INTRODUCTION

The societal significance of catalysis and the growing practical importance of single-site heterogeneous catalysts

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The concept of single-site heterogeneous catalysis, herein defined and extensively illustrated, offers a strategy for the design of new solid catalysts. By capitalizing on the opportunities presented by nanoporous materials to assemble a wide range of new, well-defined, catalytically active centres, it is possible to bring about numerous environmentally benign processes that can replace traditional methods of chemical production. The latter often employs aggressive, corrosive or hazardous reagents. By using both microporous (less than 20 Å diameter) and mesoporous solids (20–500 Å diameter), abundant scope exists for the construction and application of shape-selective, regio-selective and enantioselective catalysts.

Keywords: nanoporous solids; selectivity; benign reagents; renewable resources; clean technology; sustainability

1. Background

It would be difficult to overestimate or exaggerate the practical importance of heterogeneous catalysis. Think of the products of petroleum and natural gas upon which civilized life now relies. All the following are manufactured through the agency of solid catalysts: fuels (for transport and heating), fabrics, flavours, fragrances, fertilizers, certain foodstuffs and most pharmaceuticals. Moreover, many of the molecular building blocks for the production of a wide range of the commodities used in everyday life are also generated catalytically: propylene, benzene, toluene, xylene, benzaldehyde, terephthalic acid, adipic acid, caprolactam (precursor of nylon 6) and a variety of monomers for polymeric composites.

In fundamental, academic terms, the phenomenon of catalysis is endlessly fascinating and perennially new. Its study presents a multiplicity of intellectual and technological challenges. If we are to understand how and why certain molecules transform readily and others do not when they impinge upon an active

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One contribution of 14 to a Special feature ‘Recent advances in single-site heterogeneous catalysis’.
Introduction. Heterogeneous catalysis

It is necessary, continually, to devise, develop and deploy new techniques of investigation. This is equally true if our aim—and it is one of prime importance—is to know more about the nature of the active site itself. Without a detailed understanding of the atomic architecture of the catalytically active centre, we are unlikely to be in a position to improve existing catalysts or design superior new ones (Thomas 1997).

Because they readily facilitate the separation of products from unreacted reagents, and also because they are amenable to the various processes of thermal reactivation, heterogeneous catalysts (which almost invariably involve solid, active phases) are much more convenient to use than homogeneous ones. Consequently, they now figure eminently in the drive towards green chemistry, clean technology and sustainability. Those scientists concerned with such topics are currently exploring new ways of generating both energy and novel materials and in this regard, solid catalysts are of pivotal importance.

There is now an exigent need to design and develop catalysts that can cope with and transform readily available reactants in an environmentally benign manner. No longer is it acceptable to employ oxidants that are as aggressive as concentrated nitric acid, or as environmentally unacceptable as CrO₃. Instead, catalysts need to be created that can function selectively with O₂ or air or H₂O₂ or other hydroperoxides that create few or not deleterious by-products. Other desiderata include catalytic systems that generate no salts, and also those that require no solvents. In addition, a liquid reactant that is to be converted with high a selectivity into a sequence of desirable products should, if feasible, be exposed to an appropriate multifunctional catalyst that enables a sequence of successive conversions to be carried out in one pot. It is energetically demanding and otherwise inconvenient to have to use two or more distinct catalysts under different conditions from one another. (It has long been known that separate reactors and different catalysts in each is a costly method of manufacture.)

Over and above all these important considerations, there is the increasingly necessary drive to produce the materials (and energy) required for civilized life from sustainable sources such as carbohydrates and fatty acids from the plant and vegetable kingdom and from various forms of biomass. This, in essence, is the cardinal aim of sustainability.

With all these considerations in mind, single-site heterogeneous catalysts (SSHCs), as have been described elsewhere (Thomas et al. 2005; Thomas 2012), and are the central theme of this special issue, hold the key to success in addressing the challenges adumbrated above.

2. Definition of a single-site heterogeneous catalyst

The principal characteristic of an SSHC is that all of the active sites present in it are identical in their atomic environment and hence in their energy of interaction with a reactant. The active sites are also spatially separated, thus ensuring constancy of energy of interaction with incoming species (figure 1). The sites are also readily accessible to reactants because they themselves are distributed in a spatially uniform manner over the surface of the nanoporous (open-structure) solid where they are located.
There are two broad classes of SSHCs (Thomas 2008, 2012), which have much in common with one another. In one class, a nanoporous crystalline framework of very high surface area, largely internal, typically 1000 m$^2$ g$^{-1}$, contains spatially well-separated active centres that can be introduced during synthesis and readily characterized by \textit{in situ} and \textit{ex situ} spectroscopes and other techniques (such as those outlined in the article by Zecchina & Groppo 2012). Figure 1\textit{a},\textit{b} shows a real-space (high-resolution electron microscopic) projection image and a schematic, respectively, of this category of nanoporous SSHCs.

In the other class, again the solid matrix that accommodates the active centres is nanoporous of very high (internal) surface areas but the matrix itself is not crystallographically ordered. However, the pores themselves may (or may not) be ordered in arrays.

In the first class, typified by zeolitic molecular sieve solids such as the ZSM-5 shown in figure 1 and microporous aluminophosphates (ALPOs), the diameters of the pores leading into the interior cages and channels generally fall in the
3.8–12 Å range. Over 190 distinct structural types of these microporous solids have so far been identified. However, in theory, judging by recent computational exercises, many millions more could, in principle, exist (Klinowski & Thomas 2007). In general, fourfold coordination (of vertex atoms such as Si, Al and P) prevails. However, again in principle, there can be five- and sixfold linkages, with even greater numbers of hypothetical (and real) structures. The SSHCs made up of microporous solids may be so engineered, by the techniques of solid-state and inorganic chemistry that ‘heteroatoms’ (typically FeIII, MnIII or CoIII ions in place of AlIII or SiIV ions in place of PIV) may be placed in spatially isolated positions where they are separated by distances so far (typically 10 Å) away from the other heteroatoms that each is effectively an isolated single site. With this class of SSHC, shape-selective catalysis is greatly facilitated: certain reactants, because of size and shape, may readily reach the active centres that are predominantly located inside the catalyst. Likewise, certain products may more readily diffuse out of the vicinity of the active centre, whereas bulkier ones are not able to do so. The advantage of this class of SSHC is that bifunctional as well as mono-functional catalysts may be designed. That is to say, acidic (e.g. Brønsted or Lewis acid active sites) and redox active sites may be housed within the same catalyst. The article by Li et al. (2012) gives an up-to-date account of the various kinds of microporous ALPOs and their framework-substituted (metal) derivatives designated MAPOs, or silica-substituted (SAPOs) analogues. When, for example, a CoII ion replaces an AlIII ion in an ALPO microporous solid, a Brønsted acid catalyst (e.g. CoIIALPO-18) results. This, along with other ALPOs where cations in the II oxidation state isomorphously replace AlIII constitutes very good SSHCs for the catalytic conversion of methanol to ethylene and propylene (Chen & Thomas 1994). When, however, transition-metal ions such as CoIII, MnIII or FeIII substitute for AlIII in the framework of the ALPO, redox catalysts, suitable for the selective oxidation of linear alkanes (Raja & Thomas 1998), cyclohexane (Raja et al. 2000) and toluene (Raja & Thomas 2006), in air or O2 are formed. The article by Corá et al. (2012) gives a quantum-mechanical interpretation of the way in which these SSHCs catalysts activate C–H bonds aerobically and at relatively low temperatures.

In addition to the so-called zeotypic microporous solids (typified by zeolites, ALPOs, MAPOs and SAPOs), there are other, recently exploited, microporous solids that are potentially—and in several cases are already—powerful new variants of microporous SSHCs. Foremost among these are the metal-organic frameworks (MOFs), and are discussed in this special issue, especially by Maksimchuk et al. (2012), and by Ronachiari et al. (a full account of ways of engineering MOFs as potential catalysts has been given by Ferey (2008), Corma et al. (2010) and Ronachiari and by von Bokhoven (2010) and Ronocchiari et al. (2012)).

For the sake of completeness, we should also mention other types of SSHCs that fall into the first category, namely certain polyoxometalates (Kholdeeva 2006), pillared clays (Jones 1985) and also the fascinating extra-framework cations in zeolites, which is the subject of the article in this issue by Pidko et al. (2012). While it has long been known that La3+ ions located as extra-framework entities in zeolite-Y constitutes one of the most powerful catalytic cracking (in hydrocarbons) catalyst—see Thomas (2011) and Schüessler et al. (2011) for
a recent discussion of how cation hydrolysis of this ion liberates protons that are the key agents for the formation of carbocation and carbenium ions required to ‘crack’ a paraffin and other hydrocarbon molecules—only relatively recently, as Pidko et al. (2012) explain, have we grown to recognize the vital role that extra-framework (single-site, but multinuclear) species play in such important catalytic reactions as the conversion of benzene to phenol using nitrous oxide (see Panov et al. 1993).

In the second class, typified by ordered or disordered mesoporous silica in which the diameter of the pores may be so arranged (by appropriate methods of synthesis) as to fall, controllably, within the range of ca 20–300 Å, the active centres that may be subsequently grafted or anchored to their inner surfaces may be of many different kinds. Specific examples are transition-metal ions such as TiIV anchored via Ti–O–Si bonds to the support, or a variety of bimetallic or trimetallic clusters consisting of up to ca 20 atoms, for example Ru6Pd6 or Ru5PtC.

Many bimetallic and trimetallic clusters may be inserted into the interior walls of the (inert) silica and be firmly anchored to them (figure 2).

It is important to emphasize that these minute ‘molecular metallic’ nanoclusters are very different electronically from nanoparticle platinum group metals, such as a 10 nm diameter one composed of Pt. In the latter, there are more than $10^8$ atoms; moreover, these nanoparticles possess a continuous range of electronic energies. In contrast, a Pt3 nanocluster has discrete energy levels—not a band. Moreover, the highest occupied molecular orbital is considerably higher in energy in the three-atom cluster than in one containing 309 atoms or $10^8$ atoms (figure 3).

All this means that the ease of transfer of electron to or from a reactant molecule impinging upon a nanocluster is much facilitated compared with the same transfer to or from a nanoparticle. In other words, catalytic turnover is facilitated on nanocluster mono-, bi- or trimetallic entities in comparison with nanoparticles or bulk counterparts of the same composition.

Figure 3. Computed energy levels of outermost electrons in a nanocluster Pt$_3$ compared with the corresponding computed levels in a much larger cluster Pt$_{309}$. Note that the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) for the small cluster are much higher (by ca 1.5 eV) than the corresponding orbitals in the large cluster. This fact is, in part, responsible for the better catalytic performance of small clusters compared with that of nanoparticles (of typical diameter 3–10 nm). (Thomas & Raja 2010—Reproduced from Springer.) (Online version in colour.)

We have already alluded to two examples of the second category of SSHCs; but there are many more, as described fully elsewhere (Thomas 2008, 2012). To summarize, some of the more important other examples, we have:

— Cr$^{II}$ sites anchored on to silica (see the article by Zecchina & Groppo 2012), which are exceptionally powerful polymerization catalysts for the conversion of ethylene to polythene.
— Ni$^{II}$ sites that convert ethylene to propylene (Iwamoto & Kosugi 2007).
— Mo$^{VI}$ sites that catalytically convert methanol to formaldehyde (see Shannon et al. 1998).
— Many metal complexes that may function in a variety of different catalytic contexts as described in this issue by Diaz et al. (2012). See also Jones (2010).
— Binuclear Ti$^{IV}$ entities that catalyse the formation of vitamin E intermediates (see Kholdeeva et al. 2007).

We shall recall later the growing practical importance of SSHCs of both types that have been discussed in this section. Before proceeding to do so, however, it is instructive to draw attention to other features of this type of heterogeneous catalyst.
3. Single-site heterogeneous catalysts facilitate the fundamental study and deeper understanding of heterogeneous catalysts

So far as the first category of SSHCs is concerned—that is, those in which heteroatoms such as Al$^{III}$, Ti$^{IV}$ or Sn$^{IV}$ ions introduced into a zeolitic molecular sieve such as silicalite (figure 4) so as to generate either Brønsted or Lewis acid active centres—it is possible by X-ray absorption, UV–visible, diffuse–reflectance, high-resolution NMR spectroscopy and other techniques described (see Marchese et al. 1997; Wegner et al. 2012; Zecchina & Groppo 2012) to determine the precise atomic environment of the active centre. (Seldom is it feasible to do so with those heterogeneous, solid catalysts which are composed of close-packed structures, although there are a few exceptions—see Zambelli et al. 1996.)

With the second category, those in which active sites are grafted onto the inner surfaces of mesoporous silica, there are the twin advantages of knowing from in situ X-ray absorption spectroscopic studies that follow the full and detailed course—synthesis, activation, actual catalytic turnover, the expiry of catalytic activity and its regeneration—of all the structural variants of the catalyst from its precursor to active state. This sequence was described by Maschmeyer et al. (1995) in the case of the tripodally anchored Ti$^{IV}$–OH group (shown in figure 5). We shall return shortly to the quantum-mechanical interpretation of these individual interpretation of these individual steps.

First, however, it is prudent to outline descriptively the individual steps involved in the assembly of this efficient epoxidation catalyst. By using an organometallic precursor of the appropriate type, we can ensure that the
Figure 5. The catalytic cycle, including density functional theory calculated energies, for the epoxidation of an alkene $R\text{CH} = \text{CH}_2$ to its epoxide by a four-coordinated Ti$^{IV}$ active site at a mesoporous silica surface. *In situ* X-ray absorption studies (XAFS) established the nature of the bare active site and also the steady-state coordination of Ti$^{IV}$. Summarized XAFS data are shown at the right-hand side of the figure. (Catlow *et al*. 2005—Reproduced from The Royal Society.) (Online version in colour.)

individual active sites are spatially well separated in the final catalyst. The specific example involves using titanocene dichloride \{\((C_5H_5)_2TiCl_2\)\} as the precursor. It interacts with the silanol (Si–OH) groups at the mesoporous silica surface—fig. 2 of the article by Ward *et al*. (2012) for an illustration of this step—and, in the presence of an added, simple amine, the titanocene loses its chlorine atoms and ends up as a half-sandwich compound, with just one cyclopentadiene (cp) as shown in figure 6. Because the cp groups still attached to each anchored Ti atom exert mutual, van der Waals repulsion, this ensures that the Ti$^{IV}$ active centres that are finally generated (by gentle oxidation of the C$_5$H$_5$ moieties) are spatially well separated. X-ray absorption (XAFS) spectra establish beyond doubt the precise structure of the four-coordinated Ti$^{IV}$ active centre. It has a pendant OH group (a titanol) and is tripodally attached to the silica. See also Corma *et al*. (1998).

XAFS measurements conducted during the cause of a typical heterogeneous reaction, such as the epoxidation of an alkene (cyclohexene) with an alkyl hydroperoxide (ROOH), reveals that at steady state (see Sankar *et al*. 2001), the Ti$^{IV}$ centre takes up sixfold coordination (from its original faces) but it remains in the IV oxidation state. Combined XAFS and density functional theory (DFT) analysis leads to the reaction mechanism shown in figure 5. It follows the classic Eley–Rideal mechanism: the alkylhydroperoxide reactant is first bound to the active centre, then the cyclohexene reactant plucks off one of the oxygens bound to the Ti (a Lewis acid centre) to yield the epoxide, thereby exposing afresh the four-coordinated, Ti$^{IV}$-centred active site (Catlow *et al*. 2005).

preparation and \textit{in situ} study (XAFS and FTIR) of a single-site Ti(IV) epoxidation catalyst from Ti(Cp)$_2$Cl$_2$ and mesoporous silica.

Figure 6. \textit{In situ} X-ray absorption fine structure spectroscopy (XAFS), shown at the extreme left, coupled with \textit{in situ} FTIR (not shown), can trace the conversion of the precursor organometallic titanocene dichloride (whose entry into a single mesopore of the silica is shown schematically at bottom right) via the bound half-sandwich intermediate, top right, into the final spatially separated tripodally attached titanol (OH Ti≡(OSi)$_3$) active site. (Thomas 2012—Reproduced from Imperial College Press and World Scientific Press.) (Online version in colour.)

Further understanding of the nature of the catalytically active centres present in the second category of SSHC (i.e. those that are attached to the inner surfaces of mesoporous silica) stems from the convenient chemical fact that small fragments of silica, the so-called silsesquioxanes (otherwise known as polyhedral oligomeric silsesquioxanes, POSS), may be readily prepared. Pioneering work, especially by Feher \textit{et al.} (1989, 1992) and later by Abbenhuis (2000), showed that small entities such as Si$_8$O$_{12}$R$_8$ (where R is an organic group linked to the silicons of each vertex of a cube), or incompletely formed cubes, such as that shown in fig. 4 of the article by Ward \textit{et al.}, can be readily dissolved in a homogeneous solution. An active centre can easily be attached to one of the vertices. It therefore means that a direct comparison can be made on the performance of the same catalytically active centre in a homogeneous state, on the one hand, with a heterogeneous catalyst on the other. It transpires (see Thomas \textit{et al.} 1999) that their performance in these two distinct states is very similar. It also enables the influence of slight changes in atomic environment (e.g. changing HO–Ti–(OSi)$_3$ to HO–Ti(OSi)$_2$(OGe) to be ascertained). It emerges that the change in performance of these two particular catalysts as between a heterogeneous (single-site) and homogeneous (single-site) is similar (Thomas \textit{et al.} 1999).

Our discussion here divides conveniently into two. In the first, we are concerned with the anchoring (or immobilization) of an organometallic species on the inner walls of mesoporous silica in which the ligand attached to the metal possesses chirality. It has been demonstrated (see summary in Thomas & Raja 2008; Thomas 2012) that a given chiral organometallic catalyst, when anchored (covalently or ionically or by strong hydrogen bonding) to the concave surfaces of mesoporous silica, exhibits enhanced enantioselectively in its performance, compared with that which it has when bound to a flat or convex surface. To take specific examples, complexes composed of either Pd$^{III}$ or Rh$^{I}$ metals bonded to (inexpensive) diamino ligands of a specific chirality and anchored within the channels of mesoporous silica are very effective enantioselective SSHCs in selectively hydrogenating substrates such as methylbenzoyl formate to biochemically desirable products. In similar vein, Corma & Garcia (2002) used Mo$^{VI}$ complexes of chiral ligands (derived from hydroxyproline) and heterogenized onto the inner surface of (stabilized Y zeolite) to effect asymmetric oxidation of geraniol. Here, the enhanced enantioselectivity arises from steric congestion encountered by a prochiral substrate (see Thomas & Raja 2008).

In the second category, the chirality resides on the walls of the nanoporous MOF solids within which a single-site (active centre) is introduced. Recent workers in this field include Rosseinsky (Vaidhyanathan et al. 2006; Wu & Lin 2007; Ma et al. 2009). The full significance, and potential in asymmetric catalysis, is described in the article by Song et al. (2012), where the intriguing development of dual active site for sequential asymmetric catalysis is elaborated.

(b) Single-site photocatalytic systems

The extensive studies of Anpo et al.—see Anpo et al. (1994, 1997, 1998) and Anpo & Thomas (2006)—have amply demonstrated that both extra-framework ions (such as Cu$^{+}$ in zeolite ZSM-5) and anchored oxychromium species functions as single-site photocatalysts in a number of environmentally significant circumstances. One such reaction that is effected photochemically with these SSHCs is the reduction of CO$_2$ with H$_2$O (Anpo et al. 1997). Another is the breakdown of NO (Anpo et al. 1994). Yet, another example is the general decomposition of undesirable molecules with SSHCs (Anpo & Thomas 2006) as well as the selective oxidation of CO in the presence of H$_2$ (Kamegawa et al. 2007).

Using both zinc-modified zeolites (see Li et al. (2011) and Wei et al. (2012)) as well as novel uranyl naphthalene–dicarboxylate coordination polymeric compounds (see Xia et al. 2010), Chen and co-workers, as outlined in their contribution in this issue, have made detailed quantitative studies of single-site photocatalysis involving porous structures. It is clear from their paper that much may be expected in future from the deployment of such nanoporous solids for the important reactions that Chen et al.—e.g. the coupling of methane to yield ethane—have already begun to explore.

In addition, Yamashita et al. (in this issue) focus on the importance of single-site heterogeneous photocatalysts, in particular their detailed characterization and advantageous properties.
Table 1. A selection of some of the facile conversions that may be effected under benign conditions with air or peroxide using designed inorganic single-site heterogeneous catalysts. Many of these processes use no solvents. All these conversions as well as others have been devised in the author’s laboratory (Thomas 2012).

1. toluene to benzyl alcohol, benzaldehyde and benzoic acid. Styrene to styrene oxide and the epoxidation of cyclo-olefins, α-pinene and (+)-limonene.
2. aerobic, shape-selective oxidation of cyclohexane and n-hexane to adipic acid. Conversion of cylohexene by H₂O₂ to adipic acid.
3. regio-specific oxidation of linear alkanes (at the CH₃ termini) in O₂.
4. bromine-free synthesis of terephthalic acid from p-xylene using air as oxidant.
5. single-step production of ε-caprolactam from cyclohexanone; also a single-step process for producing the oxime of c-hexanone with NH₃.
6. generation of hazardous reagents in situ for Baeyer-Villiger oxidation of ketones to lactones. In situ generation of hydroxylamine from NH₃.
7. one-step production of niacin (vitamin B₃) and other nitrogen-containing pharmaceutical chemicals.
8. one-step solvent-free hydrogenation of polyenes.
9. asymmetric synthesis of pharmaceutical intermediates.
10. regioselective and stereoselective allylic aminations.

4. A brief summary of the practical value of single-site heterogeneous catalyst in the drive towards clean technology and sustainability

Here, we enumerate specific examples of demonstrated laboratory processes that have emerged through the use of SSHCs. Such is the rapidity with which SSHCs is now being deployed that the advances recorded in this author’s monograph completed in mid-2011—table 1—have been further extended in ways that clearly demonstrate their importance in enhancing the prominence of green chemistry and clean technology, while also offering real prospects of establishing a renewable chemicals industry that goes beyond petrochemicals (see Christensen et al. 2008; Gandini 2008; Vennestrom et al. 2011).

As described by Osmundsen et al. (2012), lactic acid, a typical renewable chemical, is an important commodity chemical currently produced from carbohydrates by fermentation. But it is now feasible, using Lewis acid SSHCs, to prepare lactic acid derivatives by the combined esterification/isomerization of triose sugars (see also Holm et al. 2010). West et al. (2010) have demonstrated the relative ease with which a SSHC such as zeolite H-USY (Si/Al = 6) produces lactic acid and methyl lactate from C₃-sugars. (Lactic acid, as implied earlier, is currently emerging as a building block in a new generation of materials such as biodegradable plastics and solvents.)

Terpenes occur extensively in the materials of the living world (Monteiro & Veloso 2004). They are natural products, the structures of which are built up from isoprene units. Guidotti et al. (2009), Ravasio et al. (2004) and Santo et al.’s (2012) article remind us that SSHCs (especially TiIV-oxo-centred ones on mesoporous silica) are well-suited for their utilization as a means of obtaining bulk and high-added value chemicals.
Table 2. Single-site heterogeneous catalysts that have already been shown to be effective in the production of essential chemicals from renewable (vegetable and plant) sources. Typical examples are given here.

<table>
<thead>
<tr>
<th>nature of naturally occurring feedstocks</th>
<th>typical products</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>corn</td>
<td>adipic acid</td>
<td>Thomas et al. (2003) and Editor's Comment Science (2003)</td>
</tr>
<tr>
<td>biomass</td>
<td>substitute fuel (dimethylfuran)</td>
<td>Roman-Leshkov et al. (2007)</td>
</tr>
<tr>
<td>carbohydrates</td>
<td>aromatics lactic acid derivatives</td>
<td>Carlsson et al. (2009)</td>
</tr>
<tr>
<td>terpenes and terpenoids glucose</td>
<td>epoxides and derivatives</td>
<td>Guidotti et al. (2007, 2009)</td>
</tr>
<tr>
<td></td>
<td>fructose (in aqueous medi at low pH)</td>
<td>Nikolla et al. (2011)</td>
</tr>
<tr>
<td>fatty acid methyl ethers</td>
<td>epoxides and derivatives</td>
<td>Guidotti et al. (2006)</td>
</tr>
</tbody>
</table>

So far as fatty acid methyl ethers that also occur extensively in the natural world are concerned the work of Guidotti et al. (2000, 2007, 2009), as well as the Dal Santo et al. article, gives ample evidence of the great utility of SSHC in selectively oxidizing them to useful epoxides and other derivatives.

Biomass is currently being intensively investigated as a feedstock with the aim of producing both biodegradable polymers, such as polylactic acid, and also transportation fuels to replace those that, at present, are derived from oil and gas. Carbohydrates constitute some three-quarters of renewable biomass, so that the quest for new catalysts to convert them to useful products continues to intensify (see Roman-Leshkov et al. 2007; Carlsson et al. 2009; Nikolla et al. 2011). Carlsson et al. (2009), have reported that with ZSM-5 (Si/Al = 60), which is a better SSHC than zeolite Beta-Ru, aromatics with carbon yields in excess of 30 molar carbon per cent were obtained from glucose, xylitol, cellobiose and cellulose.

A desirable transportation fuel, explored by Dumesic and co-workers in the University of Wisconsin (see Roman-Leshkov et al. 2007), is 2,5-dimethylfuran (DMF). The latter has a higher energy density (by 40%), and a higher boiling point than ethanol, and it is not soluble in water. Catalytic schemes have been formulated to generate 5-hydroxymethyl-furfural (HMF; from carbohydrates) and then to remove, catalytically, two oxygen atoms from HMF to form DMF. Nikolla et al. (2011) have shown that HMF may be readily synthesized from carbohydrates using Sn-zeolite Beta. This last SSHC facilitates isomerization of glucose to fructose in aqueous media at low pH. As these workers point out, glucose is the most abundant monosaccharide and the cheapest hexose, which make it a promising candidate as raw material for the production of HMF.

Table 2 summarizes a few of these key advances in green chemistry, clean technology and the use of renewable feedstocks, all achieved through the agency of SSHCs.

We conclude this article by recalling a few other examples of continuing developments involving SSHC for the more efficient utilization of petrochemical feedstocks.

(a) More efficient use of existing (traditional) feedstocks for the production of bulk chemicals

(i) Brønsted acidic microporous single-site heterogeneous catalyst for hydroisomerization (dewaxing) of alkanes

Hydrotreating, which induces long-chain alkanes to isomerize as well as to break up into smaller and/or branched daughter molecules, is a major practice in the petrochemical industry. It relies crucially on having an adequate concentration (on the internal faces of microporous zeotypes) of Brønsted active sites (as in figure 1). At the heart of dewaxing, and hydroisomerization in general, is the concept and reality of shape-selectivity, mentioned earlier.

At the Brønsted acid sites on the internal surface of a dewaxing microporous catalyst, a linear alkane is converted to a protonated cyclopropane (carbocationic) intermediate that then proceeds to the product molecules, the nature of which is governed by the topography and tortuosity of the pores in the chosen catalyst.

Dewaxing catalysts are required, inter alia, to ensure that diesel and other fuels flow freely and have low viscosities. A full discussion of how the choice of new SSHCs for dewaxing can be facilitated is given in the author’s recent monograph (Thomas 2012, §4.3.2).

(ii) Brønsted acidic microporous single-site heterogeneous catalysts for the dehydration of alkanols: environmentally benign routes to ethylene, propylene and light elements

Here, we are concerned with the production of the ever-increasing need for ethylene from ethanol, a readily sustainable feedstock (bioethanol). We also deal with the more mature, but rather enigmatic, process of converting methanol to light olefins: the so-called methanol-to-olefin (MTO) conversion.

With there being no shortage of ethanol (from biosources), SSHCs such as those depicted in figure 7 can smoothly dehydrate ethanol (ca 80% conversion and 95% selectivity) to ethylene at temperatures as low as ca 420 K.

So far as the MTO conversion is concerned, Chen & Thomas (1994) showed that MAPO-18 SSHCs (with M = CoII, MgII, MnII or ZnII) are very efficient in producing both ethylene and propylene, with just traces of butene under mild conditions. There have since been enormous efforts expended in understanding and perfecting this reaction. These developments are described in §4.4.2 of the author’s monograph (2012).

(iii) The catalytic conversion of ethylene to propylene

To effect this important conversion (figure 8)—propylene as a structurally important polymer is in even greater demand now than ethylene, important as the latter is for packaging and other purposes—the Japanese worker, Iwamoto and co-workers (Iwamoto & Kosugi 2007) constructed a trifunctional SSHC catalyst, summarized in figure 8.

Using a specially designed SSHC composed of mesoporous silica containing exposed acidic sites and metal-centred metathesis ones, they succeeded, with their so-named Ni MCM-41 catalyst, to effect a conversion of over 50 per cent...
Heterogeneous catalysis

microporous (ca 4 Å diameter pores) Brønsted acid catalysts

Figure 7. All three of these microporous SSHC, composed of framework-substituted aluminium phosphates, exhibit high Brønsted acid catalytic activity in the dehydration of ethanol and methanol to produce ethylene and other light olefins. (Thomas et al. 2009—Reproduced from Springer.) (Online version in colour.)

Figure 8. An outline of the mechanistic details involved in the use of a trifunctional SSHC for the production of propylene from ethylene. (Iwamoto & Kosugi 2007—Reproduced from The American Chemical.) (Online version in colour.)

of the ethylene with a selectivity of some 55 per cent towards propylene at a temperature of ca 400°C. Clearly, there is ample scope for further improvement in this novel catalyst.

(iv) Nanoporous single-site heterogeneous catalysts for converting light alkanes to alkenes and aromatics

The British Petroleum Company as long ago as the early 1990s reported their so-called Cyclar process, which converts light alkanes, particularly ethane and
Table 3. Important practical properties of nylon 6.

1. nylon 6 fibres are tough, possessing high tensile strength as well as elasticity and lustre.
2. high stability in O₂: does not degrade readily.
3. resistant to abrasions: readily made into any desired shape: readily sterilized.
4. lightweight: low aptitude to absorb water.
5. electrically insulating: durable: adheres to rubber readily.
6. may be manufactured in many colours because of ease with which it can be dyed.
7. softening temperature may be significantly increased by incorporation of thin lamellae of montmorillonite clay to form nanocomposites usables as components of car engines.

aNanocomposites with carbon nanotubes also feasible.

A. Hasegawa et al. (2003).

propane (which are present in several sources of natural gas), into aromatics, the key feature of their nanoporous (ZSM-5) catalyst being the presence of gallium (see Thomas & Liu (1986)). This Ga/ZSM-5 catalyst has not yet been fully commercialized, but its importance must not be underestimated, because it has been confirmed that it causes first dehydrogenation of the light alkane and subsequently aromatization of the thus produced alkenes. The full mechanism of this reaction has yet to be evaluated, but computational work, first by Bell and co-workers (see Gonzales et al. 1999) and more recently by Pidko et al. (2007), has revealed that the gallyl ion (GaO⁺) is the single site that is crucial in this conversion, which is of significance when oil supplies are depleted but natural gas sources are not.

5. Nylon 6

Nylon 6 possesses a range of commercially attractive properties that make it extremely important as a synthetic material; these are summarized in table 3. Over and above all these uses, many of which are shared by other forms of nylon (e.g. nylon 6,6), it is readily degraded (recycled) using, for example, superheated steam. Unlike other nylons that, after use, often end up in landfill, nylon 6 (polycaprolactam) can be reprocessed and the individual monomic units recovered. It is, therefore, an environmentally friendly form of nylon.

Existing routes for the manufacture of nylon 6, e.g. the Raschig process (which uses hydroxylaminehydroxysulphate and oleum and generates massive quantities of unwanted ammonium sulphate), are usually environmentally unfriendly.

In 2005, the author and his colleagues (Thomas & Raja 2005), building on earlier work using nanoporous bifunctional SSHC (Raja et al. 2001), demonstrated a route, outlined in figure 9, to the production of cyclohexanone oxime that was environmentally benign. Moreover, this process does not generate unwanted by-products, it uses air (or O₂) as the oxidant, is solvent-free and has the added merit of generating the key reactant (hydroxylamine) in situ, within the nanoporous SSHC. This breakthrough is now under commercial development, both for the manufacture of the key oxime and the nylon 6.

Figure 10 shows which of the various options of SSHCs that may be designed is the most effective for the benign production of nylon 6.

Figure 9. A summary of sequence of conversions that produce ε-caprolactam (and its linear polymer, nylon 6) from cyclohexanone (1) via its oxime (2).

Figure 10. Illustration of the supremacy of the bifunctional nanoporous catalyst, composed of CoIII (redox) and MgII (Brsönsted) active centres for the solvent-free production of caprolactam and nylon 6 without generating unwanted solid products. (Online version in colour.)

References


Introduction. Heterogeneous catalysis


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Introduction. Heterogeneous catalysis


