Chemistry on the inside: green chemistry in mesoporous materials

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An overview of the rapidly expanding area of tailored mesoporous solids is presented. The synthesis of a wide range of the materials is covered, both inorganically and organically modified. Their applications, in particular those relating to green chemistry, are also highlighted. Finally, potential future directions for these materials are discussed.

Keywords: silica; mesopores; catalysis; environment

1. Introduction

The chemical industry today is one of the most important manufacturing industries in the world. The ability of chemists to produce a wide range of different molecules, both simple and staggeringly complex, is very well developed, and nowadays almost anything can be prepared, albeit maybe only on a small scale. On an industrial scale, a great variety of products is synthesized, using chemistry which varies from simple to complex. Unfortunately, many of these processes generate a great deal of waste—often more waste is produced than product.

One of the major challenges for chemistry is therefore the development of new methods for the clean production of these chemicals. So-called end-of-pipe solutions, i.e. treating the waste generated from reactions to render it less harmful, are of limited value in the long term. In the last few years a new, intrinsically more powerful, approach has been pioneered. Green chemistry, as it has been called, involves the redesign of chemistry, such that the desired products from a reaction are produced without generating waste. This massive undertaking involves a wide range of approaches, from the invention of new reactions to developing new catalysts which allow more selective reaction to take place, to biotransformations and novel engineering concepts, which can also be used to minimize waste.

One of the newest areas in the realm of catalysis is that of tailored mesoporous materials, which are finding many uses as highly selective catalysts in a range of applications. A mesoporous material is one which has pores with diameter in the range of 2–50 nm (for comparison, a typical chemical bond is of the order of 0.1 nm). Such materials can be thought of as being analogous to the zeolites, which came to prominence in the 1960s. Zeolites are highly structured microporous inorganic solids (pores less than 2 nm), which contain channels and pores of very well-defined sizes, in which catalytic groups are situated. A wide range of zeolites is known, each having different pore sizes and channel dimensions. Many are used in large-scale industrial applications.

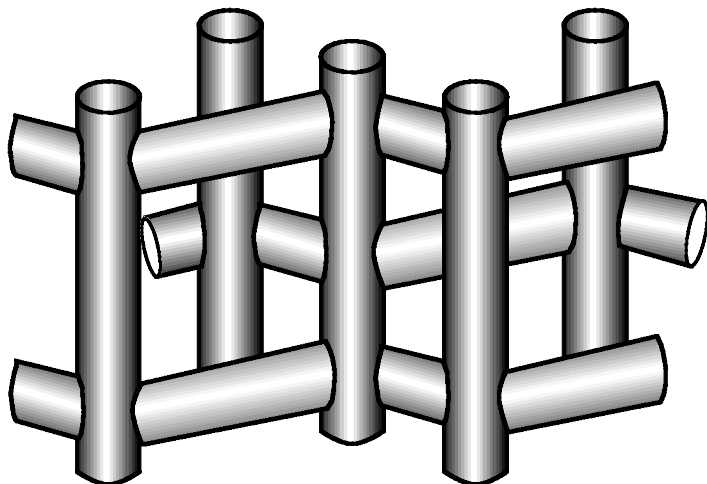*Phil. Trans. R. Soc. Lond.* A (2000) **358**, 419–430

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Figure 1. Representation of the pore structure of HZSM5, one of the most important zeolites industrially. The vertical cylinders represent one pore network, and the other cylinders an interconnecting network.

Zeolites are prepared by the linking of basic structural units around a template molecule. The structural units are typically based on oxides of silicon and aluminium, and the templates are usually small molecules such as tetraalkylammonium halides. Under the right conditions, the silicon and aluminium oxide precursors will polymerize around the template to form a crystalline three-dimensional matrix containing the template molecules. The template molecules can be removed by calcination, i.e. by treatment at high temperatures in air, where the template is effectively burnt out of the structure. This leaves a highly regular structure, which has holes where the template molecules used to be. These holes are joined to form pores and cages. It is in these pores and cages, also of very regular size and shape, that the catalytically active groups can be found (see figures 1 and 2).

Zeolites based on silicon and aluminium are acidic catalysts and are extremely thermally stable. This makes them ideal for use in the petrochemical industry, where some of the largest scale and most high-energy transformations are carried out. These transformations are carried out in the gas phase at high temperatures and involve small molecules such as dimethyl benzenes and small alkanes. Since the catalytic groups of the zeolite are found within the structure, the molecules must be able to diffuse into the structure before being able to react. The sizes of the pores and channels of the zeolites are designed to be very close to the dimensions of the molecules to be reacted. This means that small changes in size and shape can dramatically alter the ability of the molecule to reach the active site. Under 'normal' conditions, molecules react according to their electronic properties, i.e. since the electrons in the molecule must be rearranged during a reaction, their exact positioning and energy within the molecule usually determines both the rate and the nature of the reaction in a given situation. Harsh conditions usually allow many different reactions to take place, and are thus to be avoided if, as is almost always the case, a selective reaction is required. However, in the case of zeolites, the only molecules which can react are those which can fit into the pore
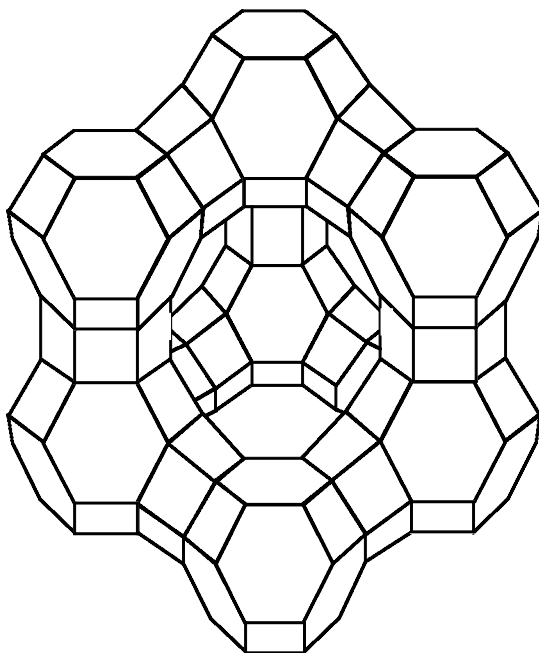
Figure 2. The structure of faujasite, a more open, larger-pore zeolite.

structure and get to the active site. Similarly, the only products which can be formed are those which are of the right shape and size to escape from the catalytic sites, migrate through the pores, and out of the catalyst. This phenomenon is known as shape selectivity, although size selectivity might be a more accurate description.

An example of this is the commercial process for preparing *para*-xylene, the precursor to terephthalic acid, which is polymerized to give poly(ethylene terephthalate). In this case, the mixture of xylenes obtained from crude oil is reacted in a zeolite (known as HZSM5). The relative rates of diffusion in and out of the pores are sufficiently different (by a factor of *ca.* 10^4) to allow the extremely efficient and selective conversion of all the isomers to the desired *para* isomer, which is the narrowest and can thus move through the structure most rapidly (see figure 3).

This type of selectivity is extremely valuable, as it gives chemists the opportunity to direct reactions in different ways to those available using conventional systems. With this in mind, chemists have searched for many years for materials with the same degree of uniformity displayed by the zeolites, but with larger pores. This would allow the concept to be extended to larger molecules such as pharmaceutical intermediates, and other highly functional compounds.

The pore size of most zeolites is less than 1.5 nm. This microporosity limits their utility in most areas of chemistry, for which mesoporous materials would be necessary. Unfortunately, attempts to use larger template molecules in the zeolite synthesis, an approach which should lead to larger pore size zeolites, have met with very little success. Some zeolitic materials have been prepared, but none which have both mesopores and significant stability. A new methodology is thus required.
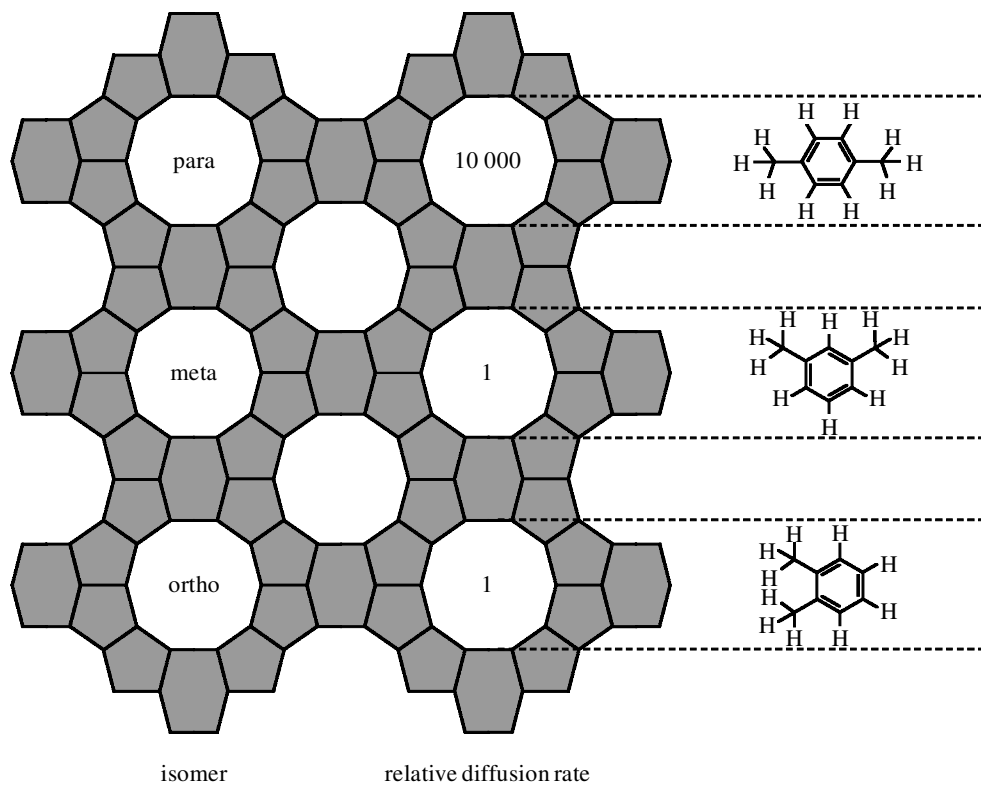
Figure 3. Relative diffusion rates in HZSM5. The shaded areas are the pore walls, the unshaded parts the vertical pore system from figure 1.

2. New mesoporous materials

In the past 20 years or so, the field of supramolecular chemistry has become enormously important, with Lehn, Cram and Pedersen winning the Nobel prize in 1987. The concept of supramolecular chemistry is that molecules can self-organize into definite structures, without forming covalent bonds, but rather through weaker interactions such as hydrogen bonding or hydrophobic interactions. One example of the latter, although not at all new, is the ability of molecules containing a polar head group and a long non-polar hydrocarbon tail (surfactants) to form micelles in polar, aqueous environments. These micelles form because the water-repelling hydrocarbon tails huddle together in the centre of a sphere, or sometimes a cylinder, to avoid contact with water. The polar head groups then form a layer on the surface of the sphere or cylinder, forming a barrier between the hydrocarbon tails and the water. The best-known example of these micelle-forming materials is the detergents. The diameter of the micelles depends on the exact nature of the surfactant, but is typically of the order of 2–4 nm. These dimensions are exactly those required for the pores in a mesoporous catalyst. The high profile of supramolecular chemistry helped to highlight such systems, and chemists from Mobil were the first to realize that this chemistry could be applied to catalyst design. Whereas initial approaches to mesoporous zeolites relied on larger and larger template molecules, Mobil researchers found that they could use
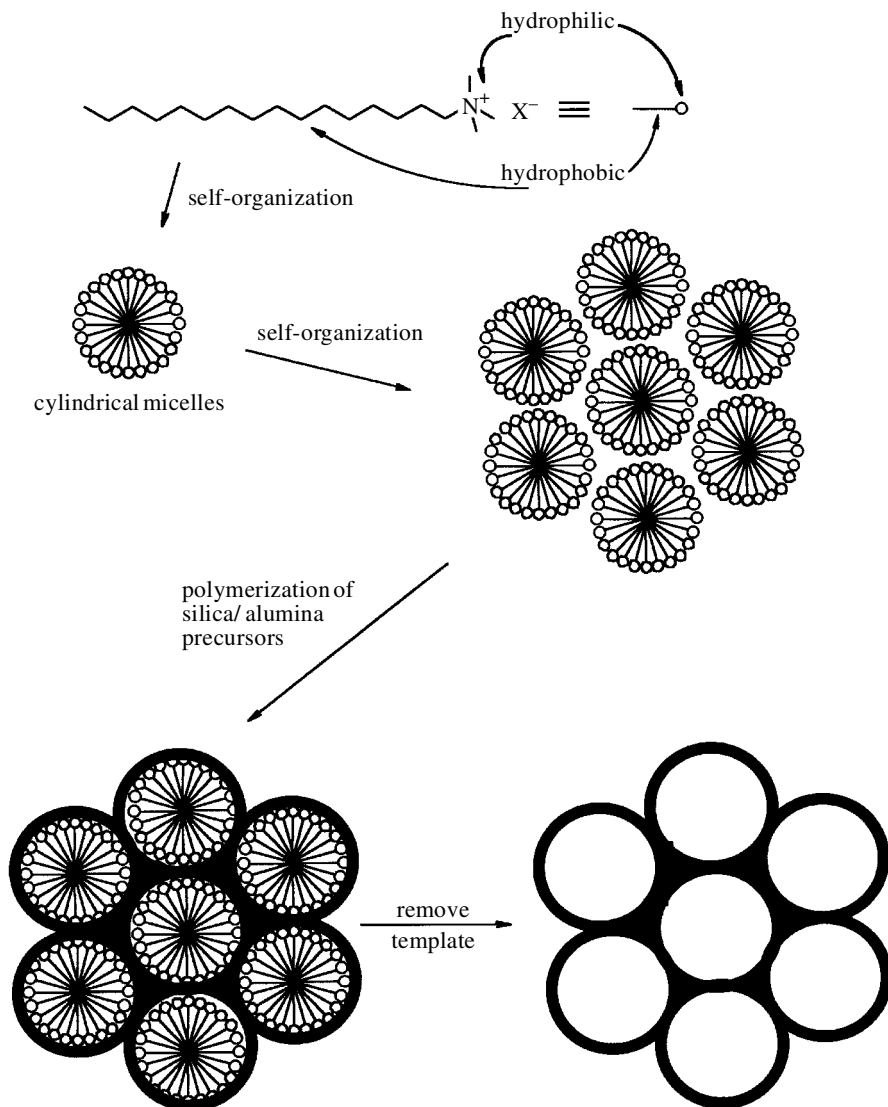
Figure 4. Preparation of MCM materials. The diagram shows self-assembly of the surfactant into micellar arrays, followed by condensation of silica around the micelles.

supramolecular assemblies of molecules as templates (Kresge *et al.* 1992). They chose long-chain quaternary ammonium salts as the micelle forming agent, and polymerized Si and Al precursors around these using conditions similar to those for zeolite manufacture (see figure 4).

These materials, known as MCMs (from Mobil composition of matter) can be prepared with a range of pore sizes. As the pore size is essentially the diameter of the micelle template, it is easy to estimate the pore size obtained with a given template. For example, an MCM made with a dodecyl trialkylammonium (C_{12}) template would have a pore diameter roughly twice the length of the dodecyl trialkylammonium

Figure 5. Expansion of a micelle by inclusion of a hydrophobic guest into the
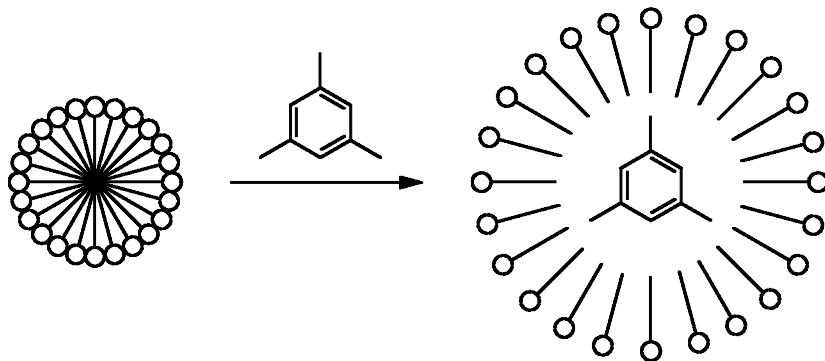hydrophobic interior of the micelles.

cation, *ca.* 2.2 nm. As the chain length of the template molecules decreases, there
comes a point where they do not form micelles. This happens around C_8, meaning
that the smallest pores achievable using this method are *ca.* 1.8 nm. Luckily, this is
almost ideal in many ways, since the largest zeolites have pore sizes of *ca.* 1.3 nm,
almost seamlessly extending the range of pore sizes available to the chemist. At the
other extreme, as the chain length increases, the ability of the quaternary salt to
form micelles decreases, due to lack of solubility, and the largest template molecule
which can easily be used is the C_{18} trialkylammonium salt. This gives a pore size of
ca. 3.7 nm. This range of sizes is sufficiently broad to allow ingress and reaction of
many large molecules, but the Mobil researchers managed to increase the pore dimen-
sions even further by expanding the micelle. They did this by inserting hydrophobic
mesitylene (trimethylbenzene) molecules into the interior of the micelle. The ratio-
nale is that the mesitylene molecules will preferentially exist in the hydrocarbon
interior of the micelle, rather than in the aqueous environment outside the micelle,
causing the micelle to expand (see figure 5).

MCM materials grown using these expanded micelles have pore sizes from 4.0 to
6.5 nm, depending on the quantity of mesitylene added during synthesis. A further
consideration in porous materials is the shape of the pores. Molecules have to diffuse
through the pores to feel the effect of the catalytic groups which exist in the interior
and, after reaction, the reaction products must diffuse out. These diffusion processes
can often be the slowest step in the reaction sequence, and thus pores which allow
rapid diffusion will provide the most active catalysts. It is another feature of the
MCMs that they have quite straight, cylindrical pores—ideal for the rapid diffusion
of molecules.

3. Different templates

The use of different templates allows the preparation of materials similar to the
MCMs. The long-range order typical of the MCMs is often reduced (not necessarily
a big problem for most applications), but this is often compensated by a greater
flexibility, allowing a wider range of materials to be prepared. Two main classes
of templates have been used other than the quaternary ammonium salts described
earlier. By far the more versatile appears to be a neutral amine system, initially
described by Pinnavaia. These materials are commonly called hexagonal mesoporous

silicas (HMSs) (Tanev & Pinnavaia 1995). Many different materials have now been prepared using this new route, which has many advantages over the original method. The preparation conditions are often much milder, the amine template can be easily recovered by washing, rather than the destructive calcination required to completely remove the quaternary template.

The utility of these methods has been extended well beyond the initial silica and aluminosilicate materials to cover a wide range of other materials incorporating many elements, usually as a minor, but important component with silica being the predominant component. For example, titanium containing materials have received a lot of attention recently, perhaps as a natural extension of the titanium silicate zeolites, which are now being used in a number of industrial applications. Indeed, the range of mesoporous materials containing elements other than silicon as the predominant species is growing rapidly.

In a further extension, the incorporation of organic molecules into these materials has been shown to be possible by several research groups. The more interesting variants are those where the organics are introduced during the synthesis of the material, with alternative approaches relying on the modification of pre-formed MCMs and HMSs (Macquarrie 1996; Burkett *et al.* 1996). The one step approach has the advantage of allowing very high levels of organic incorporation, a potentially very important feature of catalysts. It is also possible to introduce more than one organic group, thus paving the way to highly refined catalyst properties based on one catalytically active group, and another functional group modifying the polarity or affinity of the surface. There also appear to be several minor, but significant, differences in the behaviour of the materials, depending on the exact synthetic route used.

4. Applications

The initial applications of MCMs were, perhaps not surprisingly, simply attempts to reproduce zeolite chemistry on larger molecules. This chemistry is based on the fact that the aluminium centres in zeolites cause a negative charge to exist on the framework of the solid; this charge must be balanced by a cation. When the cation is a proton, the material is an acid, and some zeolites are very strong acids indeed. However, the acidity of the corresponding MCMs is considerably lower, and this has limited their applicability somewhat. Nevertheless, the MCMs are often very effective as mild acid catalysts. Much work has therefore been aimed at the production of other materials using the same concept, but with either different templating systems, or with combinations of elements other than Si and Al in the framework.

One method which has been successfully applied to increase the acidity of these systems is the immobilization of aluminium chloride onto the pore walls. Aluminium chloride is itself a very strong acid, and is one of the commonest in industrial chemistry. It is used in a wide range of transformations, but cannot be recovered intact from reactions. Its destruction leads to large quantities of waste being generated. Aluminium chloride has been successfully attached to the walls of HMS materials, without any reduction in activity, i.e. the resultant material has the same activity as unsupported aluminium chloride (Clark *et al.* 1997). A major advantage over free aluminium chloride is the ease of removal of the solid catalyst from reaction mixtures, simplifying the process and reducing waste dramatically. A second important advantage is the ability to control product distributions by tailoring the pore size
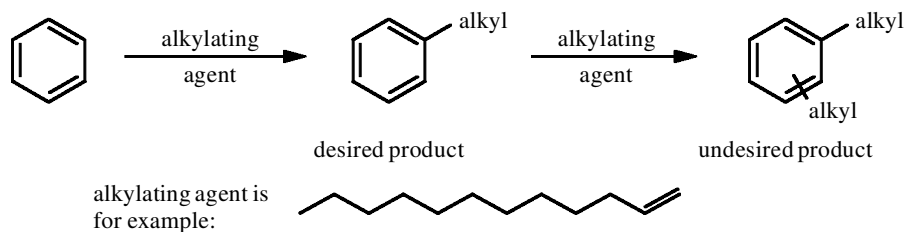
Figure 6. General scheme for the synthesis of linear alkyl benzenes, precursors to surfactants. Control over pore size if the catalyst can suppress the second alkylation almost completely.

of the material. This is best illustrated by the preparation of linear alkyl benzenes (LABs), which are precursors to detergents and are produced on a massive scale using either aluminium chloride or hydrogen fluoride, both of which have many problems associated with their use. The general scheme is shown in figure 6.

As can be seen, the reaction will proceed to the monoalkylated product, but does not stop there. The alkylated product is more reactive than the starting material, and will alkylate again, giving products which are useless. Control over this aspect of the reaction can only be achieved with difficulty in traditional systems, and very high dilutions are used to control the product distribution. The use of the new meso-porous materials allows a more concentrated (and thus more efficient) process to be developed. This is because the dialkylated product is bigger than the monoalkylated product. Careful choice of the pore size of the material will mean that the space inside the pore is too small for the dialkylated product to form, but is big enough for the desired monoalkylated product to form readily. Thus, the reaction can run selectively at high concentrations, solving the selectivity problem and using a catalyst which can be easily recovered. Waste is thus reduced dramatically.

The titanium–silicon MCMs and the related titanium–silicon HMSs are analogues of TS-1, a zeolite discovered in the 1980s by Enichem, an Italian chemical company which showed that TS-1 is an excellent catalyst for the selective oxidation of a variety of simple, small molecules. Such transformations are among the most important in organic chemistry, as they allow the introduction of a huge range of important functions into the basic hydrocarbon feedstocks derived from oil. Larger pore size versions of this material would allow a much wider range of organic molecules to be functionalized. Results with the Ti containing MCM and HMS materials have shown that these materials are indeed capable of carrying out many of the reactions of TS-1, but without the limitations of size which hampers the zeolite (Zhang *et al.* 1996). For example, one of the important applications of TS-1 is the hydroxylation of benzene to phenol, and then further to quinone. Larger molecules such as naphthalenes do not react, as they cannot fit into the pores of TS-1. Ti containing MCMs and HMSs are known and will accommodate such molecules. One important target is the synthesis of vitamin K3. Current practice still involves the use of acidic chromium reagents, which are used stoichiometrically in large quantities, and are highly toxic. Some success has been reported with the use of Ti containing mesoporous materials of this reaction type, and further progress is expected.

The organically modified versions of these materials have also been investigated as catalysts. Simple amine containing materials have been prepared by three different routes: post-modification of an MCM, and *in situ* preparation of both MCMs and HMSs. These materials are capable of the fast and efficient catalysis of several
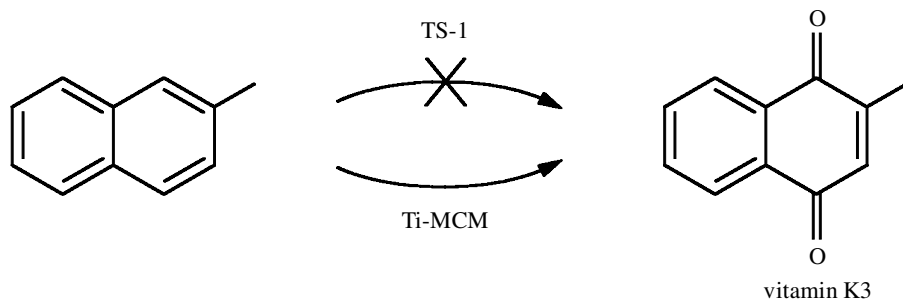
Figure 7. Possibilities for the synthesis of vitamin K3.

reactions with excellent selectivity. Activity is greater than that found with modified silicas, as is stability of the catalyst. The increased amount of amine groups which can be attached to the HMS and MCM materials gives them even more of an advantage over the traditional catalysts. Initial results on a catalyst with both amine and phenyl (non-polar) groups indicate a real rate increase over the simple amine-only material. The reasons for this are not yet understood, but may be due to the catalyst surface becoming less polar, and therefore improving the transport of reagents and products onto and off the surface. Many important reactions can be carried out with such solid bases, and their uses in synthetic chemistry will increase. In particular, many reactions which either do not generate any side products (additions or isomerization) or generate water (condensation reactions) are amenable to catalysis using these materials. We have published studies on the Knoevenagel condensation and the Michael addition, which show that the materials are capable of very efficient and selective catalysis of these important reactions (Macquarrie & Jackson 1997; Macquarrie *et al.* 1998*a*).

Thiol substituted materials have been found to be excellent adsorbents for heavy metals. The sulphur atom of the thiol group is known to complex strongly to heavy metal ions, with gold and mercury being two particularly interesting examples. The higher amounts of thiols which can be attached to the HMS and MCM materials means that their capacity for binding these metals, and removing them from, for example, drinking water, is much greater than that achieved with traditional materials (Mercier & Pinnavaia 1997).

Solid acids can also be prepared from these materials by oxidation of the thiol group to the sulphonic acid. This generates materials with acidity close to sulphuric acid (again one of the most commonly used acids industrially). The material can be easily recovered and easily handled; since the acidity resides within pores, it cannot come into contact with living tissue. Important transformations, such as esterification, have been reported using these materials (Bossaert *et al.* 1999). The scope for such materials in future is enormous.

More sophisticated materials have been made by attachment of transition metal complexes to the surface. These materials are designed to enhance the basic activity of the metal ion, by providing it with an environment tailored to make it as active as possible. The heterogenization of such (normally homogeneous) complexes has attracted a lot of attention, since the heterogeneous equivalents can be much more easily separated and recycled than the homogeneous ones, leading to much less waste being produced. These materials have been shown to be very active in a range of reac-

tions, leading to many important product types. One particularly important area of chemistry is the selective preparation of one of a pair of mirror images of a compound. This enantioselective catalysis requires great control over the exact chemical environment of the catalytic site, and is one of the major challenges in synthetic chemistry. Many drugs and agrochemicals have two mirror images, only one of which is useful, the other being useless or even dangerous. As an example of mesoporous materials containing enantioselective metal-centred catalysts, the group of Daniel Brunel in Montpellier has published work on alkylation using zinc species (Brunel *et al.* 1998). Selectivity was good, approaching that achievable with conventional systems. Further refinement of these systems will lead to improvements in the design of the catalytic site, and its surrounds, and the prospects for this area of catalysis are good.

Such solid materials are often favoured as *catalysts* because they can be easily separated from the liquid reaction medium and reused. This means that less waste is generated during the (often complex) separation steps at the end of a synthesis. In principle, the same advantages in separation would also apply to *reagents* in a reaction. Here, the use of materials such a zeolites and MCMs has been less important. This is because the vast majority of the material does not play an active part in the reaction, and thus a vast amount of solid has to be used to deliver a relatively small amount of reagent. One of the great benefits of the new method is that the amount of material can be reduced dramatically, in some cases no more than would be used with conventional systems. For example, a supported peracid has been discovered recently which has an effective molecular weight equal to that of the most commonly used conventional material (Macquarrie *et al.* 1998*b*). Peracids are important reagents in the preparation of epoxides, very important compounds in synthetic chemistry. With this new material, the amount of solid added to a reaction, in order to achieve complete reaction is only *ca.* 7% of that needed with peracids prepared using traditional approaches.

5. Future prospects

The future of these materials is very exciting indeed. Further work will reveal advanced catalytic systems, possibly containing more than one type of active site, and the control over pore dimensions will allow an ever-increasing level of control over selectivity towards the desired product. The ability to incorporate polarity-modifying groups will also play a major role in transport processes, of great importance in both catalysis and membrane processes.

Many other opportunities exist due to the enormous flexibility of the preparative method, and the ability to incorporate many different species. Very recently, a great deal of work has been published concerning methods of producing these materials with specific physical forms, such as spheres, discs and fibres. Such possibilities will pave the way to new application areas such as molecular wires, where the silica fibre acts as an insulator, and the inside of the pore is filled with a metal or indeed a conducting polymer, such that nanoscale wires can be fabricated. Initial work on the production of highly porous electrodes has already been successfully carried out, and the extension to unidirectional bundles of wires will no doubt soon follow (Attard *et al.* 1997).

The ability to produce discs and spheres of defined size and structure will be of great importance when the very promising initial results from catalytic studies are

applied on a larger scale. Processes using heterogeneous catalysts require the ability to control particle size and shape in order to ensure good mixing of all the reaction components, and separations after reaction (Gill & Ballesteros 1998).

A further application of this technology will certainly be the fabrication of membranes of these materials. Membrane reactors have shown great utility in many systems, where one component of a reaction mixture can be separated by permeation through a membrane, thus driving a reaction forwards (Ogawa *et al.* 1998).

Looking further ahead, the pores in these materials could be considered as analogous to ion channels in cell walls. If a hollow sphere of HMS or MCM material could be fabricated with, for example, an enzyme (or other cell component) inside, one could imagine this as being an 'inorganic cell'. The encapsulation of the enzyme inside the cell could then possibly be used to protect the enzyme from harsh conditions outside the cell, while allowing reaction components to diffuse in, react, and diffuse out again. Already, some effort is being expended on silica–biological composites, with significant advances being made. Given the enormous strides made since the discovery of the MCMs in 1992, such major advances will no doubt become reality in the early years of the 21st century.

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