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PERSPECTIVE

Modified silicas for clean technology

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A wide variety of novel materials can be prepared through the chemical modification of silica gels with organic and inorganic functionalities. In addition to their use in chromatographic separations, they have been increasingly used as catalysts in liquid phase organic reactions. It is the application of these materials as viable, more environmentally friendly, alternatives to traditional homogeneous catalysts that forms the main body of this review. Their use as efficient materials for the selective pre-concentration of trace metals from aqueous systems is also discussed.

1 Introduction

In recent years there has been increasing pressure on the chemical industry from governmental authorities to develop more environmentally friendly processes.[1] The main area of concern is the large volumes of waste and toxic effluent produced by a variety of chemical processes. Improvements can be made in several ways, such as using alternative reagents and catalysts, increasing the efficiency of the process, easier separation of products from reactants and recycling reagents/catalysts. This eliminates the requirement for laborious and inefficient extraction processes.

One of the major contributors to waste in a chemical process is the separation of product/catalyst from the reaction mixture. This stage often generates large volumes of waste effluent (typically salts and contaminated aqueous streams). Also, the process of extracting the catalyst can often destroy the catalyst. Thus, elimination of this step would be favourable and is one of the major goals of green chemistry.[1]

One area of research that has seen increasing interest, in this context, is in the use of supported reagents as alternatives to more traditional reagents and catalysts.[2] The main area of investigation has been in the preparation of solid catalysts, although other uses include the removal of contaminants from waste effluent streams. As the supported reagent is in a separate phase from both the reactants and the products, this means that it can easily be removed from the reaction mixture.

It has been shown that the type of support material used is a critical factor in the performance of the resulting supported reagent catalyst.[3] Two main factors should be considered when employing a material as a support. First, the material needs to

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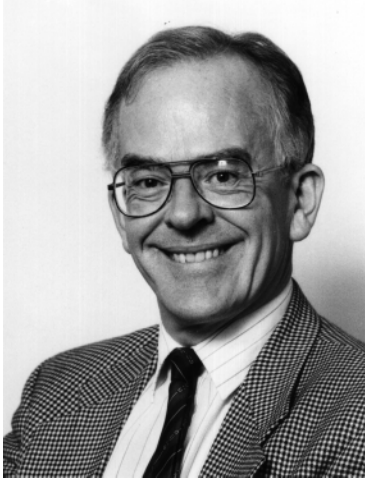
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be stable both thermally and chemically during the reaction process (including the separation stage in batch processes). Secondly, the structure of the support needs to be such that the active sites are well dispersed on its surface and that these sites are easily accessible. Generally, this requires the support to have a reasonably high surface area (typically >100 $m^2 g^{-1}$) and, for most liquid phase processes, it should have a mesoporous structure (*i.e.* >20 Å pore size to allow easy diffusion of reactants to the active sites). A variety of both organic and inorganic materials has been investigated.[3,4] One of the most effective is silica gel as this offers high thermal and chemical stability (except for a few small nucleophiles, notably OH^- and F^-). In addition, silica can possess high surface areas (>600 $m^2 g^{-1}$) and with pore sizes ranging from microporous to mesoporous (5 to 500 Å).

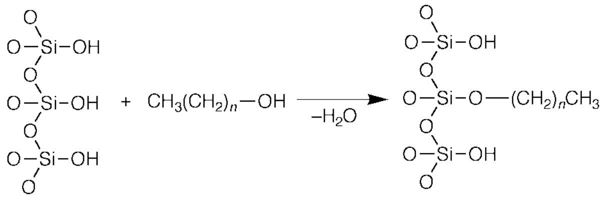
The silica surface consists of two types of functional groups, siloxane (Si–O–Si) and silanol (Si–OH). Thus, silica gel modification can occur *via* the reaction of a particular molecule which either the siloxane (nucleophilic substitution at the Si) or silanol (direct reaction with the hydroxyl group) functions, although it is generally accepted that it is reaction with the silanol function that constitutes the main modification pathway. It should be noted that the discussion in this review will be limited to the *chemi*sorption of active species onto the silica surface (*i.e.* chemical reaction between the inorganic/organic species and the silanol function). It should be recognised, however, that silica materials may be modified *via* physisorption of active species leading to a variety of useful supported reagents.[5–7] However, their use is often limited in terms of stability and reusability.

The use of modified silicas for applications such as High Performance Liquid Chromatography (HPLC) and Gas Chromatography (GC) has been extensively investigated.[8–10] Indeed, it is from these systems that a major contribution towards the various techniques of modifying silica gels has arisen.[11] In recent years, silica gels modified with both inorganic and organic functionalities have been used in other areas, notably in clean technology and particularly in green chemistry.[12] Their use has been mainly in catalysis, although, as will be discussed, modified silica gels have also been used in the separation of trace metals from aqueous systems.

2 Methods of silica modification

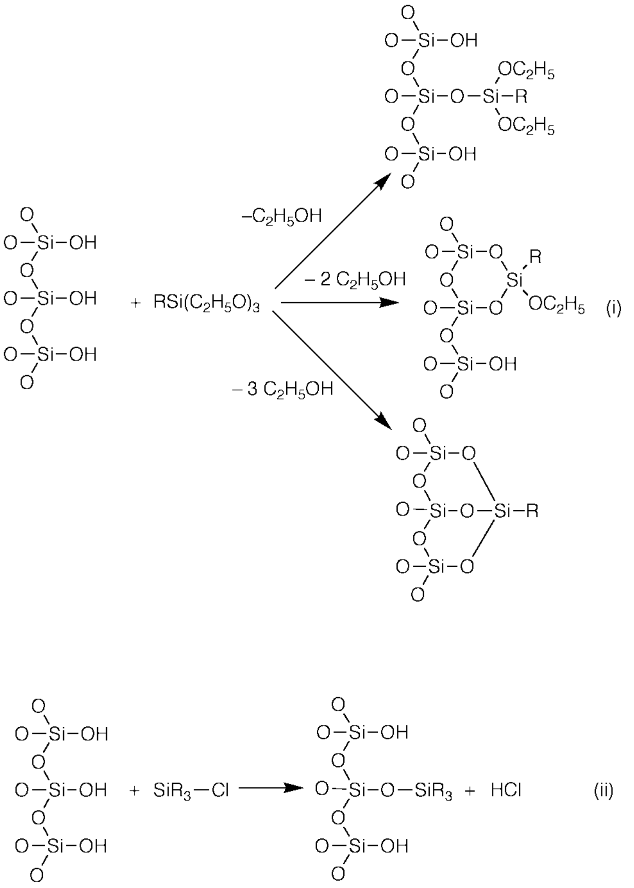
There are a variety of methodologies in which silica can be modified with organic functionalities. In this review the methods discussed will deal with the chemical attachment of organic groups to a silica surface. In our experience there are three main methods in which functional groups are attached to the silica surface: (i) through reaction between organosilanes or organic molecules and silica surface functions, (ii) chlorination of the silica surface followed by reaction of the Si–Cl with an appropriate functional molecule/reactant, (iii) incorporation of functional groups *via* sol–gel methodology followed by (where necessary) postmodification.

As previously mentioned, modification of silica gels has been developed mainly for chromatography applications. One of the first methods employed was developed by Halasz and Sebastian[13] in 1969. This involved treating an aliphatic alcohol with the silanol groups of the silica gel (Scheme 1), resulting in the formation of a Si–O–C bond. Despite exhibiting some good separations in HPLC, the bond is unstable and readily cleaved at elevated temperatures.



Scheme 1 Silica gel modification using long chain aliphatic alcohols.

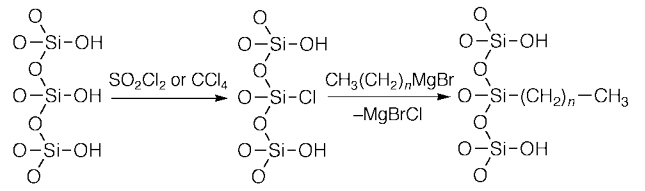
An alternative methodology is to treat the surface hydroxyls with organofunctionalised silanes, thus forming a Si–O–Si bond, which is more thermally and chemically robust than the Si–O–C bond. This can be achieved in two ways (Scheme 2).



Scheme 2 Modification of silica gel using (i) triethoxysilane and (ii) chlorosilane.

The first involves the use of trialkoxysilanes which react with the silanol groups liberating the corresponding alcohol.[12] Although a variety of trialkoxysilanes may be employed, the methoxy- and ethoxy-silanes have been shown to be the most effective due to their greater reactivity. However, the presence of three alkoxy groups means that the organosilane can react *via* one, two or all three alkoxy groups. This in turn leads to the possibility of some degree of polymerisation of the organosilane on the silica surface.[12] A second method, also developed by Kirkland and DeStefano,[14] employs the use of chlorosilanes to react with the silanol functions, thus liberating HCl. In this method thermal pretreatment of the silica gel is required (typically >100 °C for ≈18 h) to eliminate physisorbed water.

Despite the increased thermal and chemical robustness of the Si–O–Si bond (compared to Si–O–C), it is still cleaved at elevated temperatures and extremes of pH. An alternative is to form very strong Si–C bonds on the silica surface. Halasz and Sebastian developed a method in which the silica gel was first chlorinated using thionyl chloride.[13] The Si–Cl functions on the silica surface can then be treated with a Grignard reagent (or other organometallic reagents) to form Si–C (Scheme 3).[8,15,16] Alternatively, carbon tetrachloride has been used as the chlorinating agent employing fluidised bed methodology.[17] Despite the formation of strong Si–C bonds, these methods suffer from a number of drawbacks. Both thionyl chloride and carbon tetrachloride are hazardous reagents and therefore have to be handled carefully. During the chlorination of the silica both

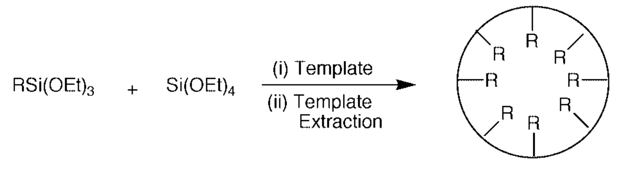


Scheme 3 Chlorination of silica surface and subsequent modification with Grignard reagent.

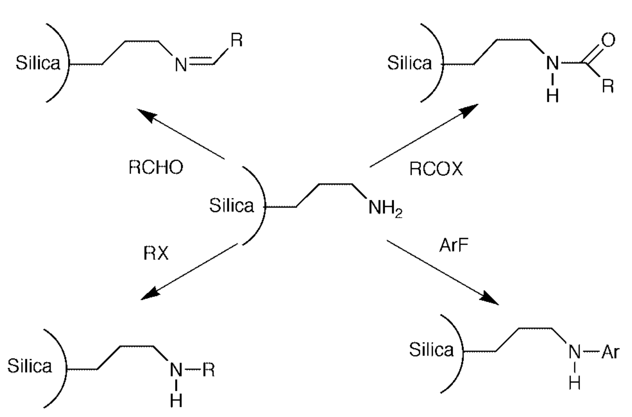
methods eliminate hazardous side-products, namely HCl, SO_2 (when using thionyl chloride) and Cl_2CO (for carbon tetrachloride). Finally, the use of organometallic reagents means that the range of functional groups that can be introduced is limited. However, this problem may be overcome by including a relatively stable functional group in the reagent which can then be derivatised in a subsequent postmodification step (*i.e.* $MCH_2C_6H_4Br$).

An alternative to postmodification is to incorporate the organofunctional groups into the solid matrix during the silica preparation. The methodology involves mixing an organoalkoxysilane with a silica precursor, typically tetraethoxysilane (TEOS). As with usual sol–gel techniques, the synthesis can be either acid or base catalysed. However, it is often difficult to control both the surface area and porosity of the final material. Thus, despite the resulting materials often possessing high loadings of organic groups, access to them by the desired substrate may be difficult.[11]

In 1992, the Mobil Corporation developed a family of silica and aluminosilicate materials designated M41S.[18,19] The materials were prepared by using cationic surfactants as templates around which the sol–gel process took place. Removal of the template resulted in materials with high surface areas and a regular array of pores. Recently, this methodology has been extended to incorporate organically modified materials.[20–24] We have recently developed materials based on the copolymerisation of TEOS and the organotriethoxysilane using a neutral surfactant (*i.e.* dodecylamine) as the template.[22–24] In addition, Mann and co-workers[20,21] have developed organically modified mesoporous silicas employing an ionic surfactant as the structure directing agent. Unlike previous sol–gel materials, the templated materials exhibit very high surface areas. In addition, the presence of a template offers considerable control over the structure of the final material. By altering the TEOS : organosilane ratio, functional group loadings upwards of 3 mmol g^{-1} have been achieved.[25] The organic groups are generally more robust than those present in the analogous post-modified materials. Furthermore, the higher surface area and regular pore structure of these materials allows greater access of reactants to the active sites. Scheme 4 shows the general preparation procedure for these materials.

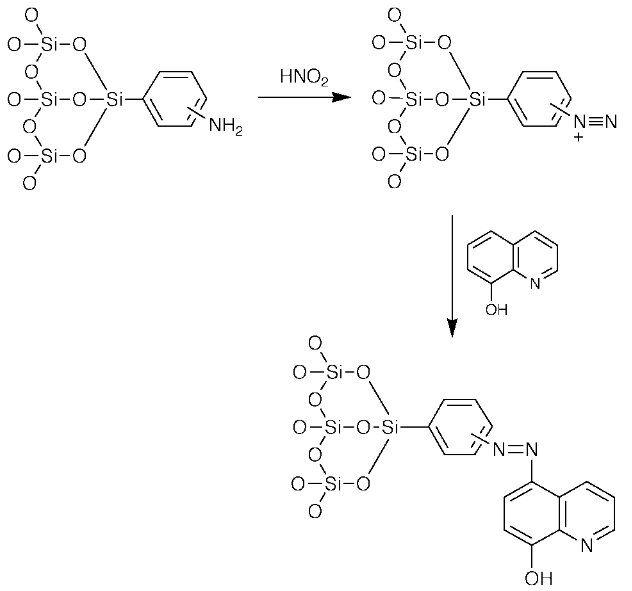


Scheme 4 Preparation of organofunctionalised silicas *via* templated sol–gel methodology.

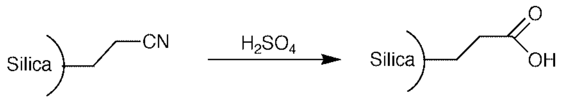


Scheme 5 Postmodification of an aminopropylsilica (AMPS).

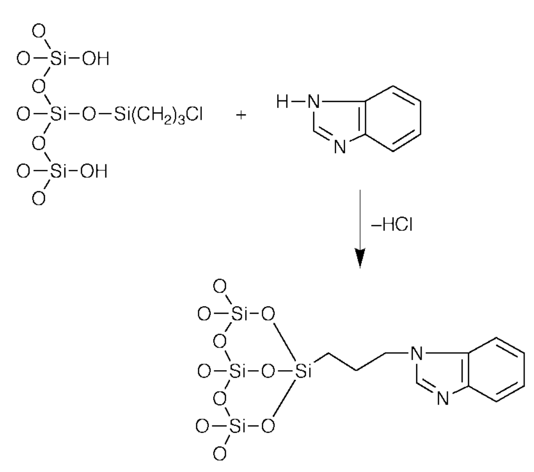
Despite the range of methodologies available, the scope of functional groups that can be incorporated into the silica framework is often limited. This can be overcome by further reaction of these groups. The most commonly used method is first to modify the silica with an alkylamine function (prepared by postmodification or sol–gel), followed by reaction with a variety of organic molecules (Scheme 5).[12] In addition Marshall and Mottola[26] have prepared modified silicas *via* post modification of an arylamine modified silica to give an immobilised quinolin-8-ol (Scheme 6). Other reported methods in this category include postmodification of cyanoalkyl silicas (Scheme 7),[27] and chlorosilane modified silicas (Scheme 8).[28]



Scheme 6 Preparation of immobilised Quinolin-8-ol.



Scheme 7 Modification of a cyanoalkyl modified silica.



Scheme 8 Postmodification of a chlorosilane modified silica.

Table 1 Major analytical techniques employed for the chemical characterisation of modified silica gels

Analysis	Technique	Information
Stability	Thermal gravimetric (TG)	Gives information on the thermal stability of the active species and whether it is chemically bound to the silica surface
	Atomic absorption spectroscopy	Used for metal containing species, stability during reaction
Loading	Atomic absorption spectroscopy	Either can be carried out by direct measurement of metal on silica surface, or by analysis of filtrate from preparation
	Titration	Used specifically for solid acids and bases
	^{29}Si MAS NMR	Can be used to determine the relative amount of Si attached to organic groups compared with Si–O–Si and Si–OH
Structure	Infrared	Mainly used for organo-modified silicas. Unmodified silica exhibits distinct bands for O–H (3800–3200), Si–O–Si (1090) and Si–OH (900 cm^{-1})
	MAS NMR	Most diverse technique, giving good information for both organic and inorganic functions. However, resolution is often lower than that of solution NMR

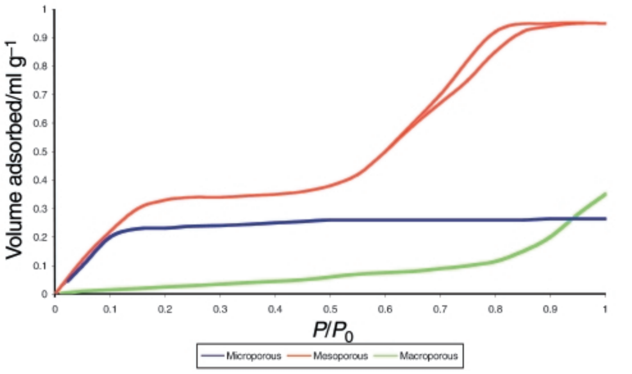


Fig. 1 Nitrogen adsorption isotherms for microporous, mesoporous and macroporous materials.

3 Characterisation of modified silicas

There are a wide variety of techniques available for the characterisation of modified silicas. In general, they can be divided into two distinct areas; (i) characterisation of the physical structure, (ii) chemical characterisation. Thus, through the combination of several techniques an accurate picture of the modified silica can be obtained. In this section a range of the most commonly used techniques will be discussed briefly.

Physical characterisation

As previously discussed, the physical structure of silica gels (high surface area, large pore volume, *etc.*) is one of the major reasons for its effectiveness as a support material. However, these features can be altered significantly during preparation (*i.e.* change in pH, temperature, use of template, *etc.*). Variations in surface area, pore volume and pore size (as well as their distribution) have a significant effect on the resulting material.[2] This includes the dispersion of the active groups and the ease in which reagents can diffuse to the active site. It is therefore necessary accurately to characterise the physical nature of the resulting material.

The adsorption of gases onto a silica surface is an extremely powerful technique for determining its physical structure. The most common adsorbate employed for this is nitrogen, although a range of other adsorbates can be used (*i.e.* argon, benzene, water). Nitrogen is adsorbed at 77 K over a relative pressure range (p/p_0) between 0 to 1. At low relative pressures (0.05 to 0.3) a monolayer of nitrogen is formed and by use of the Brunauer–Emmett–Teller (BET) method the surface area of the silica is determined.[29] At higher relative pressures ($p/p_0 >$ 0.4) capillary condensation occurs in the smaller pores. As the relative pressure increases, the size of the pores filled with adsorbate increases with all the pores being filled at saturation ($p/p_0 = 1$). From this an adsorption isotherm can be plotted, the shape of which provides information on the pore structure (Fig. 1). In general, silica gels possess pores in the mesoporous range giving rise to a type IV isotherm (Fig. 1), although a significant amount of micropores can be present.[11] One important feature of the adsorption isotherm for mesoporous materials is the formation of a hysteresis loop at relative pressures >0.4. This arises due to the adsorption–desorption process being non-reversible (amount of adsorbate on the desorption branch is always greater than the amount on the adsorption branch). In addition, pores are generally not perfect cylinders so that adsorption/desorption will be affected by the irregular shape of the pore (the “ink-bottle” effect).[30]

In general, the modification of a silica gel leads to a decrease in surface area, pore size and total pore volume. However, the silica structure is usually unaffected, with the shape of the isotherm of the modified material being the same as that of the parent silica. It should be noted that the silica structure may be altered if the modifying reagent contains (or produces) small basic anions (*i.e.* OH^-, O^{2-} or F^-).

A second important method of characterising the physical structure of modified silicas is the determination of its particle size. This can greatly alter the activity of the resulting material, by increasing the diffusion of reagents to the active sites. The particle size distribution can easily be determined by using a particle size analyser. For more detailed analysis scanning electron microscopy (SEM) has been employed to investigate the size and shape of individual particles.[31]

With the development of the M41S type materials, transmission electron microscopy (TEM) and powder X-ray diffraction have increasingly been used to characterise these materials on the nano-scale.[32] Thus, individual pores may be observed and the degree of pore structure ordering determined.

Chemical characterisation

As can be seen, the techniques employed for the physical characterisation of modified silica materials are, in the main, applicable to all modified silicas. However, this is not the case when investigating the chemical nature of the same materials. The range of techniques available is large and very much dependent on the modified silica under investigation. Therefore, the aim of this section is briefly to discuss the most commonly used techniques for chemical characterisation.

To obtain an accurate picture of the nature of the active species on the silica surface a combination of techniques should be employed. There are three important points that should be addressed in order to achieve this: (i) stability, (ii) loading, and (iii) structure of the active species. Table 1 gives brief details on some of the most commonly used techniques for characterising modified silicas.

The list of techniques presented in Table 1 is not exhaustive. However, combinations of these techniques can be used to characterise the vast majority of modified silicas. In addition, the characterisation of solid acids to determine the strength, type (Brønsted or Lewis in nature) and distribution of sites has widely been studied by spectroscopic titration methods using IR or NMR active probes, such as ammonia and pyridine. Corma[33] has written a comprehensive review on the techniques employed.

4 Applications of modified silicas

Until recently, the main use of modified silica materials has been for the separation of organic products in gas chromatography and high performance liquid chromatography. However, their use in chromatography will not be discussed here. The development of modified silica materials for use in clean technology has mainly been in the area of catalysis and will constitute the main subject of discussion. In addition, modified silica gels have been applied in the selective separation of trace metals from natural waters.

In catalysis

The modification of silica materials for use in catalysis has been studied extensively.[12] Early developments included adsorption of the active species (*i.e.* Lewis acids) onto the silica surface. These catalysts are reasonably active and generally exhibit useful improvements in selectivity. The fact that the functional groups are only physisorbed onto the surface of the silica meant that leaching was a significant problem. Therefore, the use of these materials will not be discussed further.

(i) Inorganically modified silicas. The immobilisation of inorganic species into a silica matrix for application in catalysis is well known.[28] As with the immobilisation of organic functionalities, supporting inorganic species is achieved *via* reaction with the surface silanol groups. It is the preparation and application of solid acid catalysts that has received the most attention. Although solid acids such as zeolites and acid-treated clays have widely been used in the catalyst industry, their use in liquid phase organic reactions is limited. The small pore structure of zeolitic materials often means that the size (and shape) of molecules that can be synthesized is restricted and many of the most successful reactions using zeolites are confined to the vapour phase.[3,29] Although acid-treated clays can possess pores in the mesoporous range, their acidity is significantly lower than that of conventional mineral acids. Thus, reactions using acid-treated clays often require harsh conditions to gain reasonable conversions.

The use of traditional acid catalysts such as $AlCl_3$, H_2SO_4, HF and BF_3 gives rise to considerable environmental concerns. Generally, they are difficult to separate from the reaction products, with the process often resulting in the production of large volumes of waste salt and aqueous effluent. It would therefore be highly advantageous to find a medium between the high selectivity and ease of recovery of solid acids and the high activity of liquid and soluble acids.

The immobilisation of aluminium chloride onto mesoporous silica gel has been widely investigated.[34–38] Drago and coworkers[34,38] have shown that strong solid acids can be prepared from both vapour phase deposition of the $AlCl_3$ onto the silica and by reaction in a suitable solvent, namely CCl_4. Although the catalysts exhibited high activity in *n*-alkane isomerisations, they showed low activity in liquid phase alkylation reactions. We have recently prepared similar catalysts by refluxing $AlCl_3$ with pre-dried silica gel in weakly complexing aromatic hydrocarbon solvents, in which the reagent is slightly soluble.[35] The resulting catalysts exhibit high activity in aromatic alkylations using a variety of *n*-alkenes, the activity being comparable to that of $AlCl_3$ itself (Fig. 2).[35,37,39,40] In addition, the selectivity towards the desired monoalkylated product was significantly better than that of the unsupported reagent, and the solid catalysts are reusable. By using an MCM-41 type silica (a member of the M41S family of materials possessing a hexagonal array of pores) as a support, selectivity towards monoalkylation was significantly improved. This is believed to be due to catalysis taking place within the narrow pore structure of the catalysts. The active sites on the surface of these solid acids are believed to be predominantly isolated $OAlCl_2$ (strongly Lewis acid) and highly polarised neighbouring OH (strong Brønsted acid) species.

Table 2 Comparison of activities and selectivities of the various immobilised BF_3 catalysts in the alkylation of phenol with oct-1-ene

Catalyst	Phenol conversion (%)	Octyl phenyl ether selectivity (%)
$BF_3(H_2O)_2/SiO_2$ (EtOH)	30	61
$BF_3(H_2O)_2/SiO_2$ (recycled)	6	97
$BF_3(H_2O)_2/SiO_2$ (C_6H_5Me)	4	78
$BF_3{\cdot}OEt_2/SiO_2$ (EtOH)	3	85
$BF_3{\cdot}OEt_2/SiO_2$ (C_6H_5Me)	<1	92

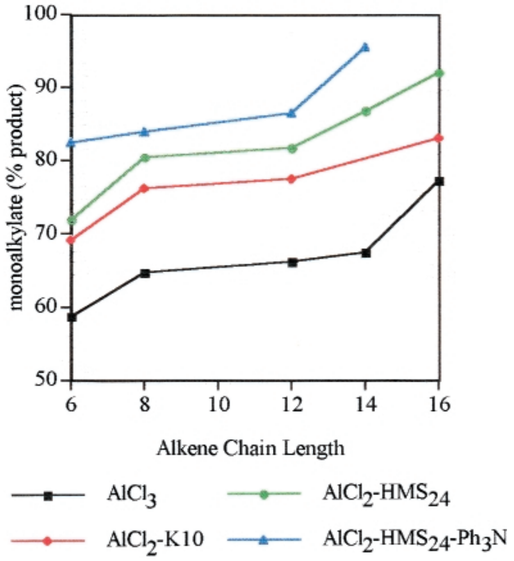
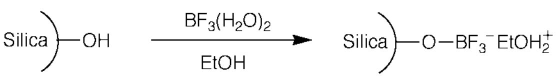


Fig. 2 Comparison of catalyst selectivities towards the monoalkylation of benzene using a variety of *n*-alkenes (K10 is an acid treated clay, HMS_{24} is hexagonal mesoporous silica possessing 24 Å pores).

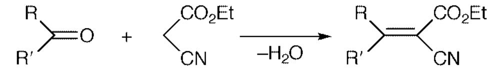
We have recently extended this methodology to preparing catalysts based on silica supported BF_3 solid acid catalyst.[41] As with the supported $AlCl_3$ catalyst, the active site is believed to be formed *via* the reaction of the Lewis acid with the surface hydroxyl groups (Scheme 9). Unlike catalysts prepared directly from reacting silica with BF_3 vapour,[42] the silica surface was modified using various BF_3 complexes. Thus, the acidity of the resultant catalyst could be tuned to some degree by using different BF_3 precursors. The catalysts exhibited good activity in the alkylation of phenol with oct-1-ene, with the stronger Brønsted acid catalysts being the most active (Table 2).



Scheme 9 Preparation of a BF_3 immobilised catalyst.

(ii) Organically modified silicas for catalysis. Over the past decade there have been several significant developments in the use of organically modified silicas as catalysts in a variety of organic syntheses. An area of catalysis which has seen much development in recent years is in the preparation of solid bases.[43] We have developed several solid base catalysts using simple aminopropyl functionalised silica materials.[24,44] As was previously discussed, the aminopropyl groups can be immobilised on the silica surface *via* reaction of the silanol groups with aminopropyltriethoxysilane (designated AMPS

Table 3 Knoevenagel reactions catalysed by aminopropyl functionalised catalysts



R, R′	Catalyst	T/°C	t/h	Yield[a] (%)	TON[b]
Ph, H	AMPS	82	0.1	99	—
Ph, H	AMP-HMS	82	36	94	—
n-C_5H_{11}, H	AMPS	82	0.2	97	—
n-C_5H_{11}, H	AMP-HMS	82	0.1	99	>6000
n-C_7H_{15}, H	AMPS	82	0.2	98	—
n-C_7H_{15}, H	AMP-HMS	82	0.15	98	>6000
c-C_5H_{10}	AMPS	82	1	98	650
c-C_5H_{10}	AMP-HMS	110	2	92	2450
Et, Et	AMPS	82	2	97	265
Et, Et	AMP-HMS	82	4	97	1127
n-C_4H_{10}, Me	AMPS	82	4	98	350
n-C_4H_{10}, Me	AMP-HMS	110	4	95	1244
t-C_4H_{10}, Me	AMPS	82	24	22	—
Me, Ph	AMPS	82	24	68	250
Me, Ph	AMP-HMS	110	36	48	47
Ph, Ph	AMPS	82	72	8	—

[a] GC yields using n-dodecane as an internal standard. [b] Number of mols of product per mol of NH_2 groups.

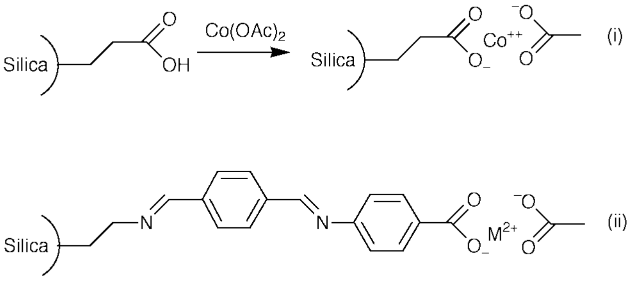
and AMP-HMS respectively†), or through *in situ* incorporation using sol–gel methodologies. The catalysts have been shown to be very effective in Knoevenagel reactions between ethyl cyanoacetate and a range of aldehydes and ketones (Table 3).

The rates of reaction for both types of solid base catalyst are largely dependent on the solvent used. Reaction rates are enhanced by using low polarity solvents (*i.e.* alkanes), due to the preferential adsorption of the polar reactants on the catalyst surface. In addition, the ability of the solvent to remove water from the reaction also increases the reaction rate. Cyclohexane was shown to be the best solvent when employing the aminopropylsilica catalyst, whereas toluene was more effective for AMP-HMS (due to its higher polarity).[45] Although in general, the HMS version of the catalyst was slightly less active, the higher loading of active sites that could be achieved meant that comparable activities can be obtained. Turnover numbers were also generally significantly higher.

As with Friedel–Crafts alkylations, the catalysts and reagents employed in liquid phase oxidations have several drawbacks. In general, they are highly toxic with the most commonly used being high oxidation state reagents of Cr, Mn and Os.[46] Reactions involving low oxidation state transition metal catalysts have been used. However, the reactions are typically carried out under harsh conditions (*e.g.* acid solvent) with promoters (*i.e.* bromide) being necessary to give acceptable rates.[47]

In recent years we have developed several oxidation catalysts based on organically modified silicas.[27,48,49] These have been shown to be more effective than previous supported reagents, which, although catalytic, possessed a lower density of active sites.[50] Catalysts have been prepared based on the immobilisation of $Co(OAc)_2$ *via* ligand exchange with a silica modified with acetate functions (Scheme 10(i)). The catalyst exhibited high conversions in the epoxidation of a variety of alkenes using a sacrificial aldehyde to form *in situ* reactive peroxy species. Several different transition metal complexes have been prepared employing the same methodology, with the complex attached to the silica *via* a long spacer chain (Scheme 10(ii)).[48] The catalysts exhibited good rates in epoxidation; surprisingly the cobalt catalyst was much less active than those of Cr or Cu with the nickel catalyst giving the best results.

The selective side chain oxidation of alkylaromatics is of particular interest to the chemical industry, with aldehydes and acids having many uses in sectors such as pharmaceuticals and perfumes. Recently, we have developed a catalyst using a silica supported Schiff base chromium complex.[49] The catalyst was prepared by initially forming the Schiff base ligand using aminopropyltriethoxysilane and salicylaldehyde. After addition of the chromium source (2:1 ligand to Cr), the complex was immobilised on the silica surface *via* reaction of the ethoxy groups with the silanol functions (Scheme 11). The catalyst exhibits high rates of ethylbenzene oxidation and is significantly better than a material based on $Cr(OAc)_3$ physisorbed on silica gel (Fig. 3). In addition, the former catalyst was more active than a similar catalyst prepared by attachment of the ligand prior to complexation of the $Cr(OAc)_3$ (unimprinted catalyst), suggesting that the Cr is more tightly bound in the former catalyst.



Scheme 10 Preparation of immobilised metal catalysts for epoxidation reactions.

A widely used method of complexing transition metals is through the use of porphyrins as ligands. However, they are expensive and are therefore not often employed as catalysts unless they can easily and efficiently be recovered. Extensive work has been carried out on immobilising metalloporphyrins on silica gels.[51,52] In general, methods have involved the postmodification of a modified silica, typically containing a nitrogen function (Fig. 4). The catalysts have been shown to be effective in the epoxidation of cyclooctene by iodosylbenzene.

In addition to the preparation of catalysts for liquid phase oxidation reactions, several studies have been made involving the preparation of silica-supported transition metal complexes for other important reactions (*i.e.* carbon–carbon bond coupling, aminations, *etc.*).[53,54] One of the most widely studied is immobilised palladium(0). Huang and co-workers[54,55] have developed a number of immobilised palladium(0) complexes,

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† AMPS is aminopropyl silica, AMP-HMS is aminopropyl hexagonal mesoporous silica.

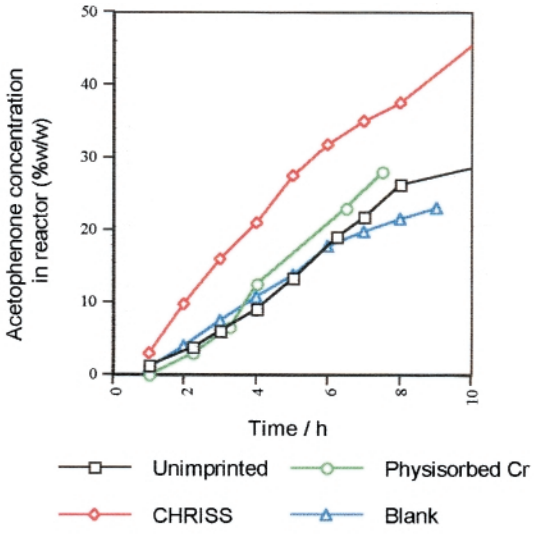


Fig. 3 Comparison of catalyst activities in the oxidation of ethylbenzene (CHRISS is chromium immobilised on a silica surface).

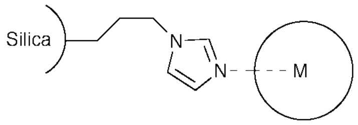
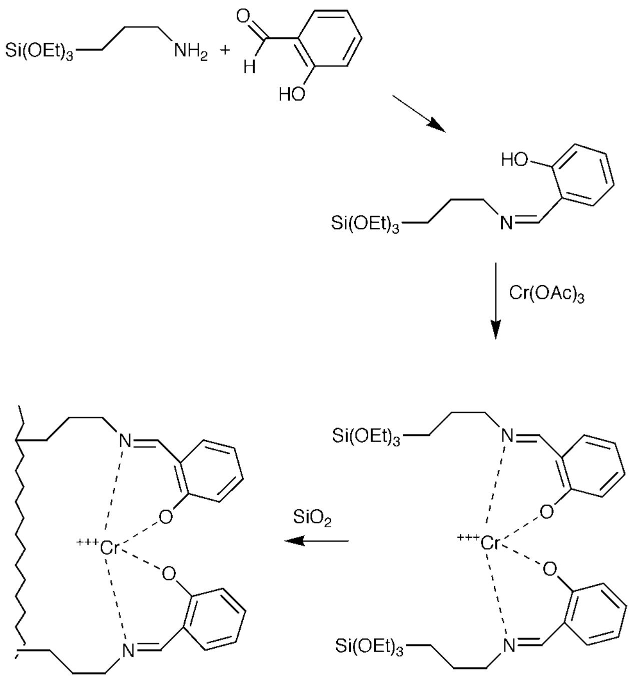


Fig. 4 An immobilised metalloporphyrin.



Scheme 11 Preparation of a chromium(III) supported Schiff base complex.

in which the palladium is bound to the silica surface by either phosphine or sulfur ligands (Fig. 5).[54,55] The phosphine supported complexes exhibit good activities in both the amination of various aryl halides[54] and the phenylation of both acid chlorides and aryl iodides,[53] whereas the catalysts in which the Pd was bound *via* a sulfur linkage were active in both the butoxycarbonylation of aryl halides and styrene arylation.[55] All the catalysts were easy to separate from the reaction mixture and are generally reusable.

Recently, Brunel and co-workers[56,57] have prepared a modified MCM-41 silica for use in enantioselective alkylations. It was prepared by first covalently bonding either a 3-chloro or 3-iodo-propyltrialkoxysilane to the MCM-41 surface; (−) or (+)-ephedrine was then attached to the modified material *via* nucleophilic substitution of the halogen with the amino group (Scheme 12(i)). The solid chiral auxiliary was then used in the enantioselective alkylation of benzaldehyde by diethylzinc to give the corresponding (*R*)- or (*S*)-1-phenylpropan-1-ol.[56] As in the homogeneous reaction ((−)-3-*exo*-(dimethylamino)isoborneol is used as the chiral auxiliary), the mechanism was believed to proceed *via* addition of the diethylzinc to the chiral auxiliary (Scheme 12(ii)). Thus, the configuration of the immobilised ephedrine controls the configuration of the final product. It was shown that the reaction rate, selectivity and enantioselectivity were all affected by the stirring rate, amount of chiral auxiliary and reagent concentrations. This was comparable to the homogeneous system, however, reaction rates and selectivities were generally lower. Two explanations were proposed. Either a significant amount of reaction was taking place on the silica surface due to racemic alkyl transfer, or there was restricted access to the catalytic sites by the reactants.

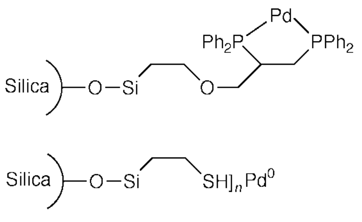
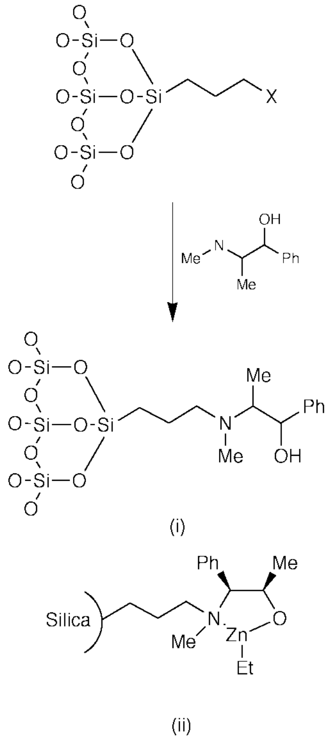


Fig. 5 Immobilised palladium complexes.



Scheme 12 Preparation of a heterogeneous chiral auxiliary (i), and addition of diethylzinc (ii).

Phase transfer catalysis is an important area of research, in which reactants in different phases (*e.g.* organic and aqueous) are allowed to react in the presence of a catalyst. As with the other catalyst systems discussed, the catalyst is difficult efficiently to recover and can easily contaminate the reaction products. Thus, immobilisation of a phase transfer catalyst (PTC) would be of great benefit if the solid analogue can operate efficiently at the liquid–liquid interface.

We have prepared a variety of supported phase transfer catalysts based on tetraarylphosphonium salts (Fig. 6).[58,59] The

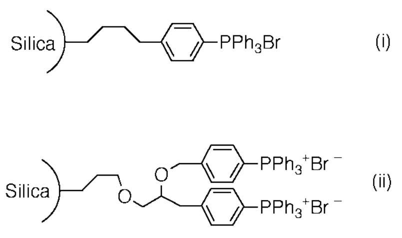


Fig. 6 Immobilised PTC (i) and bicipital PTC (ii).

catalysts exhibit high thermal stabilities and are often reusable in both a number of nucleophilic substitutions and aromatic oxidative brominations. In addition, we have prepared a supported PTC possessing two adjacent phosphonium centres (bicipital supported phosphonium catalyst).[60] Compared to the previous catalysts, the bicipital PTC exhibits significant increases in activity (per phosphonium centre) for the model nucleophilic substitution of 1-bromooctane with potassium iodide.

The immobilisation of enzymes on to silica surfaces is well established.[11,60] In biological functions (*in vivo*), enzymes are the most efficient catalysts known. Compared to the majority of chemical catalysts (both homogeneous and heterogeneous) they can exhibit high activity, are highly selective and function under mild conditions. However, in industrial applications their use suffers from two major drawbacks. In general, they are unstable at temperatures at which many industrial processes are run with activity also being lost due to variations of pH.[60] Also, their high water solubility (compared to many chemical catalysts) can result in difficulty in separating them from the final reaction products. It has been shown that in some cases the immobilisation of enzymes on solid supports can significantly reduce these problems.[60]

There are several methodologies in which enzymes can be immobilised, these include adsorption by ion exchange, incorporation into polymeric gels and encapsulation into membranes.[60] The binding of the enzyme onto a silica gel offers a number of advantages over these methods. Silica gels possess higher surface areas compared to those of organic polymer supports, thus allowing a higher loading of active sites. In addition, as the enzyme is covalently bonded to the silica gel the material possesses higher stability and so the enzyme is less easily leached. The immobilised enzyme is easy to handle and can easily be recovered from the final reaction products. One disadvantage of silica supported enzymes is their preparation. In general, a multi-stage modification process is required due to the necessity for a spacer chain between the silica surface and the active site of the enzyme (this minimises any steric hindrances during the reaction). Thus, the immobilised enzyme can be prepared either by first modifying the silica with an amine containing function, followed by addition of the spacer chain, or by modifying the silica with a long chain silane.

Owing to the high cost of preparing these materials, their use has been limited mainly to the fine chemical and pharmaceutical industries. One of the main applications is in the production of L-amino acids which are used as additives in food and in medicines (D-amino acids have no such value). This method of preparing L-amino acids is cheaper and faster than traditional fermentations. Thus, acylated amino acids are passed down a column containing the immobilised enzyme which then selectively hydrolyses the L-amino acid. The heat-treated D-amino acid (therefore leading to racemisation) may then be fed back into the column.[60]

Other applications for clean technology

As has been previously discussed, many of the more recent advances in the use of modified silicas for clean technology have been in catalysis. In this section the discussion will be extended to include other applications in which modified silicas may be employed.

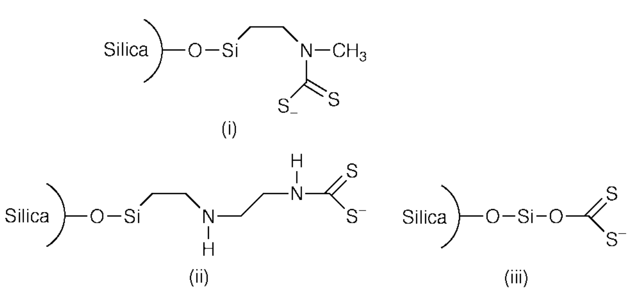


Fig. 7 Immobilised dithiocarbamates (i) and (ii), and dithiocarbonate (iii).

One area of research in which modified silicas are used for clean technology applications, other than catalysis, is in the analysis of trace components in aqueous and non-aqueous systems. A wide variety of analytical techniques has been developed to determine trace metal concentrations in natural waters.[61] The presence of even low concentrations (ppb) of some heavy metals in natural water systems can have a detrimental effect on both wild life and humans. However, at these low concentrations of metal the sample often requires pre-concentration before analysis can be undertaken. Several methods have been employed in the pre-concentration of metal ions from aqueous solutions, such as solvent extraction using a chelating agent[62] and the use of polymeric resins.[63] These methods suffer from a number of drawbacks. The use of chelating reagents (*i.e.* iminodiacetate resin) is time consuming, whereas organic resins possess low mechanical stabilities and the time taken for the metal ion to be complexed can be of the order of hours. In addition, these methods are often unselective towards the metal being analysed, with interference from alkaline earth metals being particularly problematic.[64] In recent years, the use of modified silica gels in the pre-concentration of trace metals has been investigated.[65–67] As with their applications in catalysis, modified silica gels offer the advantages of high surface areas and increased mechanical stability.

Nitrogen containing organic groups have been shown selectively to bind first row transition metals from solutions.[68,69] Thus, Marshall and Mottola[64] have prepared an immobilised quinolin-8-ol complex for the pre-concentration of copper(II) ions. By varying the pH of the solution a variety of transition metal(II) ions could selectively be extracted, even in the presence of high concentrations of alkaline earth metal ion. This makes the material useful for analysis of trace metals in natural waters where high concentrations of alkaline earth metals would be expected. Filho and co-workers[68,69] have developed several modified silica gel materials using both benzimidazole and triazole functions selectively to bind copper(II) and cobalt(II) complexes. Copper(II) was shown to complex well with the immobilised benzimidazole. However, the material was not used to chelate it from a mixture of metal ions in solution. The selectivity towards copper(II) ions is not yet known.

Leyden and Luttrell[65] prepared modified silica gels with both dithiocarbamates and *O*-alkyldithiocarbonate functions as chelating reagents (Fig. 7). The diamine complexes absorb metal ions at different rates (although all were complexed faster than organic resins). Thus, Hg^{II} and Cu^{II} were absorbed faster than Ag^{I} and Mn^{II}, with Cr^{III} being the slowest. In the case of the dithiocarbamates, all metals were extracted within four minutes except for Cr^{III}.

The presence of mercury (even at very low levels) in natural waters poses considerable environmental problems.[62] Thus, determination of mercury concentrations is of vital importance. Filho and Gushikem[70] developed a 2-sulfanyl-imidazole chelating ligand immobilised on silica gel. The modified silica exhibited high selectivity in the removal of mercury(II) ions from a mixture of metal ions in aqueous solution, when both batch and column techniques were employed. Thus, the affinity of the 2-sulfanyl-imidazole modified silica gel towards the various metals ions was $\mathrm{Hg^{II}} \gg \mathrm{Cd^{II}} > \mathrm{Cu^{II}} \approx \mathrm{Zn^{II}} \approx \mathrm{Pb^{II}} > \mathrm{Mn^{II}}$.

Mercier and Pinnavaia[71] have compared the mercury(II) absorption capacities of both 3-sulfanyl-propyl MCM-41 and HMS (both silicas possessing similar pore diameters). The HMS modified material (MP-HMS) exhibited far higher 3-sulfanyl-propyl loadings compared to those of the modified MCM-41 silica (MP-MCM-41). This was attributed to the higher hydroxyl concentration of the HMS material as a result of the template being removed by solvent extraction as opposed to calcination (SH loading was approximately 3 times higher for HMS). The rate of mercury(II) uptake was significantly greater for the MP-HMS material than for MP-MCM-41. This was explained by the larger fundamental particle size of the parent MCM-41 silica compared to that of HMS, which consists of aggregates of smaller fundamental particles,[72] therefore allowing better diffusion of the mercury(II) ions to the 3-sulfanyl-propyl sites. It was observed that the pore size of the HMS support affected the mercury(II) absorption. Thus, MP-HMS possessing a pore diameter of 1.5 nm, despite having a higher SH loading than that of MP-MCM-41 (pore diameter of 2.0 nm), had only 61% of the SH sites available for mercury(II) binding. In addition, MP-HMS (prepared by a templated sol–gel methodology) was observed selectively to bind $\mathrm{Hg^{II}}$ from a mixture of heavy metal ions ($\mathrm{Cd^{2+}}$, $\mathrm{Pb^{2+}}$, $\mathrm{Zn^{2+}}$, $\mathrm{Hg^{2+}}$, $\mathrm{Co^{3+}}$, $\mathrm{Fe^{3+}}$, $\mathrm{Cu^{2+}}$ and $\mathrm{Ni^{2+}}$).[73] The unusual low binding affinity of the thiol groups for $\mathrm{Cd^{2+}}$, $\mathrm{Zn^{2+}}$ and $\mathrm{Pb^{2+}}$ in the absence of other competing ions was attributed to only the thiol sites located on the external surface being available for binding. Conversely, the high affinity for $\mathrm{Hg^{2+}}$ was due to it being able to bind to SH sites within the pore structure of the HMS material. This again highlights the advantage of using silica gels as supports, which possess a well ordered array of pores.

5 Conclusions

This review has discussed the preparation and use of modified silica gels in clean technology. The major advances in recent years have been in the area of heterogeneous catalysis. Thus, this has constituted the main bulk of the discussion.

The immobilisation of both inorganic and organic reagents onto a silica gel surface offers a number of advantages. When employed as catalysts, reactions are generally cleaner and exhibit improved selectivity towards the desired products compared to those of traditional homogeneous methods. The catalysts are easily separable from the reaction mixture and, in many instances, reusable. Modified silica gels exhibit advantages over modified resins in that they possess high surface areas, have high thermal and chemical stabilities and are not prone to swelling. Silica gels can easily be modified with a wide variety of functional groups, thus leading to their use in numerous applications, especially in the preparation of fine and speciality chemicals and pharmaceutical compounds in liquid phase reactions. It is in these areas where environmentally unacceptable reagents and catalysts have most widely been applied and where current manufacturing processes lead to unacceptable levels of waste.

It is the development of surfactant templated silicas, such as MCM-41, that has probably seen the biggest advance in silica technology in recent years. In addition to offering high surface areas and large pore volumes, therefore enabling high loadings of active sites, the controlled pore size down to the super-micropore region offers the potential of shape selectivity in catalysis applications as well as better control in catalyst performance.[37] Recently, this technology has been applied to modified silicas prepared *via* sol–gel methodologies.[20–25] This has not only resulted in improved structural control of the final material, but by altering the silane:organosilane ratio the loading of active sites has dramatically been improved. At present the majority of the investigations have focused on the MCM-41 type materials (possessing a hexagonal array of pores). The preparation of novel materials using MCM-48 (cubic array of pores) or MCM-50 (lamellar pore structure) may offer the possibility of improved selectivity.

With increasing pressure from government for the application of more environmentally friendly chemical processes, the use of modified silicas for clean technology applications can only increase.

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