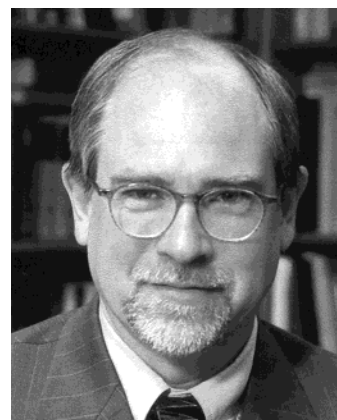
Solid catalysts provide numerous opportunities for recovering and recycling catalysts from reaction environments. These features can lead to improved processing steps, better process economics, and environmentally friendly industrial manufacturing. Thus, the motivating factors for creating recoverable catalysts are large.

Traditional heterogeneous catalysts are rather limited in the nature of their active sites and thus the scope of reactions that they can accomplish. Soluble organic catalysts can catalyze a much larger variety of reaction types than traditional solid catalysts but suffer from their inability (or high degree of difficulty) to be recycled. Since much is known about organic catalysts, the immobilization of these entities onto solids to create organic–inorganic hybrid catalysts can be accomplished with some aspects of design. The goal is to utilize the organic moiety as the active site and the solid to provide avenues to recovery and possibly recyclability of the organic active site.

These hybrids can be synthesized by a number of methods: (i) adsorption of the organic species into the pores of the support; (ii) construction of the organic molecule piece by piece within the confines



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of cavities of the support (the “ship-in-bottle” technique); (iii) attachment of the desired functionality to the support by covalent bond formation; (iv) direct synthesis into the final composite material. The types

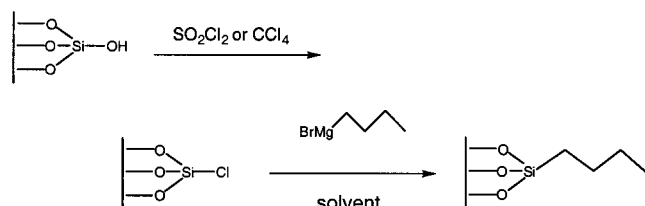
of solids used can be organic, e.g., polymers,^{1,2} or inorganic, e.g., silica and alumina. This review will focus on work reported since 1995 that involves the synthesis and catalytic applications of organic–inorganic hybrid materials (we will not discuss polymeric solids) where the organic functionality is covalently attached to porous inorganic solids. Organometallic complexes attached to the solids are discussed elsewhere in this issue. Here, we specifically address the use of organic–inorganic hybrid materials for use as catalysts. A recent special issue of *Chemistry of Materials* has compiled selected topics concerning organic–inorganic composites and deals with both the materials science and catalytic applications of these materials.³

II. Organic–Inorganic Hybrid Materials

A. Grafting of the Organic Moiety onto Solid Surfaces

There are numerous methods that have been utilized to attach organic groups to silica surfaces via the formation of covalent bonds. Chlorination of the silica surface followed by subsequent reaction with Grignard reagents can be used to form silicon–carbon bonds (Scheme 1).⁴ The use of Grignard reagents

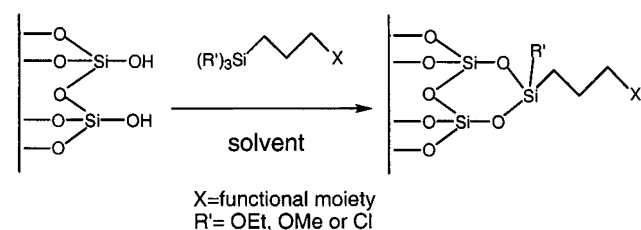
Scheme 1. Chlorination and Subsequent Reaction with a Grignard Reagent to Functionalize Silica



limits the variety of functional groups that can be tethered to the surface. However, the formation of a silicon–carbon bond between the organic moiety and the surface is desirable because of the stability of the Si–C bond.⁵

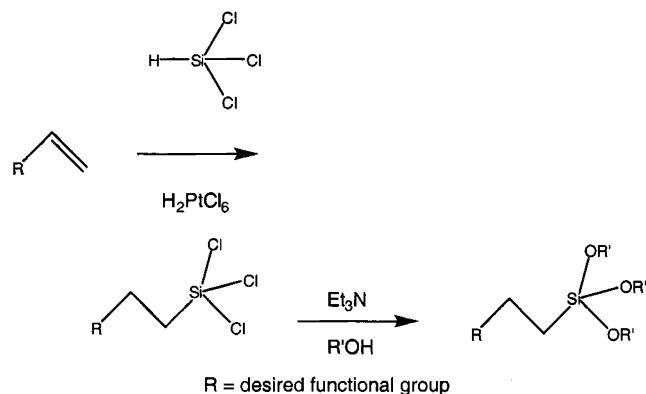
Another well-studied technique of silica surface functionalization is the grafting of organic groups onto a silanol-containing surface using a trichloro- or trialkoxy-organosilane (Scheme 2). Numerous

Scheme 2. Example of Grafting Organosilanes onto a Silanol-Containing Surface



organosilanes are commercially available. Additionally, techniques for synthesizing organosilanes are documented in the literature (e.g., Scheme 3).^{6–8} The availability of the silanol groups can determine whether the grafted silicon atom is tethered via one, two, or three silicon–oxygen bonds. These types of

Scheme 3. Synthetic Route to Organosilanes (Adapted from Ref 6)



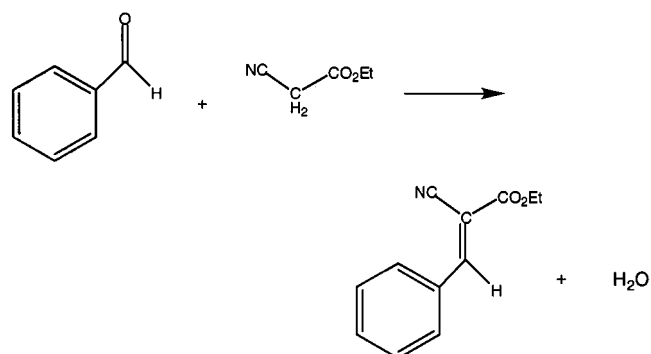
silicon atoms are denoted as T¹ (MeSi(OSi)(OR')₂), T² (MeSi(OSi)₂(OR')), and T³ (MeSi(OSi)₃) sites, respectively. The R' functionality can be either an alkyl or H (if water is present to cause the hydrolysis). In the absence of water, the chloro-organosilanes require an amine, e.g., triethylamine, for the reaction with surface silanols to proceed. This is not the case with alkoxy-organosilanes.

Several reviews concerning grafting on silicas have been published.^{5,9} Depending on the organosilane and available number of surface silanol groups, organic loadings of 0.3–2 mmol/g of solid can be obtained.⁵ The covalently attached organic groups can be sufficiently stable for recycling and reuse, and can easily be modified to create a variety of catalytic sites.

1. Amorphous Solid Supports

For catalytic applications, aminopropyl-functionalized silicas have been the most widely studied organic–inorganic hybrid solids. Angeletti and co-workers showed that these hybrid organic–inorganic solids can be effective base catalysts for the Knoevenagel condensation reaction (Scheme 4) at room

Scheme 4. Knoevenagel Condensation of Benzaldehyde and Ethyl Cyanoacetate

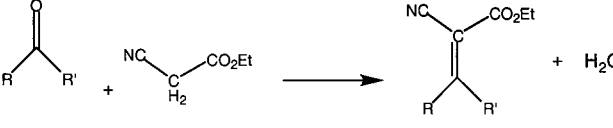


temperature in continuous flow reactors.¹⁰ The aminopropyl–silica gave yields of 66–98% for condensations of a variety of aldehydes and cyclohexanone. The loading of the amino groups was 0.79 mmol/g of silica, and the catalyst could be recycled. The basicity of the primary amine was not sufficient to catalyze the Michael addition reaction as would be expected from soluble amine reactions. However, Angeletti et al. did find that, in addition to the immobilization,

the surface provided other effects. That is, the hydrophilic silanol groups on the surface improved reaction rates by strongly adsorbing the product water molecules.¹¹

Macquarrie and co-workers later reported the use of aminopropyl–silica as a base catalyst.¹² The catalyst gave yields of 8–99%, depending on the substrate, at levels of 10 mmol of catalyst/mol of substrate (Table 1). As expected, aldehydes showed

Table 1. Knoevenagel Condensation of Various Aldehydes and Ketones with Ethyl Cyanoacetate in Cyclohexane Using Aminopropyl-Silica (from Ref 12)



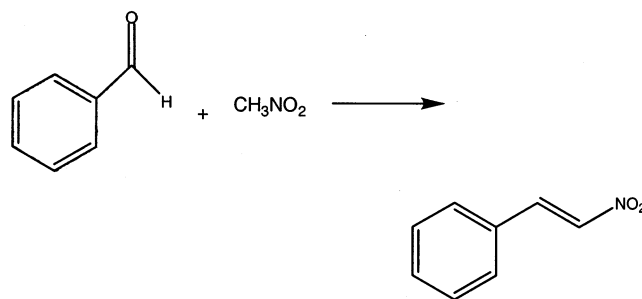
	R	R'	temp (°C)	time (h)	yield (%)
1	Ph	H	25	4	99
2	<i>n</i> -C ₅ H ₁₁	H	25	7	97
3	<i>n</i> -C ₇ H ₁₅	H	25	8	98
4	<i>cyclo</i> -C ₅ H ₁₀		82	1	98 ^a
5	Et	Et	82	2	97 ^a
6	Et	Et	82	4	65
7	<i>n</i> -C ₄ H ₁₀	Me	82	4	98 ^a
8	<i>tert</i> -C ₄ H ₁₀	Me	82	24	22 ^a
9	Me	Ph	82	24	68 ^a
10	Ph	Ph	82	72	8 ^a

^a Water removed during reaction by a Dean–Stark trap.

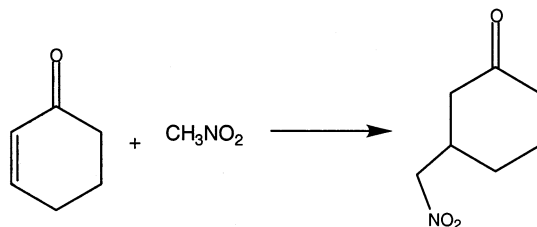
greater reactivity than ketones, and 100% yields could be approached. The loading of amino groups was around 1 mmol/g of silica. Yields in the ketone reactions improved as water was removed during the course of the reaction (compare entries 5 and 6 in Table 1). Although the catalyst could be reused by decanting of the product mixture and adding new reactants, it was deactivated after isolation from the solution and exposure to atmosphere. Infrared spectroscopy of the poisoned catalyst suggested the formation of amide groups from the reaction of the surface aminopropyl group with the ester of ethyl cyanoacetate. Additionally, the effect of solvent on the reaction rate was studied. Increases in the polarizability of the solvent decreased the reaction rate (cyclohexane > hexane > toluene > 1,2-dichloroethane > chlorobenzene). It was speculated that the low-polarity solvents were favored because of the partitioning effect onto the silica surface. That is, the polarity of the surface encourages the reactants to leave the nonpolar solvent phase and move to the surface to react with the amine groups.

The catalytic effects of grafted primary, secondary, and tertiary amines on silica have been investigated using base-catalyzed reactions such as the nitroaldol condensation and Michael addition reactions (Schemes 5 and 6, respectively).¹³ It was found that, in the supported amine systems, the catalyst activity followed the order primary > secondary > tertiary. A mechanism for the nitroaldol condensation on the supported catalyst was hypothesized on the basis of previous reports of imine formation with this type of catalyst in solution (Scheme 7).¹⁴ Experimental results from infrared spectroscopy of the working

Scheme 5. Example of a Nitroaldol Condensation



Scheme 6. Example of a Michael Addition Reaction

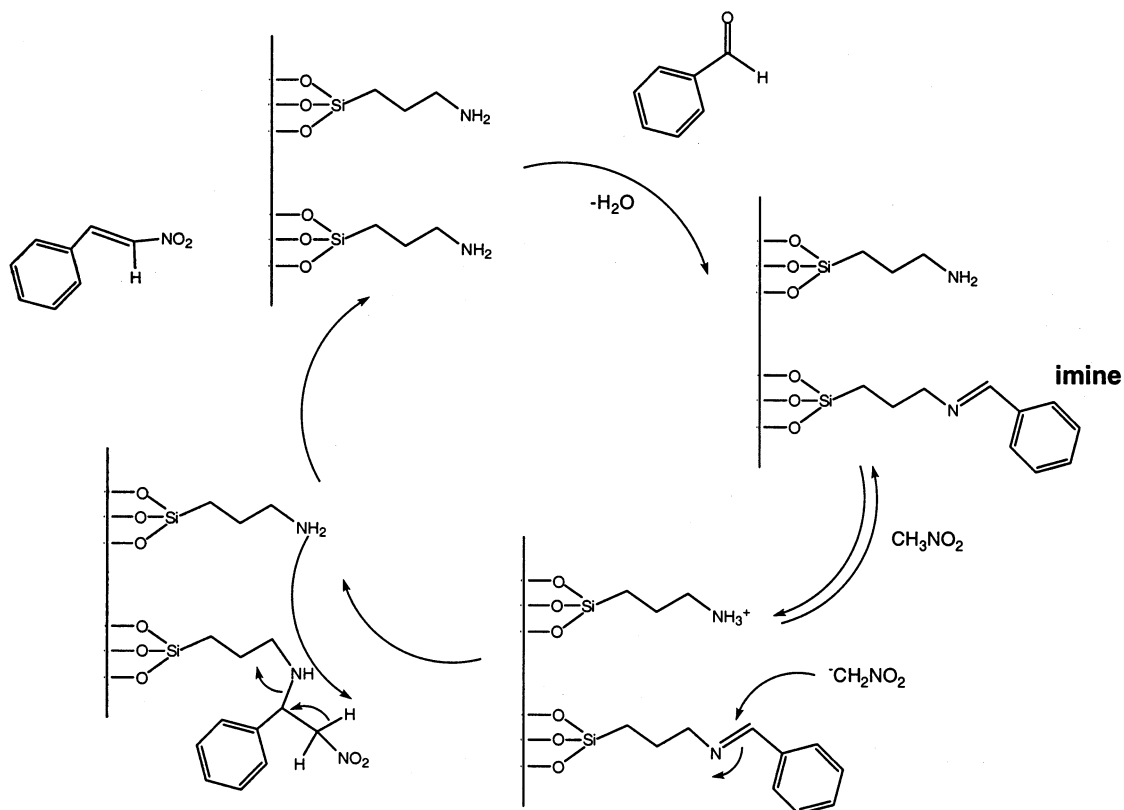


catalyst were consistent with the proposed mechanism.¹³ Variations in the substitution of the aromatic ring of the aldehydes showed little effect on the yield and selectivity of the aminopropyl-functionalized silica catalyst.

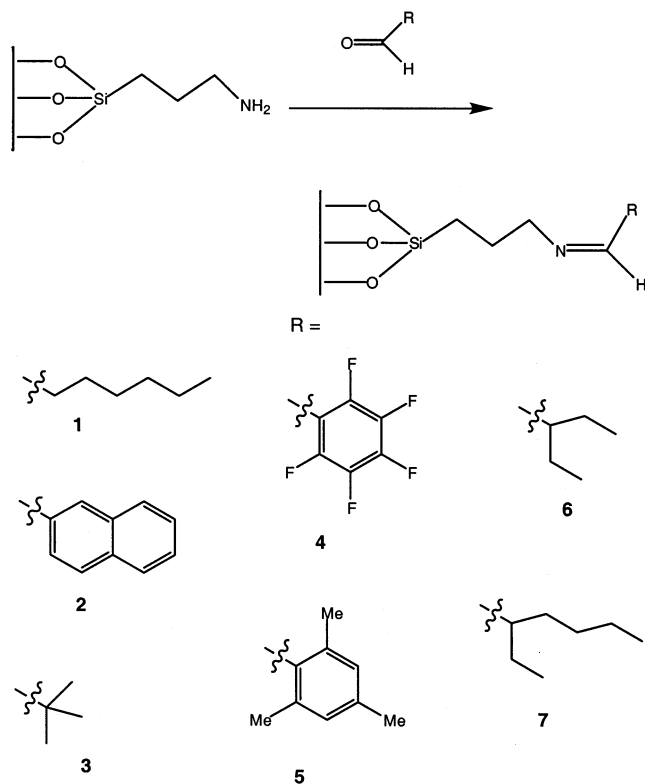
Utting and Macquarrie have investigated the use of the imine-based active sites for catalyzing the Knoevenagel condensation and Michael addition reactions.¹⁵ A variety of imine-supported silicas were prepared by modifying grafted aminopropyl–silicas (Scheme 8). IR spectroscopy confirmed the imine formation by the appearance of bands in the range of 1690–1640 cm⁻¹. Yields in the Knoevenagel condensation of pentan-3-one and ethyl cyanoacetate ranged from 23% to 99% after 5–6 h, depending on the substituent on the imine catalyst (Table 2). Substituent effects were shown to be significant in the activity of the catalyst. The Michael addition reaction of nitromethane and 2-cyclohexen-1-one gave yields of 45–58% for some of the imine catalysts tested. The stability of a phenolate-based catalyst showed that the imine bond was intact in alcohol solutions but was cleaved in acidic or basic solutions. Most of the bond cleavage (40–60% of phenolate groups lost) occurred within the first 5 h of contact with the solution media.

More recently, Macquarrie and co-workers examined guanidines tethered to silica as base catalysts for epoxidation reactions.^{16,17} The guanidine functional groups were attached either by modification of a grafted chloropropyl group or by synthesis of the guanidine silane with subsequent grafting (Scheme 9). Conversions of cyclohexenone to epoxide ranged from 40 to 85%, depending on the support and method of tethering. The grafted guanidine silane-based amorphous silica had a loading of 1.1 mmol/g of solid. These catalysts gave 55% conversion and the lowest selectivity to epoxide (42%). A guanidine-based catalyst prepared by grafting onto MCM-41 (which is referred to as “micelle templated silica”, MTS) had both improved conversion and selectivity (85 and

Scheme 7. Proposed Mechanism of Nitroaldol Condensation (Adapted from Ref 13)



Scheme 8. Imine Silica Preparation from Aminopropyl-Silica (Adapted from Ref 15)



65%, respectively) compared to the amorphous silica. It was observed that passivation of the surface hydroxyl groups by *N,O*-bis(trimethylsilyl)acetamide was required to prevent significant decomposition of the hydrogen peroxide that was used as the oxidant.

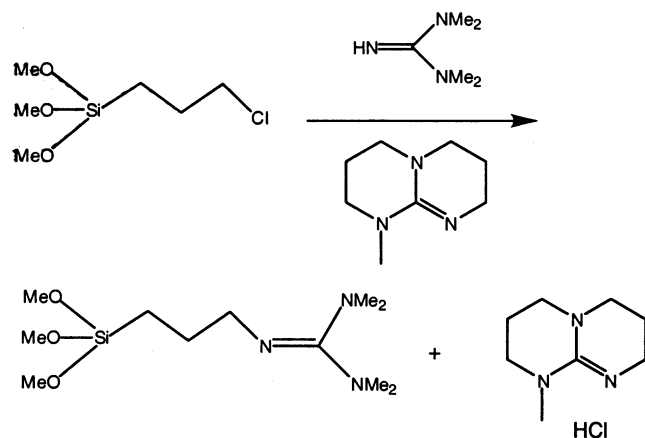
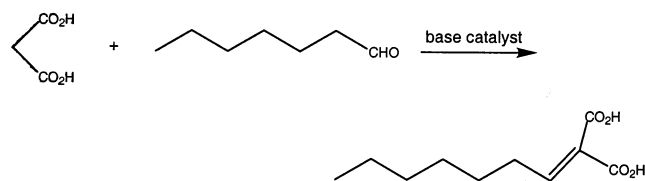
Table 2. Knoevenagel Condensation of Ethyl Cyanoacetate and Pentan-3-one Using Imine-Based Silica Hybrids (from Ref 15)

imine ^a	% yield with time						
	0.5 h	1 h	2 h	3 h	4 h	5 h	6 h
1	6.0	9.2	13.6	16.3	17.9	19.4	23.3
2	27.5	50.6	69.1	69.2	76.0	75.7	
3	44.0	58.1	69.8	72.7	76.7	82.8	
4	16.5	23.4	29.8	31.6	32.5	33.7	34.8
5	38.0	53.7	67.1	72.7	74.4	79.0	80.1
6	67.2	69.3	81.5	88.2	92.9	98.6	99.5
7	37.6	49.4	70.5	74.9	80.3	86.8	86.2

^a Imine-based silica hybrid formation depicted in Scheme 8.

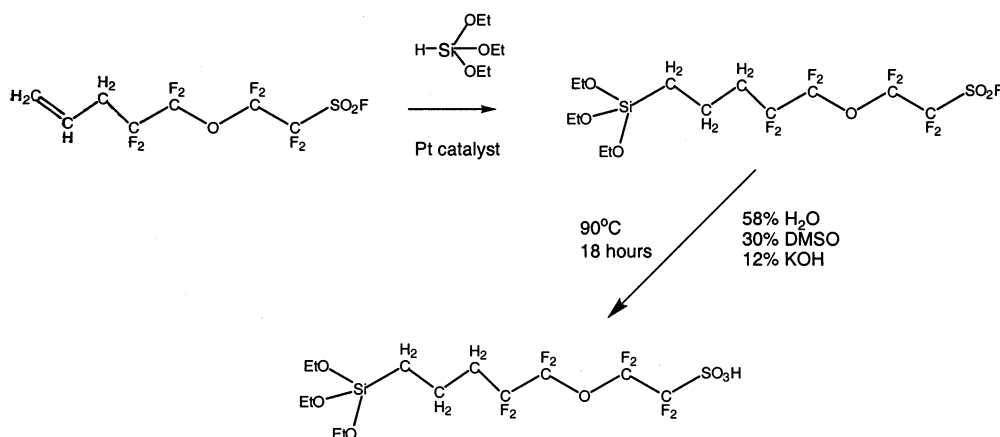
Passivation of the unreacted silanol groups was performed after grafting of the chloropropyl group. All of the guanidine-based catalysts produced a number of side products. One of the major side products, 3-methoxycyclohexanone, was formed by the Michael addition of the solvent, methanol, to cyclohexenone. A change of solvent to 2-propanol resulted in higher selectivity of 93% to the epoxide, but the overall conversion decreased to 34%.

Using guanidine-grafted hybrid silicas, Macquarrie et al. reported the ability to catalyze the Linstead variation of the Knoevenagel condensation to react malonic acid with aldehydes (Scheme 10).¹⁷ The guanidine catalysts were used to promote this reaction instead of triethylamine that typically functions as both catalyst and solvent. High temperatures are usually required for the homogeneous reaction. The elevated temperatures normally cause the malonic acid to degrade by decarboxylation, and excess quantities of the acid must be used to achieve desirable

Scheme 9. Synthesis of Guanidine Organosilanes
 (Adapted from Ref 17)

Scheme 10. Linstead–Knoevenagel Condensation
 (Adapted from Ref 17)


amounts of product. The supported guanidine catalyst gave conversions of 78–95%, with selectivities of 50% using only stoichiometric amounts of malonic acid.

Acid functional groups have also been used as organic modifiers to silica surfaces. Harmer and co-workers have attached a perfluorosulfonic moiety onto silica for use in acid catalysis applications.¹⁸ The perfluorosulfonic group is a strong acid and has excellent chemical and thermal stability. The perfluorosulfonyl fluoride silane (Scheme 11) was synthesized in a manner similar to the hydrosilylation procedure previously described (Scheme 3), using the corresponding olefin. The acid sites were generated by hydrolysis of the perfluorosulfonyl fluoride functionality. Harmer also reported the use of the perfluorosulfonic acid silane in the co-condensation of silica, using traditional sol–gel techniques. Activities of both the grafted and co-condensed silica hybrids

Scheme 11. Synthesis of Perfluorosulfonyl Fluoride Silane and Subsequent Hydrolysis to the Perfluorosulfonic Acid Silane (Adapted from Ref 18)


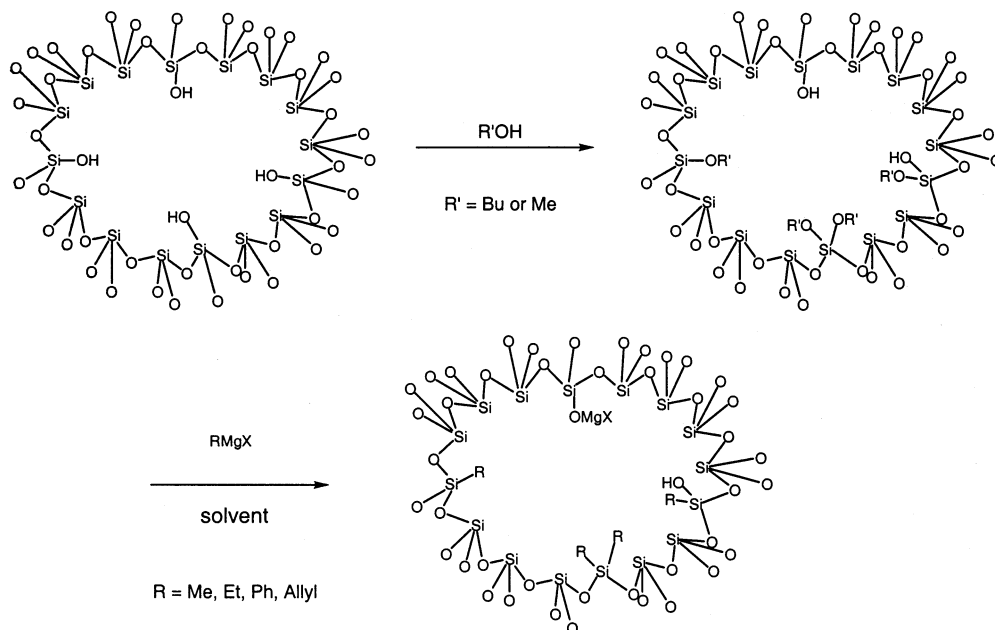
were reported as similar. The grafted acid catalyst was tested in several acid-catalyzed reactions, such as aromatic alkylation, alkene isomerization, and Friedel–Crafts acylation, and the respective conversions were 99, 95, and 89%. In the alkylation and isomerization reactions, the hybrid catalyst significantly outperformed some of the alternative solid resin catalysts currently used, e.g., Nafion resin NR 50 and Amberlyst-15. The hybrid catalyst achieved a conversion of 43% for the alkylation of benzene with dodec-1-ene at 80 °C for 1 h, conditions where the traditional acid resins gave 3–5%. It is interesting to note that the acid loadings of the solid catalysts are 0.2, 0.9, and 4.6 mequiv of H⁺/g of catalyst for the hybrid silica, Nafion NR 50, and Amberlyst-15 resins, respectively. Despite lower number density of acid sites, the hybrid silica catalyst still outperformed the resins in the reactions reported.

2. Ordered, Mesoporous Solids

The amorphous solids discussed above have large distributions in pore diameters and void volumes. The ordered, mesoporous materials, e.g., the M41S family of solids,^{19,20} have relatively uniform pore sizes and void volumes. The pore sizes of these materials can be tailored on the basis of the synthesis method used and can range from about 15 to 100 Å. Larger pore sizes of 50–300 Å can also be obtained in the SBA family of solids, e.g., SBA-15.^{21,22} The ordered, mesoporous materials can serve as more well defined supports than amorphous solids onto which organic groups can be grafted.

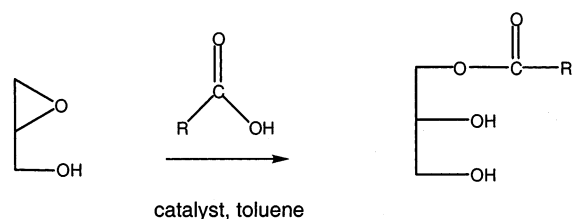
The grafting of organic functional groups onto ordered, mesoporous materials has been accomplished, and these hybrid solids have been used as catalysts.^{5,20,23,24} Numerous functionalized propyltri-alkoxy silanes have been employed to tether organic moieties onto the mesoporous silicas, and ¹³C MAS NMR was used to verify the integrity of the grafted groups. Additionally, nitrogen sorption isotherms reveal decreased amounts of pore volume as the grafted organic moiety size increased.²⁵

Grignard reagents can be used in functionalizing mesoporous materials.²⁶ In addition to the chlorinating procedures mentioned above for amorphous silicas (Scheme 1), etherification of the surface can be

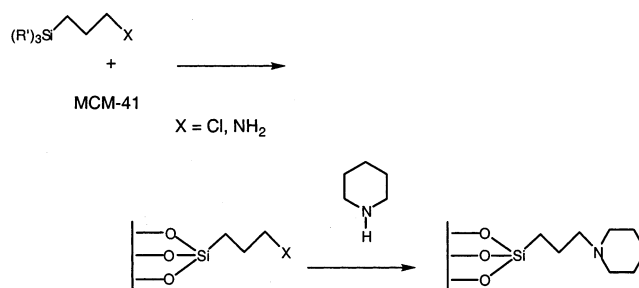
Scheme 12. Etherification and Grignard Modification of the Ordered, Mesoporous Materials (Adapted from Ref 26)

accomplished with alcohols (Scheme 12). The etherification prevents surface silanol groups from reacting with the Grignard reagent to form Si–O–MgX bonds. The Grignard reagent cleaves Si–OR' functionalities to form a carbon moiety attached directly to surface Si. However, this procedure gave surface silicon atoms with multiple organic groups attached ($\text{Me}_2\text{Si}(\text{OSi})_2$ and $\text{Me}_3\text{Si}(\text{OSi})$). The formation of these sites was attributed to the breaking of the framework Si–O bonds. It was speculated that the harshness of the refluxing alcohol temperatures for the etherification caused the cleavage and hydrolysis of the Si–O–Si framework bonds. Replacement of butanol with methanol to lower the refluxing temperature eliminated $\text{Me}_3\text{Si}(\text{OSi})$ sites but not $\text{Me}_2\text{Si}(\text{OSi})_2$ sites, indicating that some framework hydrolysis still occurred. Bulkier substituents on the Grignard reagents gave lower organic incorporation in the final organic–inorganic hybrid material.

Traditional catalysts for α -monoglyceride synthesis (Scheme 13) are tertiary amines and ammonium

Scheme 13. Monoglyceride Synthesis from Glycidol and Fatty Acids

salts, but they are difficult to isolate from the product. Brunel and co-workers introduced amine species into MCM-41 silicas by the grafting method and used the solids as base catalysts (Scheme 14).²⁷ The materials were analyzed by IR and MAS NMR spectroscopy, elemental analysis, and thermogravimetry. Pore sizes of around 31 Å and high pore volumes were obtained. Pure-silica MCM-41 and chloropropyl-

Scheme 14. Preparation of Amine-Containing MCM-41 Hybrids for Monoglyceride Synthesis (Adapted from Ref 27)

grafted MCM-41 did not provide catalytic activity as expected. However, it was shown that the surface silanol groups caused the glycidol to polymerize. For the amine-containing catalysts, the polymerization competed with monoglyceride synthesis to give yields of 16–70% monoglyceride. The piperidine-functionalized MCM-41 was more active than the primary amine-containing solid. The steric hindrance around the piperidine was speculated to prevent the glycidol from reaching the surface and thus limited the side polymerization to give improved yields. Unreacted silanol groups were passivated by the addition of hexamethyldisilazane vapor. Poisoning of the surface silanol sites increased the yields from 62 to 90%.

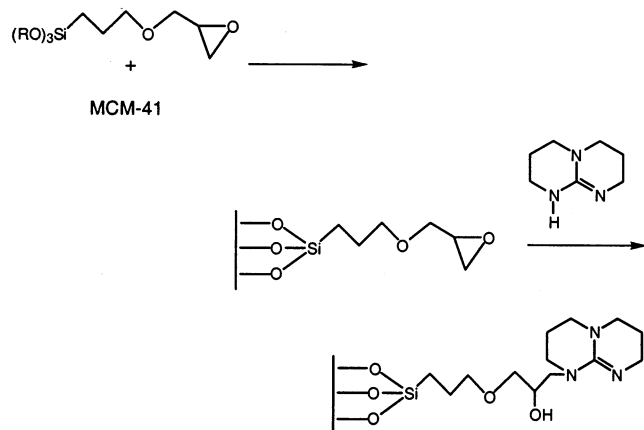
Amine-containing-MCM-41 mesoporous materials were studied by Brunel and co-workers as catalysts for the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate.¹⁴ Nucleophilic displacement of chloro- and iodopropyl-MTS materials by piperidine were used as catalysts and compared to piperidine alone as a homogeneous base catalyst. The solids were investigated by IR and ¹³C MAS NMR spectroscopy, X-ray diffraction, and nitrogen sorption. Organic loadings of 0.7–1.7 mmol/g were obtained, and the available pore volume decreased with increased functional group size. The primary amine was more

active than piperidine, nearing 100% yield after 2 h. A mechanism was proposed that involved imine formation of the primary amine with the aldehyde (similar to the nitroaldol condensation shown in Scheme 7). This mechanism was supported by the observed activity of the primary vs tertiary amine. Both catalysts (aminopropyl and piperidinopropyl) were recyclable.

Sartori and co-workers used aminopropyl-functionalized MCM-41 as a catalyst for the nitroaldol condensation of aldehydes and nitroalkanes.²⁸ The activities of the amine sites were found to follow the order primary > secondary > tertiary (98, 34, and 5% yields, respectively, under identical reaction conditions). The mechanism for the reaction was speculated to be through the formation of an imine, as described above. Recycling of the primary, aminopropyl catalyst was reported, and consecutive yields of 98, 95, 95, 90, and 84% in 5 sequential reactions were obtained.

Jacobs and co-workers introduced a guanidine moiety into MCM-41 via grafting methods.²⁹ MCM-41 (or amorphous silicas) were grafted with (((trimethoxysilyl)propoxy)methyl)oxirane and then reacted with 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) to create guanidine base catalysts (Scheme 15). The

Scheme 15. Synthesis of Guanidine Hybrid Materials (Adapted from Ref 29)



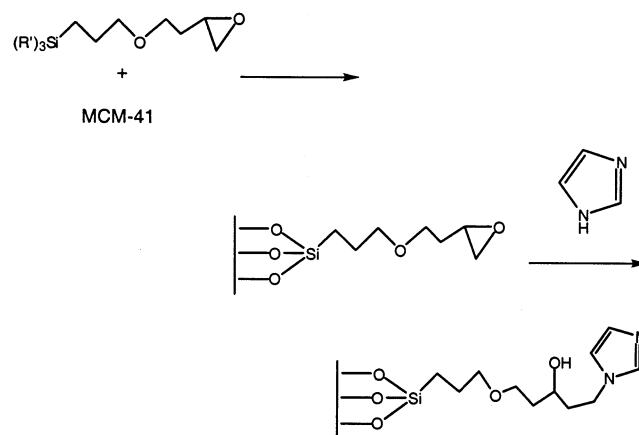
investigators used an oxirane ring opening reaction to attach the TBD to take advantage of mild synthesis conditions (298 K for 10 h) and to prevent the formation of acids (HCl and HBr) that could poison the base sites. Successful synthesis of the hybrid material was verified by NMR and IR spectroscopies and nitrogen sorption. The catalyst was active for the Michael addition of ethylcyanoacetate or diethyl malonate to various ketones and enones and gave yields of 34–100%. Reaction conditions were mild (313–353 K), and the rates were fast (reaction completed in 0.5–5 h). The most difficult reaction was the addition of diethyl malonate to cyclohexenone, which required 60 h to achieve only 2.7% yield at 353 K. Additionally, the reaction of ethyl cyanoacetate with methyl vinyl ketone gave 34% yield using the TBD-containing MCM-41 solid but only 7% for the TBD-containing amorphous silica hybrid under identical reaction conditions. It was speculated that, in general, the MCM-41 hybrids are more active as

catalysts than the amorphous silica counterparts due to higher organic loadings. The utility of the MCM-41 hybrid was further demonstrated by use in the Knoevenagel condensation of ethyl cyanoacetate or malononitrile with various aldehydes at extremely mild conditions (293–343 K). Yields ranged from 9 to 98%, depending on the reactants.

Kantam and Sreekanth have recently used the TBD-containing MCM-41 hybrid materials as base catalysts to perform transesterifications of β -keto esters.³⁰ The hybrid materials were prepared by grafting of (((trimethoxysilyl)propoxy)methyl)oxirane onto MCM-41 and subsequent modification with TBD, as described above (Scheme 15). The TBD-containing materials were active as catalysts for transesterifications by a wide variety of alcohols, giving yields of 45–100%, depending on the ester and alcohol. The catalyst was active with primary, secondary, tertiary, allyl, and alkynic alcohols, where they were aliphatic (saturated and unsaturated) or aromatic. The catalyst was recyclable for several reaction cycles, showing only slight loss in yield.

Recently, imidazole groups were grafted onto mesoporous materials for use as base catalysts in the Knoevenagel condensation between ethyl cyanoacetate and benzaldehyde.³¹ The immobilization was performed through an alkoxy silane linking, (3-(glycidyloxy)propyl)trimethoxysilane, similar to the guanidine work by Jacobs et al. (Scheme 16). The meso-

Scheme 16. Immobilization of Imidazole on Ordered, Mesoporous Materials (Adapted from Ref 31)

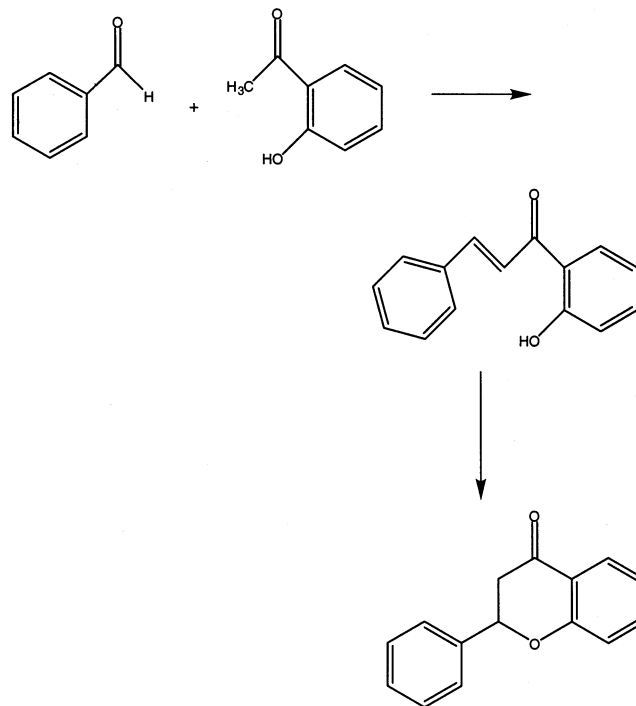


porous materials MCM-41, MCM-48, KIT-1, SBA-1, and SBA-15 were used as the supports. Functional group attachments were verified by IR spectroscopy. Loadings on KIT-1 of 0.65–1.80 mmol/g of support were obtained. About 50% of the (glycidyloxy)propyl functionalities reacted with imidazole to form a supported base moiety. Conversion with the imidazole-KIT-1 catalyst was 64%, which is less than the homogeneous imidazole-catalyzed reaction (96%) at similar reaction conditions. Repeated use of the solid catalyst showed a decrease in conversion. It was speculated that the active sites were poisoned due to benzoic acid contamination in the benzaldehyde. Treatment of the recycled catalyst with 2% KOH/ethanol improved its reactivity.

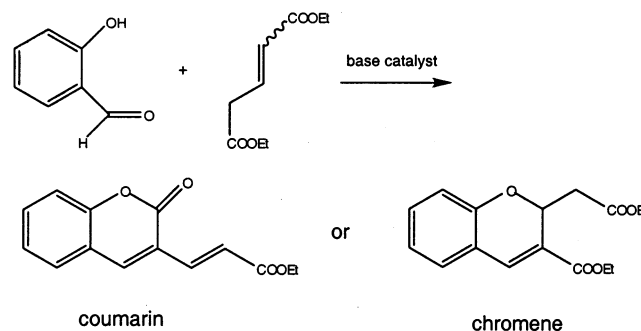
Corma and co-workers grafted a quaternary ammonium-containing organosilane onto MCM-41 silica^{32,33} for use as a Bronsted base catalyst. A commercially available quaternary ammonium chloride organosilane was grafted onto MCM-41, followed by ion exchange to the hydroxide form. Ion exchange of the chloride to hydroxide was accomplished with a 0.21 M solution of tetramethylammonium hydroxide ((TMA)OH) in methanol (MeOH). Ion exchange was allowed to occur for 10 min, after which the solids were isolated and washed thoroughly with MeOH. The structure of MCM-41 remained intact after the ion exchange, and ²⁹Si MAS NMR and elemental analyses indicated no leaching of organic groups occurred. Most of the quaternary sites were exchanged to hydroxyl anions.³³ The organic loadings were 0.88–1.22 mmol/g, and the catalysts were active for the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate, giving conversions of 77–88% after 2 h at 60 °C in CHCl₃ as solvent.³² Rodriguez et al. showed that good yields were obtained with high polarity solvents (EtOH > CH₃CN > HCCl₃ > Cl₄C).³³ However, conversions improved to 90–95% in 30 min under solvent-free conditions. Recycling of the catalyst showed no deactivation or leaching. The initial rates of reaction were proportional to the number of organic moieties, indicating full accessibility of the organic groups within the support. Michael addition reactions of various ketones with ethyl cyanoacetate were also accomplished with these grafted solids. The catalysts were very selective for the Michael addition product. Conversions of 35–72% were obtained within a few hours, at temperatures ranging from 20 to 80 °C. These reaction conditions were more mild than those used with other solid base catalysts such as Cs–MCM-41.³⁴ The hybrid solid was also able to catalyze the aldol condensation and subsequent intramolecular Michael addition of benzaldehyde and 2'-hydroxyacetophenone to yield flavanone at 130 °C in a solvent-free reaction (Scheme 17).³³ Conversion of 65% with a 78% selectivity was obtained in 8 h.

Rodriguez et al. reported the use of their Bronsted base catalyst in the synthesis of chromenes and coumarins (useful as pharmaceutical intermediates, dyes, and fragrances).³³ These compounds can be synthesized by the base-catalyzed condensation of salicylaldehydes with diethyl 2-pentenedicarboxylate (Scheme 18). Use of the hybrid solids as catalysts produced the chromene with selectivities as high as 90%. Conventional liquid bases, such as piperidine, have greater selectivity to coumarins. Rodriguez et al. speculated that a mechanism such as described in Scheme 19 could explain the observed behavior. The intermediate phenoxide anion was formed in both pathways, but the subsequent cyclization to chromene was faster than to coumarin. The formation of coumarin involved the elimination of an ethoxy group. In order for the coumarin to preferentially be formed, the ethoxy leaving group must be stabilized; a strong base catalyst can effect this stabilization. Rodriguez and co-workers used (dimethylamino)naphthalene (DMAN) as a base catalyst to probe the reaction mechanism in an attempt

Scheme 17. Aldol Condensation and Intramolecular Michael Addition of Benzaldehyde and 2'-Hydroxyacetophenone to Flavanone

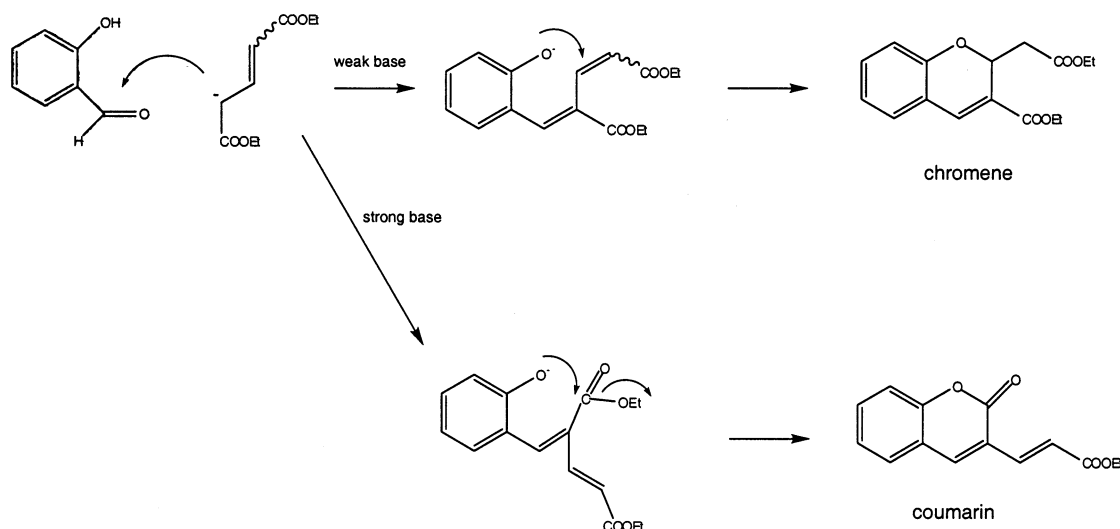


Scheme 18. Synthesis of Coumarins and Chromenes via Base-Catalyzed Condensations

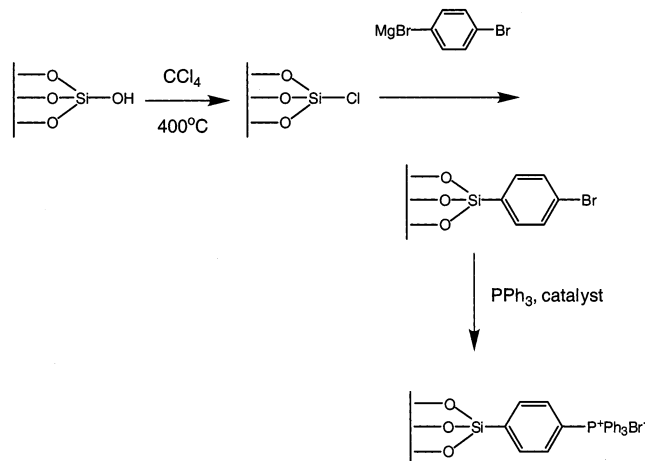


to explain the observed selectivity. The basicity of the DMAN could be controlled by choice of solvent. Results showed that the chromene pathway is preferred for base catalysts of lower strength, while coumarins are formed with stronger bases, as expected from the proposed mechanism. (TMA)OH in solution is a stronger base than the hybrid solid, and it showed greater selectivity to the coumarin formation.

Catalysts for use in triphasic reactions have also been prepared by immobilizing phase transfer catalysts (PTC) onto silica.³⁵ The immobilization of P⁺R₄X⁻ or N⁺R₄X⁻ onto a solid allows the quaternary site to act at the phase boundary between an organic and aqueous phase.³⁶ The heterogenization of the organic catalyst allows for easy recovery, which is not often possible with the homogeneous equivalent.³⁶ Traditional triphasic, heterogeneous catalysts are phase transfer catalysts immobilized onto polymer resins, and chemical and thermal stabilities are often major issues with the resin catalysts. The inorganic solids are normally more stable to harsh chemical environ-

Scheme 19. Proposed Mechanism of Coumarin and Chromene Formation (Adapted from Ref 33)

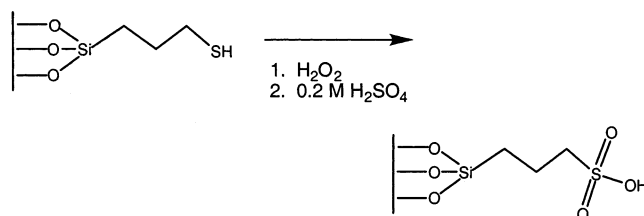
ments and higher temperatures. Phase transfer silica-based catalysts were synthesized by first being chlorinated with carbon tetrachloride at elevated temperature (Scheme 20).³⁵ Functionalization via

Scheme 20. Preparation of Silica-Supported Phase Transfer Catalysts (Adapted from Ref 35)

brominated Grignard reagents was then performed. Finally, after washing and drying, the functionalized silica was reacted with triphenylphosphine under reflux. The quaternization reactions were catalyzed by either nickel(II) bromide trihydrate (NiBr_2) or palladium diacetate ($\text{Pd}(\text{OAc})_2$). The hybrid solids were characterized by ^{13}C MAS NMR, elemental analyses, and IR spectroscopy. Organic loadings were approximately 0.4 mmol/g of brominated functional group at the intermediate step and 0.3 mmol/g of quaternized phosphonium in the final catalyst (based on elemental analyses). Clark and co-workers showed that the catalysts were thermally stable, recyclable, and active for nucleophilic substitution and oxidative bromination reactions. Decomposition of the phosphonium group was observed only at temperatures over 300°C . The unsupported phase transfer catalysts catalyzed the oxidative bromination of benzene in the presence of hydrogen peroxide with yields of 24–44% in 1 h. Silica-supported PTCs also catalyzed this reaction and were recyclable,

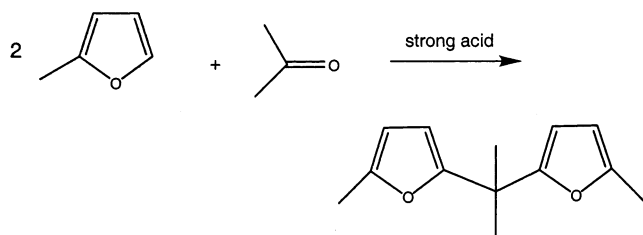
although they had lower activity (5% yields). The yields could be improved to 16% by pretreating the catalyst with ultrasound to remove trapped gas pockets. The hybrid solids also overcame poor solubility issues with traditional PTCs and worked in a greater variety of solvents.⁵

Acid sites have also been incorporated into ordered, mesoporous materials. Jacobs and co-workers prepared acid-containing hybrid solids by both grafting and co-condensation (see below) methods.^{37,38} When the hybrid materials were prepared by grafting, MCM-41 silicas were first grafted with (3-mercaptopropyl)trimethoxysilane (MPTS).³⁸ The materials were characterized by IR (to show the S–H vibration at 2575 cm^{-1}) and ^{13}C MAS NMR. It is noteworthy to mention that dimerization of the thiol groups can occur at the relatively high functional loadings obtainable in mesoporous materials. The resulting disulfide groups were detected in small amounts by ^{13}C MAS NMR. The thiol functionalities were then oxidized into sulfonic acid groups by hydrogen peroxide (Scheme 21). Functional group loadings were

Scheme 21. Oxidation of Mercaptopropyl-Functionalized Silicas To Give Sulfonic Acid Sites (Adapted from Ref 38)

1.0–1.5 mmol/g of sulfonic acid sites as determined by TGA and titration. The percentage of mercaptopropyl groups that were oxidized to acid sites was not reported. The acid catalysts were tested in the reaction of 2-methylfuran with acetone to produce 2,2-bis(5-methylfuryl)propane (DMP) (Scheme 22). Acidic zeolites (H-USY , H-*BEA) were used for comparison to the hybrid solid and quickly deactivated due to oligomerization of the furan. The sulfonic acid-functionalized mesoporous materials showed

Scheme 22. Acid-Catalyzed Addition of 2-Methylfuran and Acetone



conversions of about 57% with selectivities of 92%. The recyclability of the catalysts was not reported.

Brunel and co-workers tethered a 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) moiety onto MCM-41 silica by various grafting methods.³⁹ TEMPO is a useful homogeneous catalyst for oxidation of alcohols to aldehydes and carboxylates under mild reaction conditions. Previous work in heterogenizing TEMPO involved the immobilization of TEMPO onto supports such as polymers and amorphous silicas. The mesoporous support has a greater surface area, a highly ordered pore structure, and large number of available silanol sites for grafting compared to the previously utilized solids. The synthesis of the TEMPO hybrids is schematically outlined in Scheme 23. Loadings of 1–2 mmol/g of aminopropyl groups were obtained, as determined by elemental analysis and TGA. Of these groups, about 0.4–0.8 mmol/g of TEMPO was obtained after modification. The direct grafting of the TEMPO organosilane yielded about 0.6 mmol of TEMPO/g, as determined by TGA.

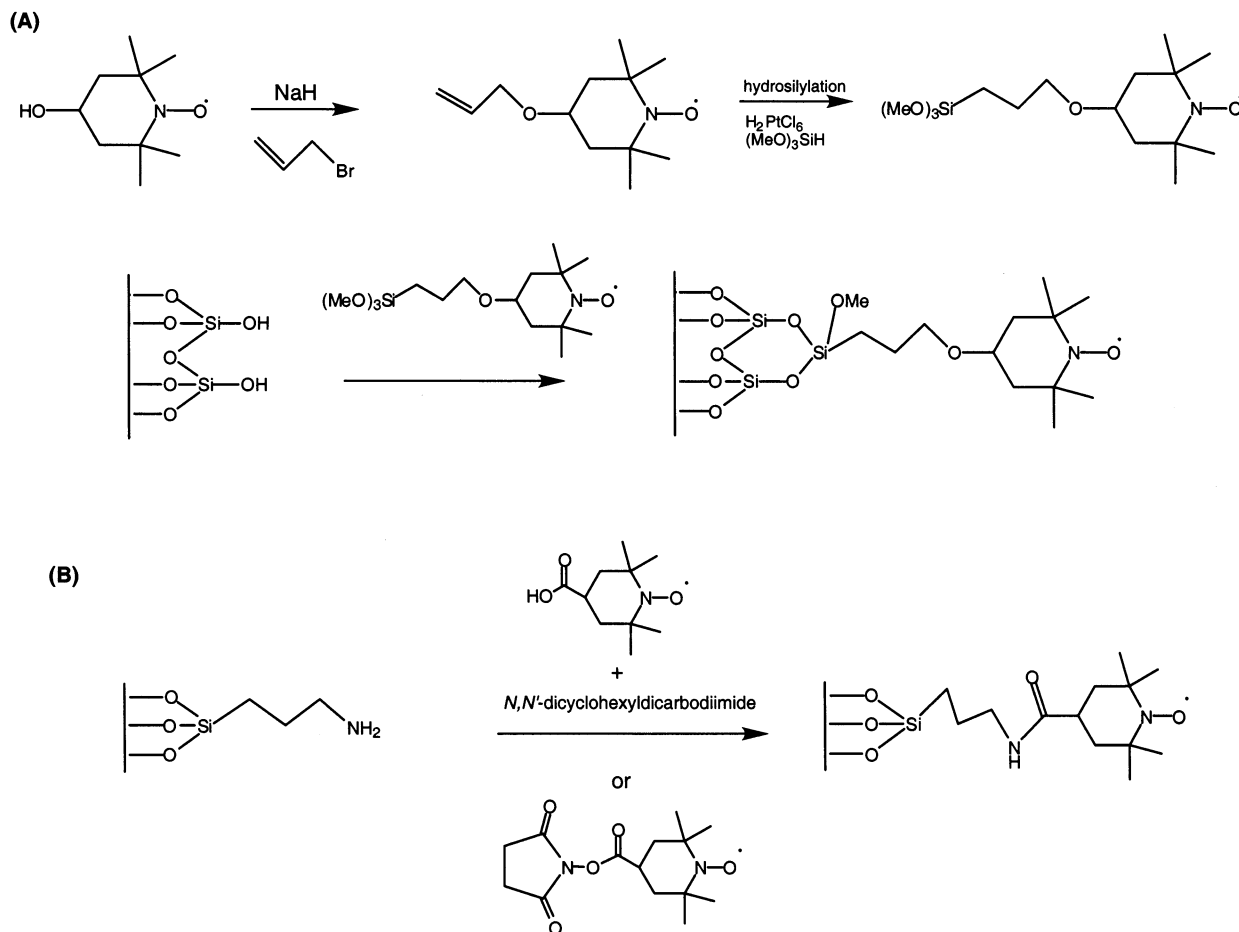
The oxidation of α -methyl glucoside, benzyl alcohol, and 1,4-pentanediol were catalyzed by the TEMPO hybrids in aqueous solution.³⁹ The α -methyl glucoside was oxidized to 1-*O*-methyl glucuronate at 0 °C with NaOCl, giving almost 100% conversion within 30 min for both the ether- and amide-TEMPO–MCM-41 catalysts. The selectivity was over 95% to the carboxylic acid product. No leaching of the TEMPO groups was observed. The catalysts were also useful in the reaction of benzyl alcohol with oxygen and copper(I) chloride in DMF. Conversion over the ether-TEMPO–MCM-41 was 35%, and selectivity to benzaldehyde was 99%. Under similar conditions, the homogeneous TEMPO gave 94% conversion and 99% selectivity. The small amount of water present in the reaction media prevented the over oxidation to benzoic acid. The lower activity of the supported TEMPO is reasonable because the proposed mechanism of the reaction requires two adjacent TEMPO molecules to be involved in a disproportionation step. The organic loading in the MCM-41 material was not sufficient to have a significant number of TEMPO moieties in close proximity to each other. Oxidation of the 1,4-pentanediol to γ -valerolactone was also catalyzed by the TEMPO-containing hybrid solids, giving 50% conversion with over 95% selectivity. The amide-TEMPO–MCM-41 was treated with hydrogen bromide prior to reaction to transform unreacted aminopropyl groups into ammonium bromides. Prior work has shown that the presence of these ammonium species can improve catalytic activity in the diol oxidation. As expected, the HBr-treated amide-

TEMPO–MCM-41 was more active than the untreated material and gave 99% conversion with over 95% selectivity under conditions similar to those of the ether-linked TEMPO.

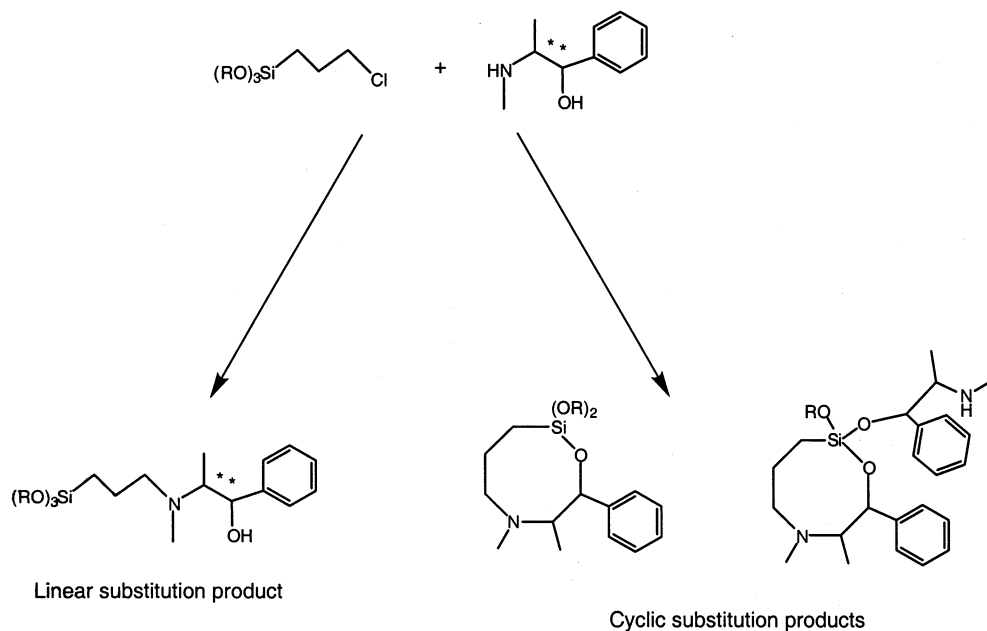
Chiral functionalities can also be grafted into silicas through similar techniques as described above. Brunel and co-workers have introduced chirality into mesoporous silicas via the grafting method.^{40–45} The chiral hybrid catalysts were then used to perform enantioselective reactions. Bellocq et al. described the immobilization of the chiral amino–alcohol (–)-ephedrine on MCM-41-type silicas via nucleophilic modification of the halopropyl groups.⁴⁰ Reaction of a chloropropylsilane with ephedrine yielded the desired ephedrine organosilane, but cyclization of the silane also occurred by replacement of the alkoxy groups on silicon with the hydroxyl group of the ephedrine (Scheme 24). A cleaner reaction was possible when the substitution occurred after grafting of the (chloropropyl)silane onto the MCM-41 solids. Although chloropropyl group loadings on the mesoporous materials were 1.2–1.4 mmol/g, only 58–76% of these were displaced by ephedrine. The ephedrine loadings ranged from 0.83 to 0.88 mmol/g. Similar grafting of amorphous silica had lower overall functional group loadings (due to lower density of surface silanol groups) of 0.5–0.9 mmol/g of chloropropyl moieties. However, a higher percentage of 60–84% of the chloropropyl moieties tethered on amorphous silica were displaced by ephedrine during modification, giving 0.44–0.53 mmol/g of ephedrine. Bellocq et al. concluded that the greater steric hindrance in the mesopores of MCM-41, compared to amorphous silica, hindered the nucleophilic attack by ephedrine. The ephedrine hybrids were then used in enantioselective addition reactions (Scheme 25). Amorphous silica hybrids produced high selectivities to the 1-phenylpropan-1-ol of 80–85% but had low enantiomeric excess (ee) of 11–22%. The MCM-41 hybrids also gave 84–87% selectivity but had 37% ee. Bellocq et al. noted that residual alkoxy groups on the functionalized MCM-41 surface for the organosilane grafting needed to be hydrolyzed by NaHCO₃ in methanol prior to addition of the ephedrine to prevent the cyclization products (as described above). Removal of the residual alkoxy groups improved the selectivity to 91% with an ee of 40%.

Further work improved the surface coverage of organic groups by utilizing a sol–gel method of functionalizing aluminosilicate mesoporous materials, Al–MTS.⁴⁵ The Al–MTS materials were exposed to (chloropropyl)silane in toluene in the presence of water and NH₄F-*p*TsOH. The chloropropyl moiety loadings were increased from 2.1 mmol/g via traditional anhydrous conditions to 4.4 mmol/g by the new tethering procedure. Modification by (–)-ephedrine then resulted in increased loadings of 1.9 mmol/g for chloropropyl-containing Al–MTS prepared by the new technique (as compared to 1.3 mmol/g for chloropropyl-containing Al–MTS from anhydrous methods). The increased organic loadings greatly reduced the available void space within the materials; Al–MTS supports of larger initial pore diameters (8.3 nm instead of 3.6 nm) were then used. The catalysts were

Scheme 23. (A) Synthesis of TEMPO–Ether–Silane and (B) Synthesis of TEMPO–Amide–MCM-41 (Adapted from Ref 39)

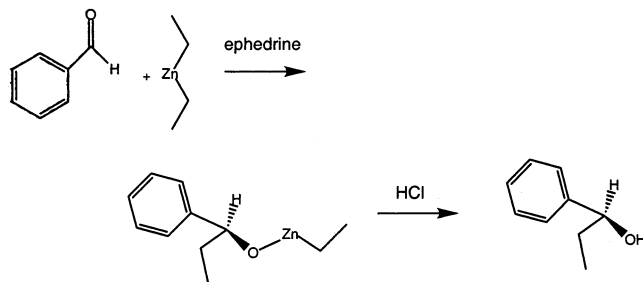


Scheme 24. Products of Nucleophilic Substitution of Chloropropylsilane and (–)-Ephedrine (Adapted from Ref 40)



studied in enantioselective addition reactions (Scheme 25). The ephedrine-containing Al–MTS catalysts prepared by anhydrous techniques gave 93% selectivity and 47% ee, similar to the ephedrine-containing MTS silicates described above. However, the ephedrine-containing Al–MTS catalysts prepared by the

sol–gel method gave 98% selectivity and 64% ee. These results were comparable to that of the homogeneous (–)-ephedrine catalyst, which gave 98% selectivity and 65% ee. The improved activities and enantioselectivity of the ephedrine-containing Al–MTS catalyst was attributed to the higher organic

Scheme 25. Synthesis of (*R*)-1-Phenylpropan-1-ol from Benzaldehyde and Diethylzinc


coverage of the surface (preventing racemic reaction on unfunctionalized surfaces) and the larger initial pore diameter, which allowed for increased accessibility to the active sites on the support.

Lasperas et al. compared the (+)-ephedrine-modified MCM-41 materials to (–)-ephedrine.⁴² As previously discussed, the (–)-ephedrine MCM-41 hybrid gave 37% ee to the (*R*)-isomer at conversions of 89–99% with selectivities of 84–89% to the secondary alcohol. The (+)-ephedrine hybrid yielded the (*S*)-1-phenylpropan-1-ol, in 26% ee, with similar conversions and selectivities. This suggests that the heterogeneous, chiral solids conform to the asymmetric induction observed in homogeneous chiral catalysts.

Recently, Kim et al. reported the anchoring of a proline derivative onto mesoporous silicas for use as catalysts in the preparation of chiral secondary alcohols.⁴⁶ The proline moiety was incorporated by modification of grafted chloropropyl species on amorphous silica, MCM-41 and SBA-15. The surface silanol groups were passivated by hexamethyldisiloxane (HMDS) after grafting of the chloropropyl silane to prevent sites for racemization to occur. The mesostructures of both MCM-41 and SBA-15 were stable throughout the modification procedure as observed by XRD. Nitrogen adsorption data showed that the MCM-41 samples had pore diameters of 23–24 Å; the SBA samples had diameters around 85 Å. ¹³C CP/MAS NMR confirmed the integrity of the proline functional groups after grafting and modification. The catalytic properties of these hybrids were tested in the asymmetric addition of diethylzinc to benzaldehyde in the presence of *n*-BuLi. The analogous homogeneous reaction system resulted in 87% yield with 93% ee. Grafting of the proline onto amorphous silica gave 41% ee at only 69% yield. Passivation of the surface with HMDS after grafting slightly improved results (43% ee and 74% yield). The MCM-41 hybrids showed better results of 84 and 96% yield (not passivated and passivated, respectively) and ee's (26 and 64%). SBA hybrids were the best catalysts of all, with 52 and 75% ee and 97 and 98% yield for not passivated and passivated surfaces, respectively.

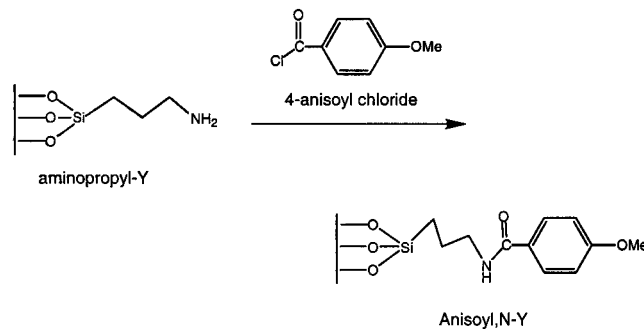
3. Microporous Molecular Sieves

The grafting of various organic moieties onto zeolites has been reported.⁴⁷ In general, modification of zeolites by organosilanes has been used to passivate the silanol groups on the external surface or to adjust the pore diameter. Brunel and co-workers function-

alized zeolite Y (calcined and dealuminated) of various Si/Al ratios with (3-chloropropyl)trimethoxysilane (CPS) and (3-aminopropyl)triethoxysilane (APS) to study the influence of the Al sites and pore size on the grafting.⁴⁷ Modification of the amine-functionalized zeolites was then performed by the addition of 4-anisoyl chloride and 2,3-butanedione. The samples were characterized by elemental analyses, IR, ¹³C MAS NMR, adsorption, XRD, and TGA.

The micropore volume of the zeolite Y solid decreased substantially by one-third or more after functionalization (Table 3).⁴⁷ Subsequent modifica-

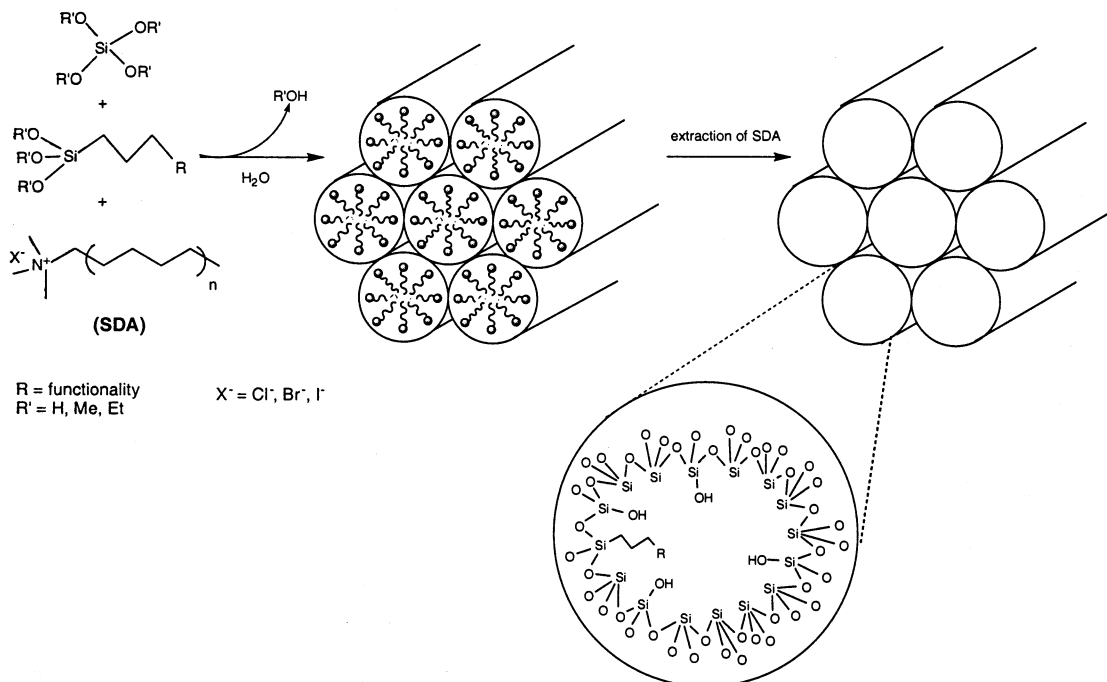
Table 3. Nitrogen Sorption Data for Organosilanes Grafted onto Zeolite Y (from Ref 47)



support (Si/Al ratio)	surf area (m ² /g)	external and mesopore surf area (m ² /g)	micropore vol (cm ³ /g)
unmodified HY (2.5)	751	48	0.31
chloropropyl-Y (2.5)	417	33	0.17
aminopropyl-Y (2.5)	479	37	0.19
unmodified HY (8)	720	126	0.26
chloropropyl Y (8)	447	90	0.16
aminopropyl Y (8)	422	92	0.15
Anisoyl,N-Y (8)	382	84	0.13
unmodified HY (17.5)	795	135	0.29
chloropropyl-Y (17.5)	537	91	0.20
aminopropyl-Y (17.5)	523	92	0.19
Anisoyl,N-Y (17.5)	431	83	0.15

tion of the amine groups further reduced the pore volume. Organic loadings were 0.97–1.48 mmol/g, as determined by TGA. Modification of the amino groups appeared to occur on about half of the amines (organic loadings of 0.46–0.61 mmol/g; however, the elemental analyses were inconsistent with the TGA data). Comparisons of available external and internal surface areas of the solid, before and after treatments, suggest that most of the functionalization occurs on the external surface and at the pore mouths of the zeolite. Diffusion limitations of the organosilanes and the high reactivity of the silanes likely produce reaction at the silanol functional groups around the openings of the pores and prevent penetration within the crystal. Most of the micropores and inner cavities of the zeolite would then be blocked by the deposited organosilane. Brunel et al. pointed out that larger, sterically hindered functional groups are much more easily grafted and are more accessible catalytic sites for mesoporous materials than in zeolites.⁴⁸ Functionalization on the external surface of the zeolite eliminates shape selectivity and nullifies some of the motivation behind using zeolites in catalysis.

Scheme 26. Co-condensation of Organosilanes and Tetraalkoxysilanes for the Assembly of Ordered, Mesoporous, Organic–Inorganic Hybrid Solids



B. Direct Incorporation of Organic Moiety: Ordered, Mesoporous Materials

Although grafting of organosilanes onto surfaces through hydroxyl groups is a well-studied and an often used method of forming organic–inorganic hybrid materials, the tethering is done by covalently attaching the organosilane to a surface silicon atom through the silicon (surface)–oxygen–silicon (external)–carbon bond in the organosilane (Scheme 2). The silicon–oxygen bond is then external to the surface and can be cleaved at conditions encountered in some catalytic reactions.⁴ Obviously, if this occurs, the solids will not be able to function as recyclable catalysts. It would be desirable to have the carbon bound directly to a silicon atom on the surface. By incorporation of the organosilane into the synthesis mixture during the formation of the solid, the functional group presents itself on the surface and the silicon in the silicon–carbon bond in the organosilane is on the surface of the material (Scheme 26). This forms a more uniform dispersion throughout the solid. In this “one-pot” method, the organosilanes are co-hydrolyzed and condensed with other silica reagents, e.g., tetraalkoxysilanes, water, and the appropriate organizing molecules (used for the synthesis of ordered, mesoporous materials and zeolites), to create the synthesis mixture. Issues of importance when selecting the preparation conditions include the solubility of the organosilane in the mixture, stability of the organic functional group under reaction conditions (pH, temperature), ease of organizing molecule (structure directing agent, SDA) extraction (for ordered, mesoporous materials and zeolites), and stability of the organic functional group during the extraction process. High loadings of functional groups (up to 3 mmol/g catalyst) can be obtained by co-condensation.⁵

To have a useful catalyst after synthesis, one must be able to extract the organizing molecules (Scheme 26) from within the pores to create porosity; calcining the material would destroy the incorporated functional groups. Extraction techniques have been developed for both mesoporous and microporous materials.^{49–53} Extraction of the SDA can be most effectively accomplished by acidic methanol solutions.³⁷ Ordered, mesoporous materials can be designed with specific pore sizes on the basis of the SDA and organic functionality used, but there is a lower limit to the pore size (ca. 15–20 Å). Several reviews concerning advances in co-condensation of mesoporous hybrid materials have been published.^{5,9,54}

Mann and co-workers reported the first incorporation of organic groups into mesoporous materials by co-condensation methods.⁵⁵ Phenyl and *n*-octyl functionalities were incorporated into MCM-41 silica by the “one-pot” method using TEOS as the silica source and hexadecyltrimethylammonium bromide (C₁₆TMABr) as the SDA. The SDA was extracted in acidified ethanol at 75 °C for 24 h. The structure of the phenyl–MCM-41 material was preserved throughout the extraction as observed by XRD. Octyl–MCM-41 was less stable to the extraction process than the phenyl–MCM-41. The mole percent of organosilane was varied to determine its effect on the assembly of MCM-41. Phenyl-functionalized MCM-41 was prepared with concentrations as high as 20 mol %, while the *n*-octyl-functionalized material remained high quality for up to 10% organosilane. TEM images of the materials confirmed the hexagonal structure, and nitrogen sorption data showed a decrease in pore size from 30 Å for all-silica MCM-41 to 24 and 18 Å for the 10 and 20% phenyl–MCM-41 materials, respectively. This work showed the possibility of directly tethering an organic functionality to the walls of the ordered mesoporous silicate (organic groups and the

presence of Si–C bond confirmed by IR and NMR studies). Slade and co-workers later showed that the addition of swelling agents, such as mesitylene, could be used in the phenyl–MCM-41 synthesis to increase the pore size of the material to around 30–40 Å.⁵⁶

Mann et al. synthesized MCM-41 materials with other functional groups such as mercaptopropyl, amine, epoxide, imidazole, and allyl.⁴⁹ MCM-41 silicas were prepared by using various organosilanes and C₁₆TMABr as the SDA at conditions of basic pH. The amine and imidazole organosilanes were also incorporated into a neutral synthesis gel using *n*-dodecylamine as the SDA. Hexagonal ordered phases were obtained and characterized by XRD. Structural order was lost at concentrations approaching and exceeding 20%. Also, the basic synthesis procedures produced more ordered materials than did neutral pH synthesis method. The SDAs were extracted by acidic alcohol solutions. The amine- and mercaptopropyl-functionalized MCM-41 silicas were stable to extraction; however, the epoxide, imidazole, and allyl silicas lost structural order. The amount of organic incorporation, as determined by ²⁹Si NMR, increased as the concentration of organosilanes increased, and ¹³C CP/MAS NMR revealed that the most of the organic groups were still intact after synthesis and extraction. Because of the alkaline conditions of the synthesis gel, the epoxide ring opened to form a diol, and the acidic extraction then substituted the β hydroxyl with a chloride.

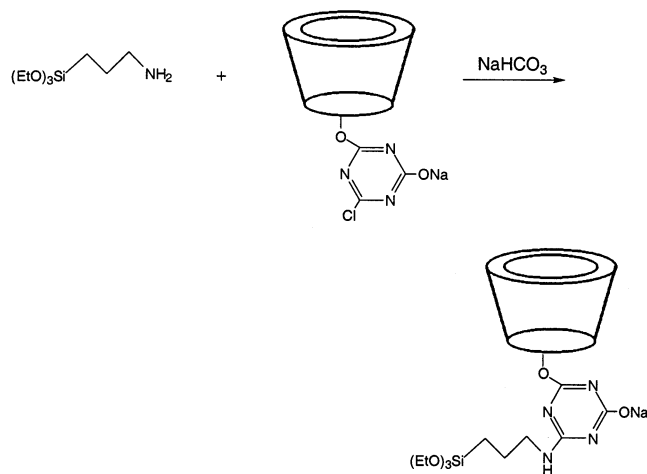
Hall et al. have reported the synthesis of a bifunctional mesoporous material via the co-condensation method.⁵⁷ Phenyltriethoxysilane and various other organosilanes (allyl and amino- and mercaptopropyl) were added to TEOS in the presence of C₁₆TMABr (SDA) under basic synthesis conditions. Ordered MCM-41 phases were obtained for materials with 20% total organosilane or less (by XRD). ²⁹Si CP/MAS NMR established the presence of Tⁿ sites. An increase in the Tⁿ sites was observed as the amount of organosilanes in the gel increased. The SDA was removed by acidic ethanol extraction at refluxing conditions. After extraction, the bifunctional materials were less ordered. ¹³C CP/MAS NMR verified the functional groups were intact. The combination of phenyl and aminopropyl functionalities gave the most stable hybrids, while phenyl and allyl functionalities provided the highest structural disorder. Pore diameters were reported to be ca. 35 Å for the bifunctional materials. Work was also performed with co-condensation methods to produce functionalized MCM-48-type materials. Only phenyl was successfully incorporated into an ordered MCM-48 structure. Hall et al. suggested that further study into the functionalization of MCM-48 would be beneficial to develop an organic hybrid material with a 3-dimensional pore structure (MCM-41 has a 1-dimensional pore structure).

Stein and co-workers incorporated an organic substituent into MCM-41 that could subsequently be modified.⁵¹ Vinyltriethoxysilane was added to TEOS and C₁₆TMABr (SDA) under basic synthesis conditions. Heating the reaction mixture to 87 °C for 24 h was found to provide solids with structural order. Extraction of the SDA was performed by refluxing

in acidic methanol solutions. XRD and TEM data showed that the structure remained ordered during extraction. IR spectroscopy and elemental analyses were used to confirm the complete removal of the SDA. ¹³C CP/MAS NMR data verified the integrity of the vinyl groups; i.e., the vinyl functionality was unaltered during the synthesis and extraction steps. The material and functional groups were thermally stable up to 280–290 °C under flowing nitrogen. Bromination of this material was performed, and IR and ¹³C CP/MAS NMR spectroscopy were used to confirm complete bromination of the vinyl groups after 6 days of reaction. Nitrogen sorption experiments revealed a pore size reduction from 22 to 18 Å after the bromination of the vinyl groups. The incorporation of a reactive vinyl group provides the opportunity to tailor the solids by postsynthetic reactions to create a wide variety of useful organic functional groups.

More recent work has involved the co-condensation of methacrylate moieties into MCM-41 materials.⁵⁸ The organosilane 3-(trimethoxysilyl)propyl methacrylate was added to a reaction mixture with TEOS and cetyltrimethylammonium chloride (C₁₆TMACl) under basic synthesis conditions to make a methacrylate hybrid MCM-41 material (MA–MCM). The presence of the methacrylate moiety was observed by IR spectroscopy in as-made samples. IR also showed the Si–C stretch at 1165–1170 cm⁻¹, similar to that listed in previous work.⁵⁹ No ²⁹Si CP/MAS NMR data were reported to confirm the presence of the Si–C bond. Extraction of the SDA by refluxing ethanol removed 30% of the C₁₆TMACl. Use of an ethanol/NaCl solution at room temperature improved the extraction to 95%, but a loss of structural order occurred. The most efficient extraction solvent was found to be acidic ethanol at reflux conditions to completely remove the SDA (verified by IR) with no structural loss. Increasing amounts of methacrylate silane decreased the order of the resulting material. Loadings of 0.23–0.28 g/g of methacrylate, relative to silica were obtained, as determined by TGA. (Hybrid materials prepared by grafting had loadings of 0.16 g/g of methacrylate, relative to silica.) The materials were thermally stable up to 200 °C under vacuum. Nitrogen sorption measurements showed a reduction of pore size from ca. 23 Å for calcined MA–MCM to 18 Å for extracted materials. Reaction with bromine demonstrated the accessibility of the functional groups.

Cyclodextrin moieties have also been incorporated into mesoporous silicas by co-condensation.⁶⁰ Cyclodextrins have useful applications in the removal of organics from water and in chiral separations. Their immobilization onto silica allows them to be used in a recoverable fashion in aqueous systems. Mercaptopropyl- and amino-functionalized mesoporous solids were prepared according to the method of Richer and Mercier⁶¹ (see below), using nonionic surfactants as SDAs to create the mesoporous structure denoted MSU.⁶² The thiol- and amino-moieties were extracted by refluxing ethanol to remove the nonionic surfactant and then contacted with monochlorotriazinyl β-cyclodextrin. Nitrogen sorption and IR spectroscopy

Scheme 27. Synthesis of Cyclodextrin-Containing Organosilane (Adapted from Ref 60)

showed no incorporation of the cyclodextrin. The MSU hybrids had pore diameters of 40–50 Å, which should have been sufficient to allow cyclodextrin (15.3 × 7.8 Å) to enter the pores. It was speculated that reaction of the cyclodextrins at pore openings prevented the remaining cyclodextrins from entering the mesopores. To incorporate the organic throughout the silica, the direct synthesis method was employed. Cyclodextrin-containing organosilanes were prepared by modification of (aminopropyl)silane (Scheme 27). The organosilane mixture was then co-condensed with TEOS in the presence of dodecylamine (SDA) to yield cyclodextrin–silica hybrid HMS materials. 1,3,5-Trimethylbenzene (TMB) was added as a swelling agent. SDA removal was performed by ethanol extraction. Cyclodextrin loadings of 0.14–0.39 mmol/g were obtained. TEM images, nitrogen sorption, and XRD patterns exhibited the expected wormhole morphology of HMS materials with approximately 40 Å pore diameters. Contrary to usual trends with co-condensed hybrids, incorporation of cyclodextrins in the synthesis gel resulted in a pore size increase of the HMS materials (30 Å for silica–HMS). It was speculated that the cyclodextrin acted as a swelling agent during the synthesis, similar to other results observed with mesitylene⁵⁶ and 1,3,5-trimethylbenzene.⁶³ Pore volumes were reduced as more cyclodextrin was added to the reaction mixture. The hybrid solids were shown to be useful in the removal of *p*-nitrophenol from aqueous solutions.

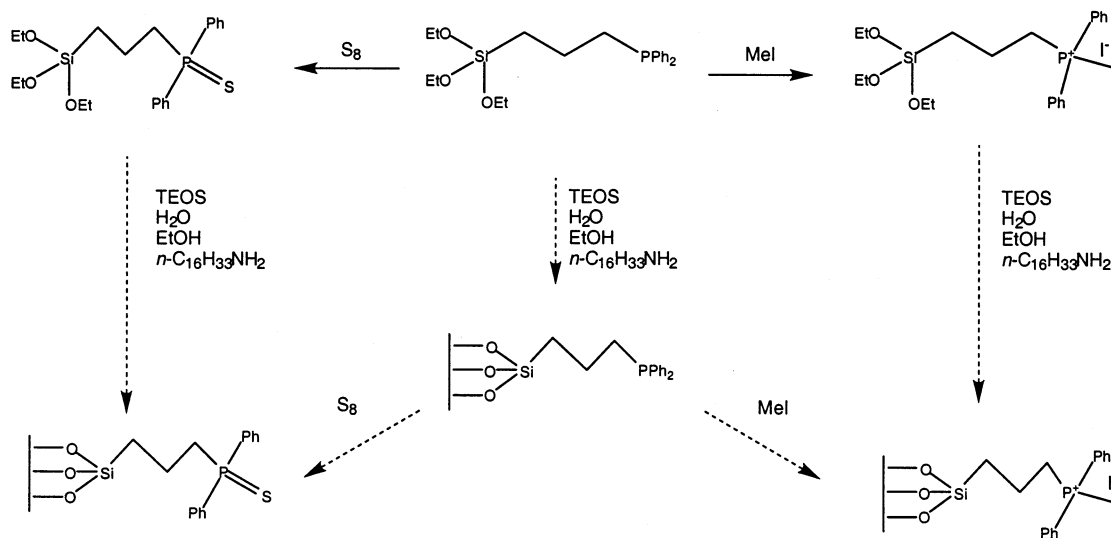
1. Base Catalysis

The initial work on base catalysis using co-condensed, mesoporous hybrid solids was performed by Macquarrie in 1996.⁵⁰ Adapting a neutral surfactant route to HMS,⁶⁴ Macquarrie and co-workers incorporated aminopropyl functional groups. TEOS and trimethoxy(3-aminopropyl)silane were hydrolyzed in the presence of *n*-dodecylamine (SDA) and water in ethanol. Room-temperature condensation occurred for 18 h. The SDA was then removed by refluxing ethanol. Complete SDA removal was obtained after three extractions. In a similar manner, (2-cyanoethyl)trimethoxysilane was also incorporated into a hybrid material. Analysis of the filtrate, IR spectroscopy

of the recovered solids, and TGA of the final material provided evidence to suggest complete SDA removal without damage to the functional groups. This synthesis method (with a neutral surfactant) resulted in a solid material that was easily extracted under relatively mild conditions, as compared to the ionic surfactant SDAs. The TGA analysis showed two high-temperature losses from the amino–MCM-41 material: a small loss at 300 °C and a larger loss at 575 °C. Similar analysis of the cyano–MCM-41 material showed only one large loss at temperatures over 500 °C. On the basis of these observations and IR analyses of materials treated to 600 °C, Macquarrie et al. claimed that both the 300 and 500 °C weight losses were from the functional groups. IR spectra showed the presence of some intact functional groups after the thermal treatment to 600 °C. ¹³C MAS NMR was not reported to confirm the IR. Macquarrie et al. pointed out that this high thermal stability had not previously been observed in other aminopropyl-functionalized silicas. Nitrogen sorption data gave pore sizes that varied from 29 to 39 Å.

In work related to the study of the Knoevenagel condensation catalysis by aminopropyl-silica formed by grafting, Macquarrie and co-workers also examined aminopropyl-functionalized mesoporous HMS materials prepared by co-condensation.⁶⁵ The HMS materials were more catalytically active than the functionalized silicas under optimized conditions (i.e., solvent). The HMS materials have higher organic loadings (2–3 instead of 1 mmol/g) and higher turnover numbers (4–5 times higher).⁵ Previous work with the grafted aminopropyl–silica (discussed in the previous section) suggested that deactivation occurred by amide formation and that there was a solvent dependency on the catalytic activity for the Knoevenagel condensation of aldehydes.¹² The HMS-based catalysts showed similar solvent effects as with the grafted aminopropyl–silica. However, the HMS-based catalysts were slightly less sensitive to the solvent effects; e.g., toluene has comparable performance to cyclohexane. It was speculated that the increased polarity of the HMS-based catalysts compared to amorphous silica improved the partitioning of reactants from the solvent phase to the active site, thus making the HMS-based material less sensitive to solvent. The amino–HMS catalysts did not reveal amide formation from the reaction of the ethyl cyanoacetate with the amine, as did the silica analogues. However, the presence of some unknown adsorbed organic species was observed on the used HMS catalysts and likely was the cause of catalyst deactivation.

Macquarrie and co-workers placed *N,N*-dimethylaminopropyl groups onto amorphous silica and ordered, mesoporous materials.⁶⁶ Loadings of 0.85–1.0 mmol/g of silica were obtained by grafting of *N,N*-dimethyl(3-aminopropyl)trimethoxysilane. IR spectroscopy indicated the presence of the N–CH₃ stretch at 2760 cm⁻¹. Additionally hybrid mesoporous materials were made by co-condensing the organosilane with TEOS in the presence of *n*-dodecylamine (SDA) to make a HMS mesoporous material. The SDA was removed by refluxing ethanol. As observed with

Scheme 28. Phosphorus-Containing Organosilane and Mesoporous Material Syntheses (Adapted from Ref 68)


aminopropyl, the *N,N*-dimethylaminopropyl functionality was thermally stable to temperatures of 400–650 °C by TGA. Functional group concentrations varied from 1.2 to 2.2 mmol/g of solid and had a pore size of around 56 Å. The higher loadings of functional groups produced less ordered materials. Michael addition reactions of nitroalkanes and carbonyl compounds were investigated using these solids as catalysts. The dimethylamino–mesoporous solids were significantly more active than the dimethylamino–amorphous silica (conversions of ca. 85 and 60%, respectively). The selectivity to Michael addition products was high for all catalysts tested. The mesoporous hybrids showed no leaching of functional groups and were thus recyclable catalysts. Some deactivation of the mesoporous hybrids was observed, but the amorphous silica analogue had greater deactivation. The new solid base catalysts showed better performance than conventional resin catalysts such as Amberlyst A-27.⁶⁷

Macquarrie and co-workers attempted to co-condense guanidine silanes into an ordered, mesoporous material for use as base catalysts in epoxidation reactions, similar to work done with grafted materials above.¹⁷ Only amorphous solids were obtained. Macquarrie attributed this to the positive charge of the guanidine moiety in synthesis mixture, citing previous examples of charged silanes not being observed to form ordered materials.⁶⁸ Material was then prepared by co-condensation of (chloropropyl)silane with TEOS into a functionalized mesoporous silica. The chloro–mesoporous material was then passivated (see previous section) and modified (Scheme 9) to form a guanidine-containing hybrid material. These hybrid catalysts had high selectivity (89%) and reasonable conversion (65%).

2. Phase Transfer Catalysis

Quaternary phosphonium functional groups can also be incorporated via the co-condensation method into mesoporous materials. Corriu and co-workers used the neutral surfactant synthesis (*n*-hexadecylamine) to co-condense (3-(diphenylphosphino)propyl)-

triethoxysilane, as well as its sulfide and quaternary derivatives, with TEOS (Scheme 28).⁶⁸ X-ray diffraction patterns showed the expected low-angle peak characteristic of the HMS type material from the neutral synthesis method for both the diphenylphosphino-organosilane and its sulfide derivative. The phosphonium organosilane did not result in an ordered HMS material. SDA removal was accomplished by refluxing ethanol. A diphenylphosphino–HMS material could also be quantitatively modified after synthesis by sulfonation and quaternization procedures similar to those used to prepare the organosilanes after 2 h in refluxing ethanol. No structural degradation was observed during these postsynthetic modifications. Pore size analyses showed that the HMS hybrid materials ranged from 30 to 36 Å. Quaternization of the phosphorus centers with benzyl bromide (1 equiv) or α,α' -dibromoparaxylene (0.5 equiv) in dichloromethane at 20 °C was performed.⁶⁹ The HMS materials had 83, 93, and 100% reaction after 72 h, showing that the phosphorus groups within the pores of the HMS were accessible. No catalysis with these materials was reported. The phosphonium-containing hybrid materials may be useful as phase transfer catalysts, like other materials described above.

3. Acid Catalysis

The incorporation of mercaptopropyl functionalities by grafting techniques is discussed above.³⁸ The thiol groups incorporated by either method can be oxidized to sulfonic acid sites (also described above). In addition to studying the grafted analogues above, Jacobs and co-workers co-condensed (3-mercaptopropyl)-trimethoxysilane (MPTS) with TEOS in the presence of hexadecyltrimethylammonium bromide ($C_{16}TMABr$) or *n*-dodecylamine as SDAs, to prepare thiol-containing MCM-41 or HMS, respectively. The SDAs were removed by extraction (acid solution or refluxing ethanol for MCM-41 and HMS, respectively). Both thiol and disulfide moieties were detected by IR and ^{13}C NMR spectroscopies. The thiol functionalities were then oxidized into sulfonic acid groups by

hydrogen peroxide (Scheme 21). The acid catalysts were tested in the reaction of 2-methylfuran with acetone to produce 2,2-bis(5-methylfuryl)propane (DMP) (Scheme 22). The sulfonic acid-functionalized mesoporous materials showed conversions of 52–85% with selectivities of 87–96%. The sulfonic acid-containing materials prepared by co-condensation methods behaved similarly to those prepared by grafting methods (see above). The recyclability of the catalysts was not reported.

Jacobs and co-workers also studied the use of these sulfonic acid-functionalized materials, prepared by both grafting and co-condensation methods, in the acid-catalyzed synthesis of monoglycerides by direct esterification of glycerol with fatty acids.⁷⁰ The mesoporous hybrids were found to be more active than other solid acid catalysts, such as H-USY and Amberlyst-15. Sulfonic acid-functionalized amorphous silica gave 51% yield, where Amberlyst-15 and H-USY had about 44% and 36% yield, respectively. Sulfonic-acid functionalized HMS material, produced by co-condensation with TEOS in the presence of *n*-dodecylamine, as described above, gave approximately 52% yield, while the grafted MCM-41 sulfonic acid-containing material gave 47–53% yield. The hybrid mesoporous catalysts were stable to recycling.

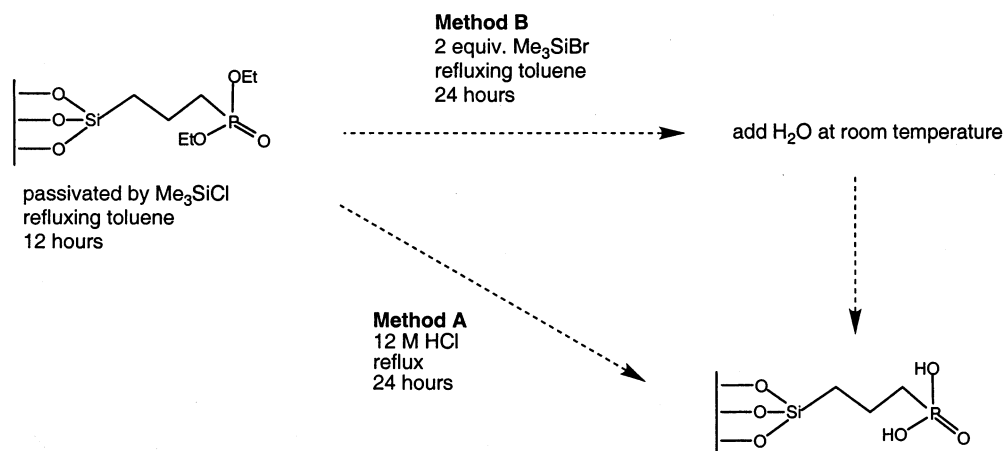
Other work involving the use of sulfonic acid-containing materials as catalysts for monoglyceride preparation from glycerol was reported by Pérez-Pariente and co-workers.^{71–73} The sulfonic acid-containing catalysts were prepared by the co-condensation of (3-mercaptopropyl)trimethoxysilane and TMOS with methyltrimethoxysilane in varying ratios (0–60 mol % of the total organosilanes from methylsilanes).⁷¹ A mixture of SDAs (C_{16} TMABr, dodecyltrimethylammonium bromide, C_{12} TMABr, and decyltrimethylammonium bromide, C_{10} TMABr) and the use of (TMA)OH instead of NaOH was used to improve the structural order of the hybrid mesoporous materials. The SDA was removed by acidified ethanol. Pore sizes ranged from <10 to 14 Å, depending on the relative organosilane ratios and SDAs used. The sulfonic acid sites were then generated by oxidation with H_2O_2 . Increasing ratios of the alkyl-containing silanes to mercaptopropyl silane resulted in an increased C/Si ratio in the final material. The incorporation of Si–CH₃ moieties was confirmed by ¹³C CP/MAS NMR.

The effect of the increased hydrophobicity from the alkyl functionality on the activity of the sulfonic acid sites in the monoglyceride synthesis was then examined.⁷² The sulfonic acid-functionalized catalyst containing no alkyl moieties gave a TON of 2 mol of fatty acid/(site × time) after 8 h of reaction with lauric acid. Increasing amounts of alkyl (up to 1.8 mmol/g of methyl groups, corresponding to 40% methylsilane) improved the TON to 6 mol of fatty acid/(site × time) during the same time. No further improvement was seen by increasing the methyl content to about 4.5 mmol/g (60% methylsilane). The selectivity of the catalysts toward the monoglyceride product was improved with increasing methyl content. Similar effects were observed with the reaction of glycerol

with oleic acid, with higher conversions observed with increasing methyl content.

Stein and colleagues have studied co-condensed mercaptopropyl silanes with tetraalkoxysilanes to create mercaptopropyl-functionalized MCM-41 hybrids.³⁷ High organic loadings of 4.7 mmol/g were obtained using (3-mercaptopropyl)triethoxysilane condensed with tetramethoxysilane (TMOS) in the presence of C_{16} TMABr (SDA) under basic reaction conditions. Higher structural order, as determined by XRD and TEM, was obtained with TMOS as the silicon source rather than TEOS, due to its faster hydrolysis rate. Homogeneity of the reaction mixture and hydrolysis rate were controlled by using a 30% MeOH aqueous solution. Hydrolysis of the silanes was allowed to occur at room temperature for 12 h, and then the mixture was heated to 95 °C for 36 h to facilitate condensation into an ordered material. The heating of the reaction mixture was important to obtain ordered materials with high organic loadings. The SDA was extracted with an acidic MeOH solution, and no structural or functional group degradation was observed (pore diameter of 14 Å). It was shown that the hybrid mercaptopropyl–MCM-41 could adsorb heavy metal ions (2.1 mmol of Hg²⁺/g of dry mercaptopropyl–MCM-41). The adsorbed mercury could be removed by extraction in HCl. The thiol could also be oxidized by nitric acid to create a sulfonic acid site that was located within the mesopores. Some structural degradation was observed by XRD, and a loss of nitrogen sorption capacity was obtained after the oxidation. However, sulfur loadings remained at 4.7 mmol/g. The treatment created some mesopores of 35–80 Å within the material due to pore collapse. However, 85% of the 14 Å pores remained intact. ¹³C CP/MAS NMR showed the presence of sulfonic acid and the loss of thiol. Titration of the sulfonic acid MCM-41 with NaCl gave a proton exchange capacity of 1.76 mequiv/g. The acid sites were used as catalysts for the reaction of ethanol with 3,4-dihydro-2*H*-pyran to give 2-ethoxytetrahydropyran. Conversions of 96% were obtained in less than 1 h of reaction time at room temperature. The organic–inorganic hybrid was therefore useful as a substitute for sulfonated polymer catalysts.

Stucky and co-workers employed a triblock copolymer SDA under acidic reaction conditions to create a mesoporous solid that incorporated a mercaptopropyl-organosilane. Like other studies, oxidation of the thiol to sulfonic acid sites was accomplished.⁷⁴ These mercaptopropyl–SBA-15 hybrids were thermally stable up to 340 °C. Organic loadings of 1.5 mmol/g (10% organosilane: total silicon sources) to 2.9 (20% organosilane) were found by TGA. About 90% of the (mercaptopropyl)silanes were incorporated into the mesoporous material during the synthesis. Further modification steps with H_2O_2 and acidification of the mercaptopropyl hybrid was required to form a sulfonic acid site (33–77% oxidation obtained with varying oxidation times) in the SBA-15 hybrids.⁷⁴ Proton exchange capacities of 0.5–1.16 mequiv of H⁺/g of silica were measured, and the amount depended on the oxidation conditions. The postsynthesis modification step reduced the structural order

Scheme 29. Synthesis of Phosphonic Acid Sites in SBA-15 (Adapted from Ref 75)

in the solid and decreased pore size (pore sizes of 47–52 Å, as compared to 55 Å for the mercaptopropyl-SBA-15). Increased oxidation times during postsynthesis modifications enhanced the number of acid sites as determined by titration but reduced structural order even further. The traditional sulfonic acid resin, Amberlyst-15, was stable to 260 °C, while the SBA-15-based material revealed stability to 450 °C. These solids thus give organic–inorganic hybrid materials with pore sizes of up to 67–73 Å and proton exchange capacities of 1.26–2.24 mequiv of H⁺/g of silica. No disulfides were observed in contrast to the results obtained by Van Rhijn³⁸ and Lim³⁷ during postsynthesis oxidation. ³¹P MAS NMR of adsorbed triethylphosphine oxide in the materials suggested the presence of strong Bronsted acid sites in the materials reacted with H₂O₂. The acidity of the sulfonic acid-SBA materials was compared to other heterogeneous acid catalysts by using the triethylphosphine oxide adsorption technique. The order of increasing acidity, as determined by the shift in ³¹P NMR resonance of the adsorbed oxide, was Al-MCM-41 < USY < sulfonic acid-SBA-15 < Amberlyst-15.

To alter the hydrophobicity of the cavity surrounding the sulfonic acid sites, Stucky et al. incorporated a second functional group, either benzyl or methyl (via a triethoxysilane), in addition to the thiol functionalities during synthesis.⁷⁴ Additionally, the oxidant H₂O₂ was included in the reaction mixture to oxidize the thiol functionalities during the bifunctional material synthesis. The sulfonic acid loadings in the bifunctional materials were similar to those of the monofunctionalized sulfonic acid hybrids (1.3 mequiv/g). XRD and nitrogen sorption analyses showed that the mesoporous materials had hexagonal order and pore sizes greater than 60 Å. ¹³C CP/MAS NMR of the bifunctional materials suggested the presence of both the sulfonic acid groups and either the benzyl or methyl moieties. No thiols or disulfides were observed in the ¹³C NMR. Although the incorporation of other functionalities was intended to influence the surface hydrophobicity and the acidity of the sulfonic acid sites, no clear conclusions were obtained. The mono- or bifunctional sulfonic acid-containing SBA-15 hybrids were not tested as catalysts. However,

these solids would likely be useful in acid-catalyzed reactions.

Richer and Mercier recently investigated the possibility of mercaptopropyl functional group incorporation by direct co-condensation in nonionic surfactant templated MSU-X mesoporous materials.⁶¹ TEOS and (3-mercaptopropyl)trimethoxysilane (0–0.05 organosilane:TEOS) were co-condensed by a NaF-catalyzed condensation process in the presence of various SDAs (Tergitol 15-S-12 (C₁₅H₃₁(OCH₂CH₂)₁₀OH), Triton-X100 (C₈H₁₇C₆H₅(OCH₂CH₂)₈OH), Igepal CA-720 (C₈H₁₇C₆H₅(OCH₂CH₂)₁₀OH), Brij-76 (C₁₈H₃₇(OCH₂CH₂)₁₀OH)) at temperatures ranging from 15 to 60 °C. The SDAs were removed by extraction with refluxing ethanol. Increasing organosilane content diminished the order for all surfactants studied. Ordered materials were obtained with organic loadings of less than 5–6% thiol. Pore diameters of 20–60 Å were determined by nitrogen sorption and depended on SDA, synthesis temperature, and organosilane content. Decreasing pore diameter was observed for increasing thiol content for all SDA systems. Elevated synthesis temperatures increased the amount of mercaptopropyl incorporated into the silica. No oxidation of the thiol functionalities or catalysis studies were presented. However, it is likely that these materials also have the potential to be useful as sulfonic acid-containing hybrid solids.

Corriu and co-workers co-condensed TEOS and diethyl ((trimethoxysilyl)propyl)phosphonate in the presence of the triblock copolymer EO₂₀PO₇₀EO₂₀ SDA under acidic reaction conditions with NaF as a catalyst to make SBA-15 mesoporous materials.⁷⁵ The SDA was removed by refluxing ethanol to yield the phosphonic acid diethyl ester-functionalized SBA-15 materials. ³¹P and ¹³C CP/MAS NMR established the presence of the diethyl phosphonate moiety in the solids. Elemental analyses gave an organic loading of 1.33 mmol/g (theoretical loading of 1.29). Nitrogen sorption showed the expected mesoporosity giving a type IV isotherm with pore size of 75 Å. The diethyl phosphonate-containing SBA-15 materials were subsequently treated with trimethylchlorosilane (Me₃SiCl) in refluxing toluene to passivate the surface silanol groups prior to the formation of the phosphonic acid sites. The acid sites were created by

two methods (Scheme 29). After treatment to give the phosphoric acid sites, ^{31}P and ^{13}C CP/MAS NMR confirmed the presence of these acid sites. Structural integrity remained after the treatments. A titration measurement of the acid sites showed 1.08 mmol/g of acid sites in the materials. Although no catalysis was reported with these materials, acid catalysis should be possible with these phosphonic acid-containing materials.

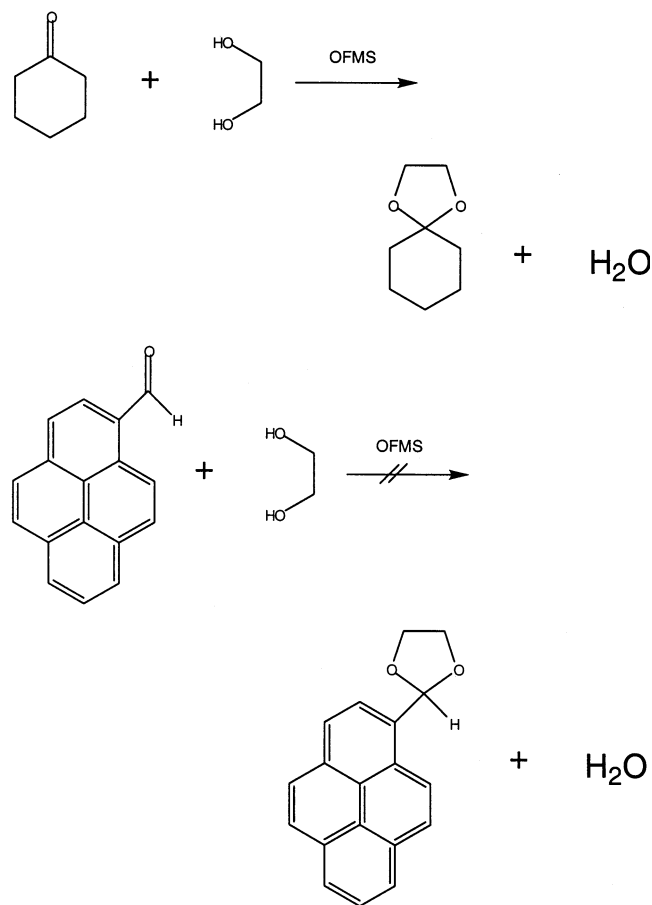
C. Organic-Functionalized Molecular Sieves (OFMS)

As previously mentioned, co-condensation of organosilanes with TEOS during formation of the inorganic structure should provide a more even distribution of functional groups than the use of grafting methods for ordered, mesoporous materials. Grafting onto zeolites has the additional complication of pore mouth clogging and is therefore unlikely to place functional groups within most of the microporous space. The ability to incorporate organic groups directly in the zeolite syntheses would be desirable to provide for uniform distribution within the void space. When an organic functional group is introduced into a zeolite during the synthesis via co-condensation, the SDA for the particular zeolite structure must be removed by some means other than calcination, to preserve the integrity of the functional group. SDA extraction, as typically used in a co-condensed, ordered, mesoporous, hybrid material as described above, requires that the SDA be smaller than the pore size of the zeolite (not always the case). The SDA must also not have strong electrostatic interactions with the zeolite framework as well. These stipulations limit the range of molecules that can be used as SDAs. Cambior et al. published a fluoride-mediated synthesis procedure for the zeolite structure *BEA that used tetraethylammonium fluoride (TEAF) as the SDA.⁷⁶ The molecular diameter of the TEAF is smaller ($\sim 6 \text{ \AA}$) than the pores of *BEA ($7.6 \times 6.4 \text{ \AA}$). The fluoride-mediated synthesis also creates an essentially “defect-free” framework that has very little residual internal silanol groups. This eliminates the usual electrostatic interactions between positively charged SDAs and the negative framework.⁷⁷ The SDA is the fluoride salt that can readily be removed by extraction.

Jones et al. correlated the temperature at which SDAs burn out of a microporous zeolite in thermal gravimetric analysis (TGA) with the ease of SDA extraction.⁷⁸ It was observed that SDA's that are removed from microporous materials under $400 \text{ }^\circ\text{C}$ tended to have less interaction with the surface and can be extracted.

Using the TEAF synthesis of *BEA, Jones et al. demonstrated that a phenethyl moiety could be introduced as an organosilane and the organic group be incorporated during the synthesis.^{52,79} The new organic–inorganic hybrids were denoted organic-functionalized molecular sieves (OFMSs). The TEAF was extracted from the OFMS pores without damaging or leaching the phenethyl groups (verified by ^{29}Si CP/MAS NMR and Raman spectroscopy). Any small amount of organic groups on the external

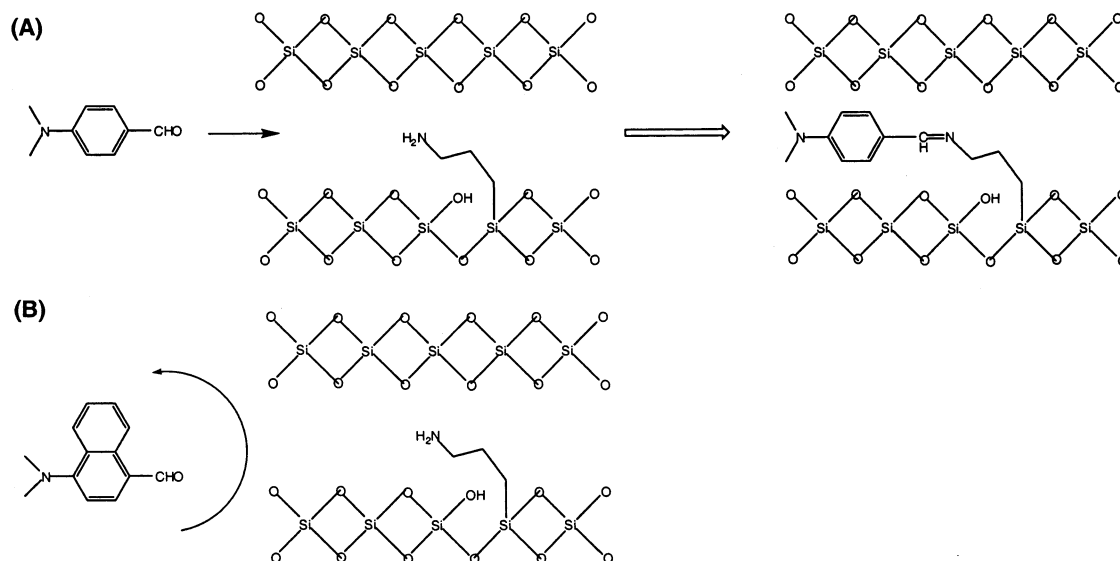
Scheme 30. Shape-Selective Behavior of OFMS Catalysts



surface of the zeolite could be removed by washing with concentrated NaOH solutions. Postsynthesis and SDA-extracted materials were sulfonated to create sulfonic acid sites, and shape-selective acidic catalysis was accomplished (Scheme 30). Poisoning experiments demonstrated that the catalytic functional groups were within the zeolite pores. This type of shape-selective catalysis is not possible with mesoporous materials and grafted zeolites.

Tsuji et al. synthesized *BEA-type OFMSs with other polar groups, including basic functionalities.⁵³ These functional groups, such as aminopropyl, tolerated SDA extraction and were demonstrated to be located mainly within the zeolite pores. Extraction studies were conducted with various solutions such as water, methanol, acetonitrile, acetic acid, pyridine, and pyridine/HCl solutions, to determine the extraction efficiency. The most efficient extraction solutions were aqueous acetic acid and aqueous HCl/pyridine. The addition of HCl increased the extraction efficiency of the pyridine and lowered the pH. The extracted OFMSs were exposed to aldehydes of differing molecular sizes, and shape-selective imine formation was observed by Raman spectroscopy (Scheme 31). The 4-(dimethylamino)benzaldehyde (DMBA) reacted with the OFMS to form an imine, while the larger aldehyde, 4-(dimethylamino)-1-naphthaldehyde (DMNA), was excluded from the pores and did not form imines. The aminopropyl OFMS was also able to perform shape-selective Knoevenagel condensation reactions.

Scheme 31. Shape-Selective Imine Reactions with OFMS Materials: (A) Reaction of 4-(Dimethylamino)benzaldehyde; (B) Reaction of 4-(Dimethylamino)-1-naphthaldehyde (Adapted from Ref 53)



A synthetic method for converting an extracted organic-functionalized MCM-41 hybrid material to an OFMS with the *BEA structure has been reported.⁷⁹ It was noted that the structural integrity of the MCM-41 sample used as the starting material was important to the purity of the OFMS obtained. Jones et al. also reported the synthesis of OFMS materials using various silica sources, synthesis temperatures, and heteroatoms in the framework. Other functional groups, such as alkenes and mercaptopropyl moieties, were incorporated into *BEA to show that a wide variety of OFMSs could be prepared and, after appropriate postsynthesis modification, used to create a large number of different catalysts.

Later work incorporated mercaptopropyl functional moieties into the *BEA structure to create thiol-containing OFMSs.⁸⁰ The thiol functionalities were then oxidized by H₂O₂ to create sulfonic acid sites. Shape-selective acid catalysis was performed to compare these hybrid materials to the sulfonic acid sites created in OFMS by sulfonation of phenethyl moieties.

D. Hybrid Materials with Organic Groups in the Network

Co-condensation techniques may also be used to create organic–inorganic hybrid materials that lack long-range order and contain the organic moiety as part of the solid network. The organic functionality may be a part of the solid network if the organosilane contains more than one silicon center (necessary but not sufficient condition for incorporation into the network). Examples of these types of materials are provided below.

Incorporation of organic groups within the network of glasses to create organic–inorganic hybrid composite materials has been reported since the 1980s. These organic–inorganic hybrids have been denoted as “ORMOSILS” (organically modified silicas) by Schmidt⁸¹ and “ceramers” by Wilkes and co-workers,⁸² and they possess mechanical and physical

properties altered from those of traditional ceramics and glasses. Much research has been dedicated over the past two decades toward studying the effects of organosilane addition on the sol–gel synthesis conditions and the applications of the resulting composites.^{83–91} Physical parameters such as morphology, porosity, transparency, and thermal and mechanical stability, as well as chemical properties such as solvent stability and hydrophobicity, can be affected by the addition of various organic substituents into the sol–gel processing of the ceramic materials. Polymerization of organic-functionalized trialkoxysilanes result in silsesquioxanes, and this area has been reviewed by Baney et al.⁹² The addition of a tetraalkoxysilane, such as TEOS or TMOS, as a cross-linking agent enables the formation of more fully condensed gels and ceramics, polysilsesquioxanes. The formation of organic hybrid polysilsesquioxanes has been reviewed by Loy and Shea⁹³ and Sanchez and Ribot.⁹⁴ A review on the applications of these organically modified silicas lists novel composite materials, chromatography and separations, chemical sensors, dyes for optical applications, and catalytic active sites for catalysis.⁸⁷ However, little catalysis has yet to be reported for these materials.

Recent work by Corriu and co-workers examined the accessibility of the functional groups imbedded within the lattice of silica xerogels.⁹⁵ Bis- and tris-(trialkoxysilyl)phosphine organosilanes and their derivatives were used to prepare xerogels.⁹⁶ The xerogels were then investigated to determine whether the organic phosphorus centers were accessible to different reagents. ³¹P MAS NMR was used to quantify the interaction. H₂O₂ and S₈ were able to completely react with the phosphorus centers of all of the xerogels. Quaternization with methyl iodide resulted in 95–100% yield. Reaction with benzyl bromide was 85–100%, showing the effect of more steric hindrance for the bulkier reactant.

Inagaki and co-workers reported the synthesis of the first ordered mesoporous silica with organic

groups evenly incorporated in the walls (“periodic mesoporous organosilicas”, PMOs).⁹⁷ 1,2-Bis(trimethoxysilyl)ethane (BTME) was hydrolyzed and condensed in the presence of the SDA, octadecyltrimethylammonium chloride (C_{18} TMACl), under basic reaction conditions. Two highly ordered mesoporous structures were obtained (depending on the synthesis conditions): a two-dimensional hexagonal mesophase (hexagonal rod morphology, denoted HMM-1) and a three-dimensional hexagonal mesophase (spherical morphology, denoted HMM-2). Unlike the co-condensed mesoporous hybrids discussed above where concentrations greater than 10–20% of organosilane resulted in disordered materials, the PMOs had 100% organosilane utilization in the condensation reaction. Inagaki et al. attributed this difference to the flexibility in the framework given by the ethane moieties. The ammonium SDA was removed by acidic ethanol extraction. The HMM-1 and HMM-2 hexagonal structures were mesoporous, having pore sizes of 31 and 27 Å, respectively. ^{29}Si and ^{13}C CP/MAS NMR spectroscopy was used to verify the presence of Si–C bonds and of the ethane bridge. None of the Si–C bonds of the BTME were cleaved during the condensation process. The organic groups were stable up to 400 °C by TGA. Inagaki et al. proposed that modification of the functional groups could produce useful catalytic materials where both inorganic and organic active sites are present.

Inagaki later reported the synthesis of a third PMO phase, HMM-3.⁹⁸ The BTME organosilane was condensed in the presence of C_{16} TACl (SDA) under basic reaction conditions. The SDA was removed by extraction with acidic ethanol. SEM and TEM images of the particles showed well-ordered decaoctahedral particles with cubic symmetry. Nitrogen sorption indicated mesoporosity with a pore diameter of 29 Å. ^{29}Si MAS NMR was used to verify that no degradation of the Si–C bonds occurred during synthesis, and ^{13}C CP/MAS NMR showed no destruction of the organic group.

About the same time, Stein and co-workers reported the use of 1,2-bis(triethoxysilyl)ethane (BTSE) or 1,2-bis(triethoxysilyl)ethylene (BTSEY) in the condensation of mesoporous silica using C_{16} TABr (SDA) under basic reaction conditions.⁹⁹ The mesoporous materials, designated “unified organically functionalized mesoporous networks” (UOFMNs), have MCM-41 structures, although they appeared less structurally ordered than the organic–inorganic PMOs studied by Inagaki. Stein et al. suggested that the samples appear to have a morphology more similar to the MSU-X wormhole channel materials of Pinnavaia⁶² than MCM-41. The SDA was removed by acidic methanol (as observed by IR spectroscopy). ^{29}Si MAS NMR data showed no cleavage of the Si–C bond occurred during material synthesis. ^{13}C CP/MAS NMR was used to verify the presence of the ethane and ethylene functional groups. Nitrogen sorption measurements confirmed the mesoporosity of the materials, with pore sizes of 21–24 Å. The UOFMN samples had greater hydrothermal stability than all-silica MCM-41 analogues.

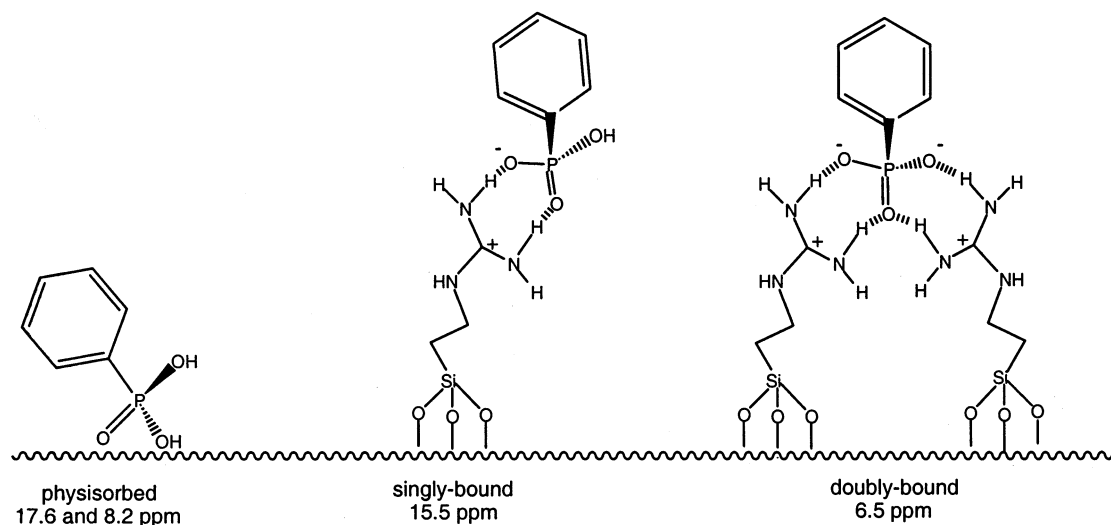
Recently, Burleigh et al. reported the incorporation of BTSE into another PMO system using the triblock copolymer, Pluronic P123, as the SDA.⁶³ The SDA was extracted by refluxing acidic ethanol. To create even larger pores, 1,3,5-trimethylbenzene (TMB) was added as a swelling agent. The addition of TMB not only increased the pore size but also altered the structural morphology. TEM images of material prepared with no TMB exhibited the expected wormhole structure with pore sizes of about 60 Å. The presence of TMB increased the pore size to 120 Å and changed the shape to cylindrical pores. Even greater amounts of TMB resulted in spherical pores of 200 Å diameter.

Ozin and co-workers also studied the co-condensation of 1,2-bis(triethoxysilyl)ethylene with TEOS using C_{16} TABr (SDA) under basic reaction conditions.¹⁰⁰ Materials with lower amounts of BTSEY had hexagonal structural order. Loss of order was observed in the materials that had higher concentrations of the organosilane. FT-Raman and ^{13}C and ^{29}Si CP/MAS NMR spectroscopies were used to confirm the presence of the ethylene moieties and the Si–C bonds. Nitrogen sorption results indicated mesoporosity, with pore sizes of about 40 Å. Additionally, Ozin and co-workers co-condensed organosilane bis(triethoxysilyl)methane (BTM) with TEOS in the presence of a C_{16} TABr (SDA) to create ordered hexagonal mesoporous materials.¹⁰¹ As increasing ratios of BTM to TEOS were used, the order in the materials decreased. The SDA was removed by acidic methanol extraction, with no degradation of the structure. Nitrogen sorption indicated mesoporosity with a pore diameter of 31 Å. The integrity of the methylene groups within the walls and presence of the Si–C bonds was verified by the use of Raman and ^{13}C and ^{29}Si NMR spectroscopies.

Ozin and co-workers also investigated other functional groups as spacers in the PMO framework.¹⁰² Various bis(trialkoxysilyl)-organosilanes were condensed in the presence of C_{16} TABr (SDA) under basic reaction conditions, creating ordered, hexagonal materials. The SDA was removed by acidic methanol extraction without structural damage. ^{29}Si CP/MAS NMR showed that benzene- and thiophene-containing PMOs had almost total cleavage of the Si–C bonds of the organic functional groups under the basic conditions of the reaction mixture. Condensation of the thiophene-containing PMO under acidic reaction conditions revealed only partial cleavage of the Si–C bonds. ^{13}C CP/MAS NMR data from these samples showed that the benzene and thiophene moieties were intact. Materials made with ferrocene, acetylene, and bithiophene spacers exhibited lower structural order and more Si–C bond cleavage.

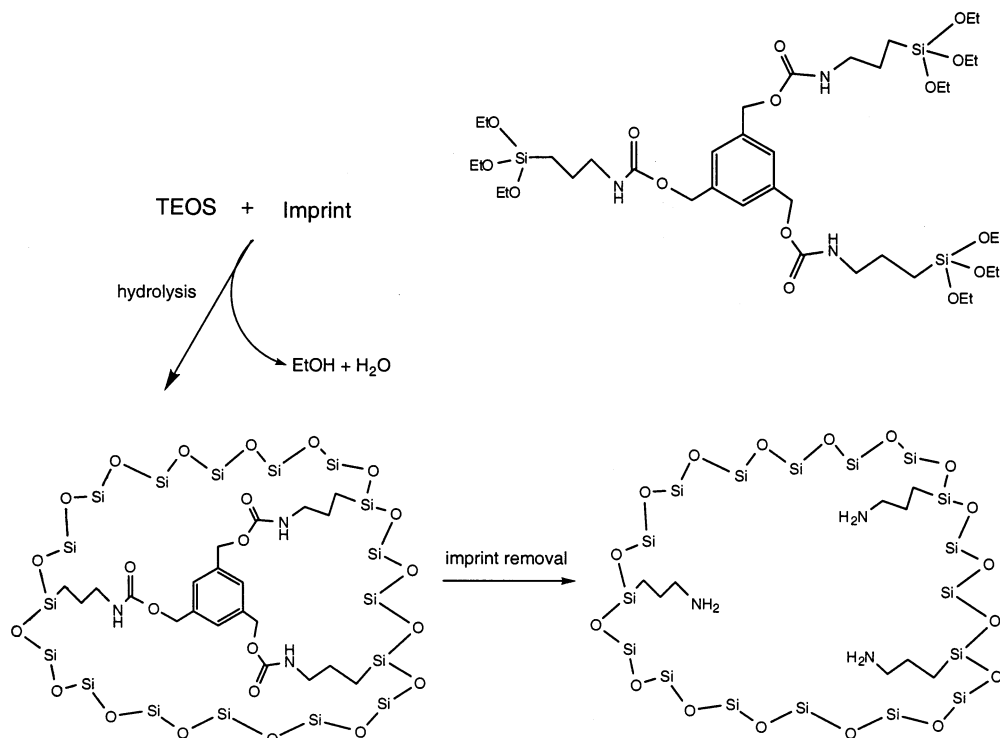
Yamamoto et al. recently claimed the synthesis of zeolites with an organic moiety within the silica lattice.¹⁰³ The “zeolite with organic lattice” (ZOL) contained an organic group that is incorporated during the zeolite assembly. Bis(triethoxysilyl)methane (BTM) was condensed in the presence of tetrapropylammonium hydroxide ((TPA)OH) as the SDA. The resulting reaction mixture was heated under autogenous conditions at 170 °C in a Teflon-

Scheme 32. Interaction Modes of Phenylphosphonic Acid with Guanidine-Functionalized, Imprinted Xerogels^a (Adapted from Ref 107)



^a ³¹P MAS NMR chemical shifts are listed for each configuration.

Scheme 33. Imprinting of Amorphous Silica^a (Adapted from Ref 105)



^a The example illustrated is for organizing three aminopropyl groups.

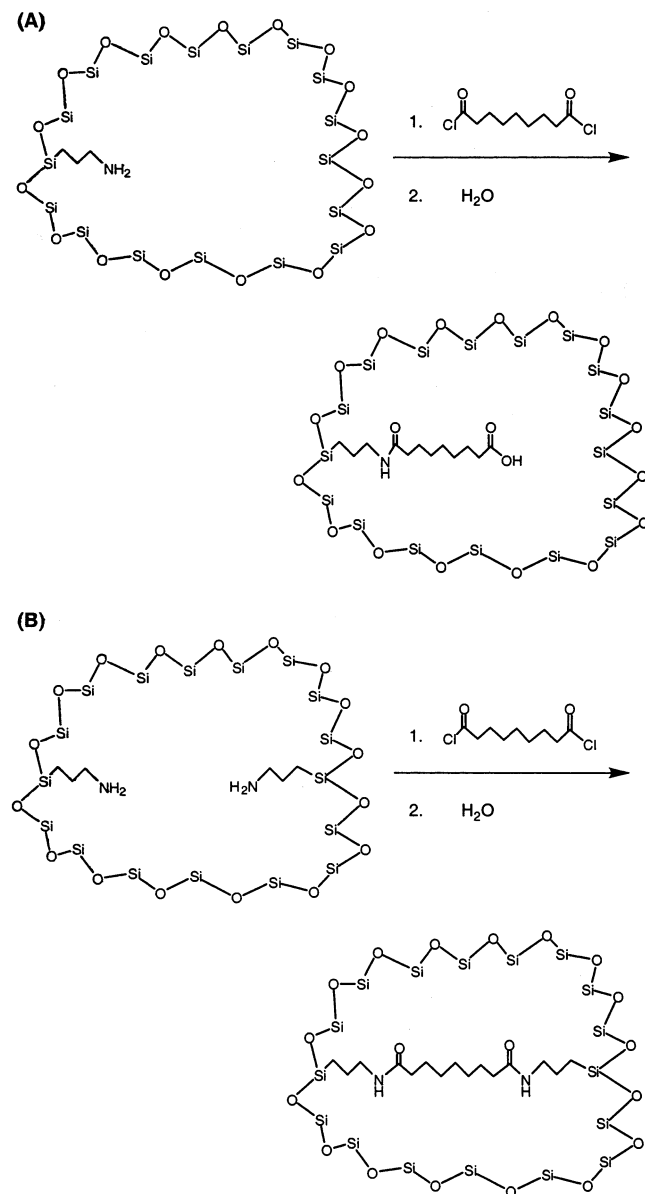
lined autoclave, either static or rotating. The organic–inorganic hybrid solid (named ZOL-1) has MFI structure, with no contaminating amorphous phase observed by XRD. ¹³C and ²⁹Si CP/MAS NMR data from the solids verified the presence of the organic moieties and Si–C bonds but also indicated some cleavage of the Si–C bonds. The SDA could not be extracted. The zeolite synthesis was then attempted with no SDA, using an aluminosilicate version of the MFI synthesis. The MFI phase, ZOL-5, was obtained after crystallization of the gel at 190 °C. ¹³C and ²⁹Si CP/MAS NMR data again showed the presence of the organic moieties and Si–C bonds, as well as some cleavage of the Si–C bonds. IR spectroscopy of the

ZOL-5 sample showed both methyl and methylene vibrations. The organic groups appeared to not affect the hydrophobicity of the zeolite, as ZOL-5 was shown to have a water sorption similar to that of ZSM-5 with comparable Si/Al ratios. Yamamoto proposed the use of the bis(trialkoxysilyl)-organosilanes with other SDAs to explore the possibility of synthesizing other zeolite phases with an organic lattice. If this early report can be verified, it will open a new area of microporous materials for catalysis.

E. Imprinted Silicas

Dickey and Pauling first demonstrated in 1949 that silica gels prepared with dye imprints specifically

Scheme 34. (A) One- and (B) Two-Point Interactions of Aminopropyl-Imprinted Silicas (Adapted from Ref 108)



adsorbed dyes with similar structures.¹⁰⁴ Since that time there has been significant efforts to create “imprinted” solids. Davis et al. have reviewed these efforts up to around 1996.¹⁰⁵ The addition of organic groups (via organosilanes) to an assembly process that also contains molecules for organizing the organic groups into a three-dimensional configuration (imprint) can be used to create a porous hybrid material with ordered functional groups (after imprint removal). For example, Makote and Collinson report the sol–gel processing of phenyl- and methyltrimethoxysilane with TEOS in the presence of dopamine as an imprint molecule.¹⁰⁶ The thin films produced from the gel, after removal of the imprint, preferentially adsorb dopamine compared to related compounds serotonin, epinephrine, and dihydroxynaphthalene.

In another type of assembly procedure, Sasaki and Alam created guanidine-containing imprinted silicas

and studied the binding of phenylphosphonic acid.¹⁰⁷ Amorphous silica xerogels were prepared by condensation of TEOS. The xerogels were then grafted with (1-(trimethoxysilyl)propyl)-3-guanidinium chloride in the presence of varying amounts of phenylphosphonic acid (PPA) as an imprint to direct the spatial orientation of guanidine-functional groups. PPA can interact with the protonated guanidine in either a one- or a two-point mode (Scheme 32). ³¹P NMR spectroscopy was used to distinguish the different binding modes. After the organic–inorganic hybrid xerogels were synthesized, the imprint PPA was removed by acidic solutions. The first extraction removed 93% of the total PPA imprint. Of the imprint remaining in the solids, 82% was bound by two guanidine moieties. Sasaki and Alam showed that the experimental binding constant for two-point adsorption was higher than for singly bound species.

Katz and Davis imprinted amorphous silica to create functionalized void spaces for shape-selective catalysis.¹⁰⁸ Imprints prepared to organize either one, two, or three aminopropyl functionalizations were incorporated into a sol–gel condensation of amorphous silica (Scheme 33). The surface silanols were passivated by trimethylchlorosilane and hexamethyldisilazane. Removal of the aromatic core of the imprint was performed by treatment with trimethylsilyl iodide in acetonitrile using HCl as a catalyst. ¹³C CP/MAS NMR data were used to prove the integrity of the imprint in the as-made silica samples. The percent cleavages of the carbamates of the imprints were 73, 74, and 22% for the one-, two-, and three-aminopropyl-functionalized imprints, respectively. Functional group loadings of 0.23, 0.23, and 0.07 mmol/g, respectively, were estimated from the adsorption of benzoic acid onto the amine sites. As expected, removal of the three-aminopropyl-functionalized carbamate was the most difficult. Argon sorption showed that the samples were microporous. The spatial distribution of the functional groups was examined by various methods including the adsorption of probe molecules. The one-aminopropyl-functionalized silica showed the expected amide (1710 cm^{-1}) and carboxylic acid (1647 cm^{-1}) peaks in IR spectroscopy after adsorption of azelaoyl chloride, while the two-aminopropyl-functionalized silica had only a single, broad amide band in the IR, consistent with the two-point binding (Scheme 34). These materials were active as catalysts and able to perform shape-selective base catalysis (Knoevenagel condensation of malononitrile with isophthalaldehyde).

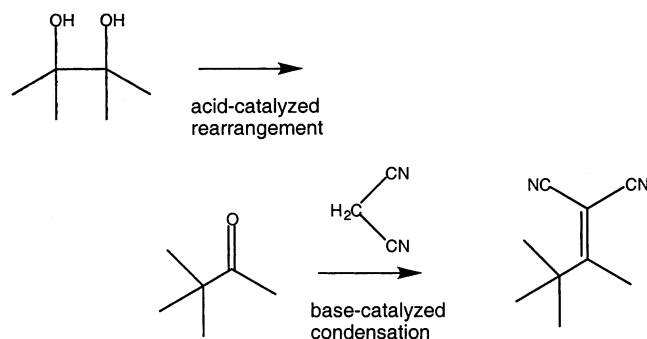
III. Future Directions of Organic–Inorganic Hybrid Materials

There are numerous organic–inorganic hybrid materials that have been prepared and characterized but not yet tested as catalysts. Additionally, very few of the materials that have been exposed to reaction conditions have been rigorously tested for reuse. Thus, there are many opportunities for investigation with currently available materials. Since much is known about how organic moieties can serve as catalysts for homogeneous reactions, many elements of “design” can be used in future developments of

organic–inorganic hybrid materials for use as recyclable catalysts.

Further work on exploring the incorporation of multiple functional group types, either randomly or in specific spatial arrangements, is merited. Recently, the ability to have both acid and base functionalities on silica was reported.¹⁰⁹ Nafion acid resin was immobilized with silica using a previously reported technique.¹¹⁰ Base functionalities, such as amines and guanidine, were also immobilized onto silica by co-condensation¹¹¹ or grafting.²⁹ Physical mixtures of the acid and base-immobilized catalysts were then used to perform sequential acid–base reactions in a one-pot reaction (Scheme 35). The ability to have the

Scheme 35. Acid- and Base-Catalyzed Reactions in One-Pot Reactions (Adapted from Ref 109)



tethered functional groups within the same silica matrix would be a desired extension of this work.

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