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Innovations in oxidation catalysis leading to a sustainable society[☆]

John Meurig Thomas[a,b,*], Robert Raja[c,**]

[a] Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, UK
[b] Davy Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London W1S 4BS, UK
[c] Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

Abstract

The strategic principles that enable simple, open-structure solid catalysts to be systematically designed so as to oxidize selectively a wide range of organic compounds in air or oxygen under mild conditions, and often without use of solvent are outlined. Illustrated examples of specific reactions, that utilize single-site catalysts that permit these conversions, include: preferential conversion of cyclohexane to adipic acid, toluene to either benzaldehyde or benzoic acid, linear alkanes to terminally oxyfunctionalized products, alkenes to epoxides, ketones to lactones, methanol to formaldehyde and ammonia to hydroxylamine, the last reaction under *in situ* conditions. Single-site catalysts open up methods for the future avoidance of ecologically harmful procedures, which are still publicized in modern textbooks, that use aggressive stoichiometric oxidants such as CrO_3/H_2SO_4, pyridinium chlorochromate, SeO_2, $KMnO_4$ and $KHSO_5$.

Keywords: Single-site heterogeneous catalysts; Selective oxidation; Clean technology; Green chemistry; Polymer recycling; ε-Caprolactam

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1. Introduction

To reach the goals that the community of scientists focussing on selective oxidation have nowadays identified one must recognize a number of important needs. These are enumerated below:

- the desirability of effecting single-step and/or solvent-free processes;
- to maximize the use of mild conditions, ideally involving benign reagents and benign catalysts;
- to replace stoichiometric oxidation processes by catalytic ones;
- to design durable heterogeneous (solid) catalysts of very high activity and selectivity that are amenable to recycling.

Finally, as well as seeking cheap, readily preparable catalysts, they should also be capable of using oxygen (preferably) or H_2O_2 (or alkyl hydroperoxides) – in order of decreasing preference – as the oxidizing agent.

To a large degree, our work in recent years has been able to satisfy these particular desiderata, and we list in Table 1, the specific selective oxidations as well as the benign catalysts that we have succeeded to develop. Many of the reactions and catalysts developed by us function effectively with oxygen or air as the oxidant. Other benign catalysts, developed by us and others [1–7], such as Ti^{IV}-centred active sites in mesoporous silica, are very good epoxidation catalysts for alkenes with alkyl hydroperoxides as the oxidant. And, with H_2O_2 as the oxidant, many other examples of benign catalysis, especially with Fe^{III}-centred silica or TS-1 (i.e. Ti^{IV} in tetrahedral sites in silicalite), are known (see Table 2).

All the new catalysts that we and other colleagues have developed and designed in the past decade or so are single-site heterogeneous catalysts. These exhibit the property of being site-isolated, with the structures of their active sites being known in atomic detail. Fuller details of precisely what we mean by single-site heterogeneous catalysts, henceforth

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* Corresponding author. Fax: +44 1223 740360.
** Corresponding author. Fax: +44 1223 336017.
E-mail addresses: jmt2@cam.ac.uk (J.M. Thomas), rr243@cam.ac.uk (R. Raja).

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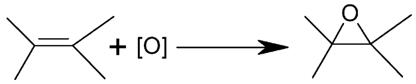
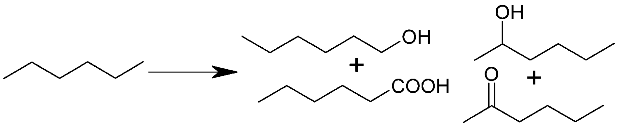
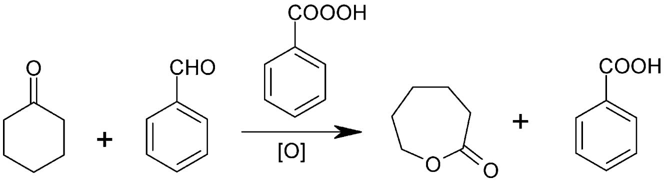
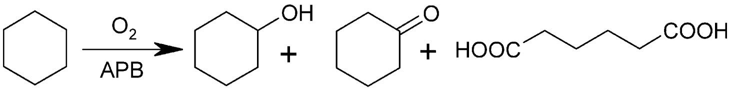
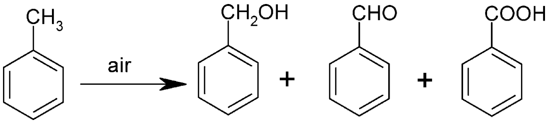
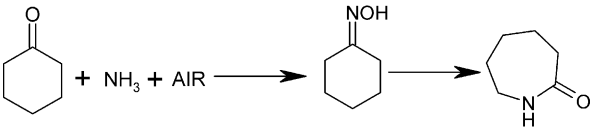
Table 1
A range of selective oxidations that can be carried out employing SSHC and oxygen or air as the oxidant [1,8]

Selective oxidations with air or oxygen	Benign catalysts
Alkenes to epoxides	
	Mn^{III}AlPO-36, TiMCM-41
	Mn^{III}AlPO-18
	Co^{III}AlPO-34
	Co^{III}AlPO-36
	Fe^{III}AlPO-31, $FeCl_{16}$Pc-Na-X, Mn^{III}AlPO-5
	Mn^{III}AlPO-5, $CoCl_{16}$Pc-Na-X
	$Co^{III}Mg^{II}$AlPO-36, $Mn^{III}Zn^{II}$AlPO-5
$CH_3OH \rightarrow HCHO$	Mo^{IV}-centred sites at silica surfaces
$_2HC = CH_2 + CH_3COOH \rightarrow CH_3COOC_2H_5$	Acid clay (montmorillonite) (interlamellar catalysts)[a]

[a] Strictly speaking this oxidation does not consume oxygen but is carried out in air.

abbreviated SSHC, are given in a recent review [8]. The advantages of SSHC are enumerated in Table 3.

2. The urgent necessity to abandon the use of stoichiometric oxidants

For far too long, chemists – especially organic chemists, as may be judged by both recent [9,10] and classic texts [11] in organic chemistry – have been cavalier, even profligate, in using ecologically unacceptable stoichiometric reagents to effect oxidation. Most of the aggressive and environmentally harmful oxidants enumerated in Table 4 are still being employed.

A leading textbook of organic chemistry, one of the premier ones in the 20th century by Fieser and Fieser [11], had this to say about the manufacture of benzaldehyde from toluene, which is used in massive amounts world-wide in a large variety of chemical, pharmaceutical and agrochemical contexts:

> “The chief technical process for production of benzaldehyde, required as an intermediate for dyes and other synthetic chemicals and in flavors and soap perfumes, utilizes toluene as the starting material. One efficient method of conversion into the aldehyde is side-chain chlorination in Pyrex glass or porcelain reactors (preferably with illumination), fractionation, and hydrolysis of the benzal chloride cut. The hydrolysis is accompanied with water at 95–100° in the presence of iron powder or ferric benzoate as catalyst, lime is then added for neutralization and the benzaldehyde is steam distilled. Benzoic acid usually appears as a by-product.”

$$C_6H_5CH_3 \rightarrow C_6H_5CHCl_2 \xrightarrow[76\%]{} C_6H_5CHO$$

Table 2
Selective oxidations with TS-1, Fe^{III}- and Ti^{IV}-centred active sites in mesoporous silica using H_2O_2 or TBHP as oxidants [2–7]

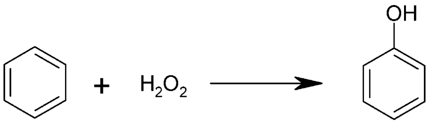
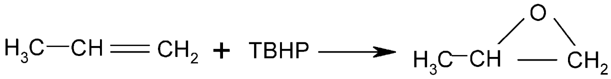
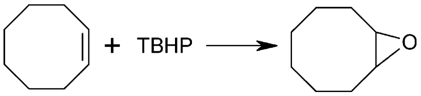
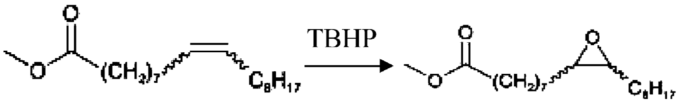
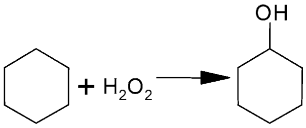
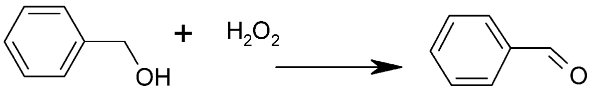
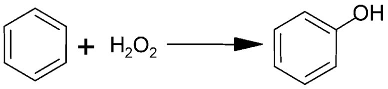
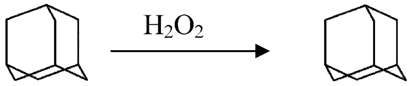
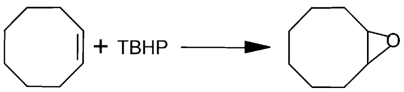
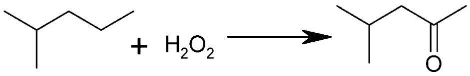
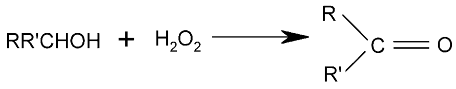
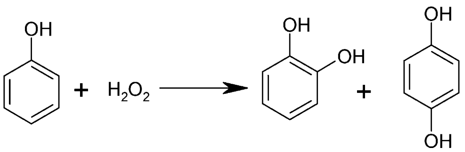
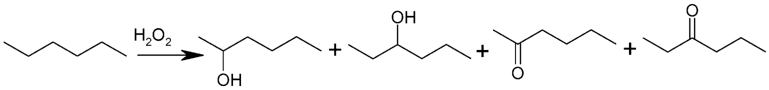
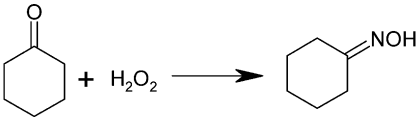
Selective oxidations with H_2O_2 and TBHP	Catalysts
	Ti^{IV}-centred mesoporous silica
	Ti^{IV}-centred mesoporous silica
	Ti^{IV}-centred mesoporous silica
	Ti^{IV}-centred mesoporous silica
	Fe^{III}-centred mesoporous silica
	Fe^{III}-centred mesoporous silica
	Fe^{III}-centred mesoporous silica
	Fe^{III}-centred mesoporous silica
	Fe^{III}-centred mesoporous silica
	TS-1
	TS-1
	TS-1
	TS-1
	TS-1

Table 3
Advantages of single-site heterogeneous catalysts

Sharply defined molecular products—regio-selective, shape-selective, enantioselective reactions
Combine the merits of homogeneous and heterogeneous processes (separation, recyclability)
Amenable to sophisticated computation (DFT) and detailed experimental studies
Molecular Fragments (e.g. silsesquioxanes) circumscribing the active site readily preparable—allow comparisons between heterogeneous and homogeneous catalysis (with same active site)
Offer strategic principles for the design of new catalysts
Considerable scope for clean technology (Benign reagents and catalysts)

Table 4
Aggressive and environmentally harmful stoichiometric oxidants

Stoichiometric oxidants
$K_2Cr_2O_7$, CrO_3, CrO_2Cl_2, $KMnO_4$, PhIO, peracids, percarbonates, perborates, H_2O_2, H_2O_2:urea, H_2O_2:DABCO, alkyl hydroperoxides, Jones Reagent (CrO_3/H_2SO_4), pyridinium chlorochromate, DMSO, H_2SO_5, $KHSO_5$, oxone, BTSP, SeO_2

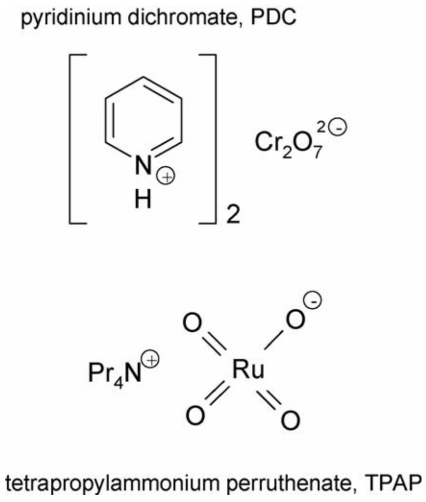
The same authors give details of another method of transforming toluene to benzaldehyde, using the classic Étard reaction:

> “A solution of two equivalents of chromyl chloride (CrO_2Cl_2) in carbon disulphide is added cautiously to the hydrocarbon with control of the temperature to 25–45°. The red colour of the reagent is discharged slowly and a chocolate-brown crystallizate separates consisting of a molecular complex containing two equivalents of the inorganic compound. The dry solid on treatment with water decomposes to give the aldehyde and an aqueous solution containing chromic acid and chromic chloride, and the aldehyde must be removed rapidly by distillation or solvent extraction to avoid destruction”.

$$ArCH_3 + 2CrO_2Cl_2 \rightarrow ArCH_3 \cdot (CrO_2CL_2)_2 \xrightarrow{H_2O} ArCHO$$

The oxidation of toluene to benzoic acid with molecular oxygen is also industrially significant for the production of ε-caprolactam via the Snia-Viscosa process [12,13]. This method uses cobalt acetate in the presence of a bromide promoter and acetic acid as a solvent, thereby generating large amounts of toxic acidic waste, leading to equipment corrosion and costly separation processes. The use of *N*-hydroxy phthalimide (NHPI) with cobalt acetate in acetic acid [14] and stoichiometric amounts of $KMnO_4$ [15] have also been reported for side-chain oxidation of aryl compounds to aromatic carboxylic acids.

More recent textbooks of organic chemistry, for example, Clayden et al. [9] give numerous examples of oxidation of alcohols. Two in particular are noteworthy. The first uses pyridinium dichromate (PDC), the second tetrapropylammonium perruthenate (TPAP) for oxidation to aldehydes (see Scheme 1). Most of the reagents detailed by Clayden et al. [9] are used stoichiometrically, but some of them may also function catalytically, such as TPAP. But even when it does function as a catalyst a stoichiometric oxygen donor (a sacrificial oxidant) is needed, and a popular one is *N*-methylmorpholine-*N*-oxide (NMO), which is reduced to the amine in the process.



Scheme 1.

In this paper we shall focus briefly on:

(i) new, powerful ways of selectively oxidizing cyclohexane, especially the use of acetylperoxyborate (APB);
(ii) aspects of the selective oxidation of cyclohexene to adipic acid, using TAPO-5 and H_2O_2;
(iii) the selective oxidation, using air or H_2O_2 of toluene to either benzaldehyde, benzoic acid or cresols;
(iv) the “green” conversion of cyclohexanone to ε-caprolactam using air and ammonia in the presence of a bifunctional, open-structure SSHC;
(v) the general advantages associated with the use (as previously emphasized by Bäckvall) [16] of “ship-in-bottle” catalysts.

3. Selective oxidation of cyclohexane

This is a subject of ancient lineage in which very many homogeneous and heterogeneous catalysts as well as photocatalysts have been employed under a wide range of conditions—see for example, the review by Muzart [17]. The free-radical reaction that takes place when cobalt acetate solutions (in acetic acid) are used for the aerial oxidation of cyclohexane, with the production of K-A oil (a mixture of cyclohexanol and cyclohexanone) is the basis of the current industrial production of adipic acid, which is formed from K-A oil using concentrated nitric acid [18]. (This generates large amounts – 2 mol per mol of adipic acid – of N_2O, a greenhouse gas that also destroys the ozone layer.)

We have shown [19] elsewhere that, in place of this multi-step, environmentally aggressive (and homogeneously catalyzed) method of converting cyclohexane to adipic acid, a benign catalyst (Fe^{III}AlPO-31), works effectively and yields 65% adipic acid—see Fig. 1.

More recently [20] we have achieved even higher selectivity (*ca.* 80%) towards adipic acid, at very high conversions (*ca.* 88%)

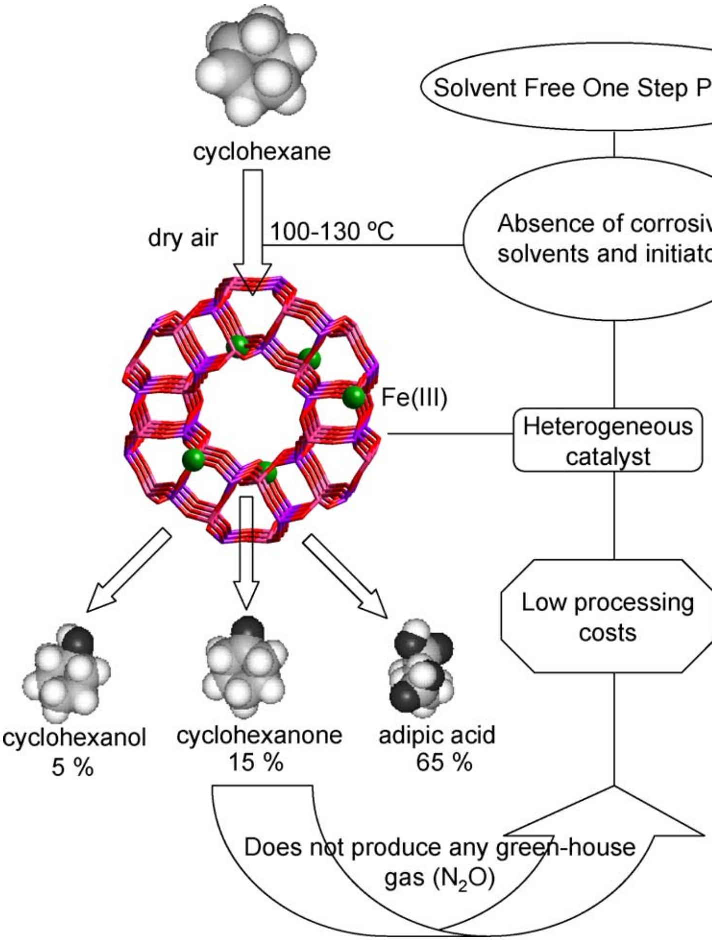


Fig. 1. One-step, solvent-free route to produce adipic acid in the presence of air and Fe^{III}AlPO-31.

of cyclohexane, using acetylperoxyborate (APB), which, as we have recently demonstrated [20], may be regarded as a convenient solid source – that may be safely stored and transported – of peracetic acid (PAA) and H_2O_2. This solid oxidant, which requires a SSHC (such as MnAlPO-5 or transition-metal-substituted phthalocyanine encapsulated on zeolite X) to initiate the liberation of the active oxygen, is also very effective in epoxidizing olefins and terpenes (Tables 5 and 6).

Table 5
Oxidation of cyclohexane using APB in the presence of Fe^{III}AlPO-31 and $FeCl_{16}$Pc-Na-X—the comparative performance with PAA is also shown

Catalyst	Oxidant	pH	Time (h)	Conversion (mol%)	Product selectivity (mol%)			
					cy-ol[a]	cy-one[b]	Adipic acid	Other acids[c]
Fe^{III}AlPO-31	APB	5.2	3	49.0	11.2	71.5	17.1	–
			16	88.6	–	11.3	81.2	7.5
Fe^{III}AlPO-31	PAA	1.65	3	61.2	6.5	48.3	21.8	23.5
			16	97.0	–	–	33.1	56[d]
$FeCl_{16}$PcNa-X	APB	5.2	3	37.5	14.5	85.3	–	–
			16	73.7	3.5	35.0	55.0	6.4
$FeCl_{16}$PcNa-X	PAA	1.65	3	41.2	9.0	65.5	18.9	6.5
			16	85.0	–	15.3	41.5	43.0[e]

Reaction conditions: cyclohexane = 2.5 g; catalyst = 0.25 g; T = 383 K; solid APB = 3.49 g (shown by titration studies to liberate 0.701 g of peroxyacetic acid and 0.045 g of H_2O_2) dissolved in 20.5 g of double-distilled (d-d) water; PAA = peroxyacetic acid (25% peroxyacetic acid solution in acetic acid) = 4.2 g + 20.5 g of d-d water.

[a] Cyclohexanol.

[b] Cyclohexanone.

[c] Other acids = glutaric, succinic and valeric acids.

[d] 10.5% CO_2.

[e] 7.9% CO_2.

Table 6
Liquid-phase epoxidation of olefins and terpenes using APB with CuCl$_{16}$Pc-Na-X, Fe^{III}- and Mn^{III}AlPO-5

Substrate	Catalyst	Oxidant	pH	Time (h)	Conversion (mol)%	Product sel. (mol%)			
						Epox[a]	Diol	Benz[b]	Others
Styrene	Mn-AlPO-5	APB	5.2	1	95.2	100	–	–	–
				4	98.8	86.5	13.5	–	–
	Fe-AlPO-5	APB	5.2	1	84.1	100	–	–	–
				4	99.1	87.3	12.5	–	–
	Mn-AlPO-5	PAA	1.65	1	97.6	15.5	35.2	39.7	9.5
α-Pinene	Mn-AlPO-5	APB	5.2	1	77.8	100	–	–	–
				4	88.6	68.7	–	–	31.2
	CuCl$_{16}$Pc-Na-X			1	35.1	96.2	–	–	3.5
				4	64.5	91.3	–	–	8.5
(+)-Limonene	Mn-AlPO-5	APB	5.2	1	78.0	100	–	–	–
				4	93.7	61.3	–	–	38.5
	CuCl$_{16}$Pc-Na-X			1	39.0	100	–	–	–
				4	67.9	78.4	–	–	21.5

Reaction conditions: styrene = 2.8 g; α-pinene, (+)-limonene = 3.7 g; catalyst = 0.25 g; T = 338 K; solid APB = 3.49 g (shown by titration studies to liberate 0.701 g of peroxyacetic acid and 0.045 g of H_2O_2) dissolved in 20.5 g of double-distilled (d-d) water; PAA = (25% peroxyacetic acid solution in acetic acid) = 4.2 + 20.5 g of d-d water.

[a] Epox = epoxide.

[b] Benz = benzaldehyde.

4. Selective oxidation of cyclohexene to adipic acid

With the ready availability (through selective hydrogenation of benzene) of cyclohexene, Japanese workers have shown that adipic acid may be readily prepared using H_2O_2 as the oxidant and a homogeneous catalyst [21]. We have also investigated this selective oxidation using a heterogeneous catalyst, TAPO-5, which is not as active as the homogeneous catalyst used by Sato et al. [21]. By application of multinuclear NMR, mass spectrometry and chromatographic analysis we concluded that the mechanism of the conversion involves the following steps (Fig. 2) [22].

5. Selective oxidation of toluene

As part of a general programme centred on the design of benign, stable, solid catalysts for the conversion of substituted aromatics to high-value products, we have investigated convenient ways of producing aldehydes, acids and cresols from toluene (Scheme 2) and *ortho*- and *para*-xylenes using

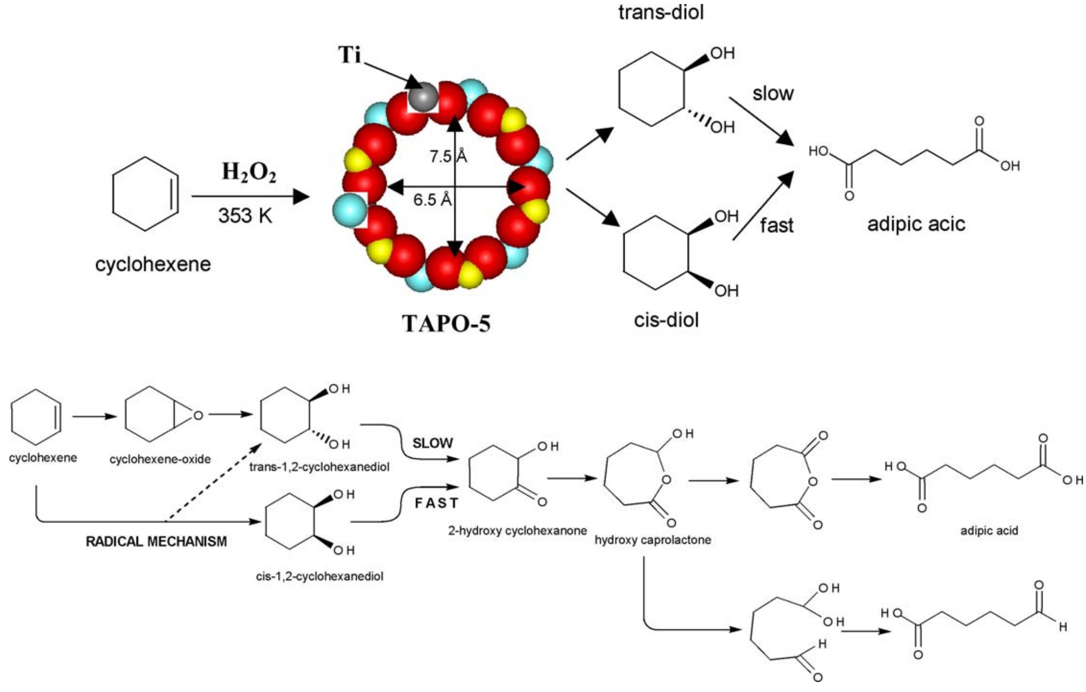
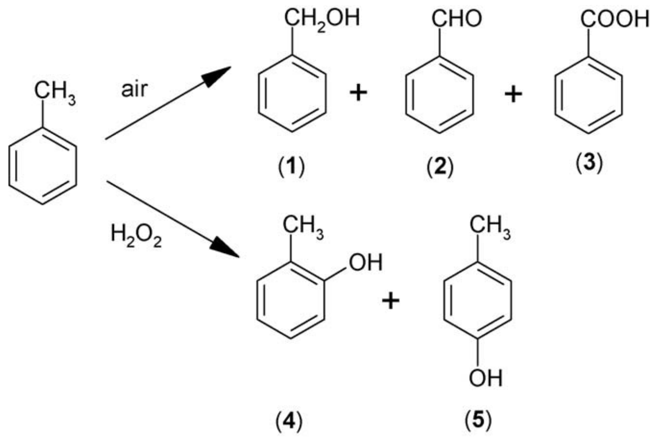


Fig. 2. Mechanistic pathway for the oxidation of cyclohexene to adipic acid using a TAPO-5 catalyst.



Scheme 2.

either air or hydrogen peroxide as the principal oxidants. Two single-site heterogeneous catalysts have been designed so as to convert toluene selectively either in O_2 (solvent-free) or in H_2O_2 to any one of the desired products (benzyl alcohol, benzaldehyde, benzoic acid, *ortho*- and *para*-cresol) each in high yield. Full details of the catalytic performance employing the above SSHC have been reported elsewhere [23]. The key results, however, are summarized in Table 7 and Figs. 3 and 4. These results compare very favourably with those of several previous [24,25] studies, where the catalysts were usually homogeneous and the reactions performed using a solvent such as acetic acid or acetonitrile.

It is noteworthy from Table 6 that the use of H_2O_2 and cumene hydroperoxide in particular, results in ring-hydroxylation (predominantly) with the zeolite-encapsulated metal-phthalocyanine catalysts displaying a higher propensity for the formation of cresols. On the other hand, the use of air as an oxidant facilitates the oxidation of the side-chain, with the microporous AlPO-catalysts exhibiting a greater influence, at higher temperatures (423 K), for the formation of benzoic acid. The kinetic plots (Figs. 3 and 4) summarize the contrasting behaviour of the selectivity profiles of these two types of catalysts. This work, of which this is only one facet, employing cheap, readily preparable catalysts, offers a clean, industrially viable and environmentally benign method of effecting oxidations of alkyl aromatics that hitherto were carried out [26,27] using high-valent metal oxo complexes (in solution) halogens, nitric acid, chromium-based [11,17] or other ecologically unacceptable catalysts.

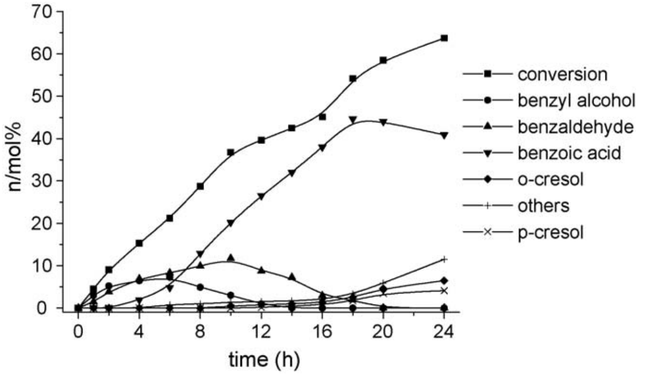


Fig. 3. Kinetic plot for the oxidation of toluene in air at 423 K with $Mn_{0.10}Al_{0.90}PO$-5—see Table 7 for reaction conditions.

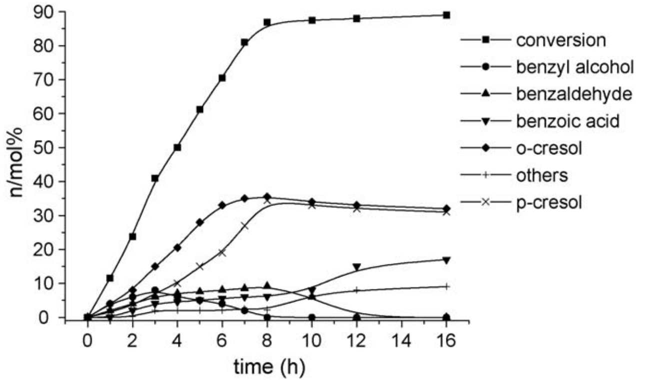


Fig. 4. Kinetic plot for oxidation of toluene with $CoCl_{16}Pc$-Na-X at 393 K using cumene hydroperoxide as the oxidant. Reaction conditions: toluene = 15 g; catalyst = 0.5 g; substrate: oxidant = 3:1 (mole).

Table 7
Oxidation of toluene using air and H_2O_2

Catalyst	*T* (K)	Oxidant	Conversion (mol%)	Product selectivity[a] (mol%)					
				1	2	3	4	5	6
$CoCl_{16}Pc$-Na-X	423	Air	11.2	–	35.5	52.5	7.0	4.5	0.4
$FeCl_{16}Pc$-Na-X	423	Air	13.5	–	45.0	43.9	6.3	3.6	1.0
$Mn_{0.10}Al_{0.90}PO$-5	423	Air	45.1	–	6.5	84.2	3.0	1.8	4.5
$Fe_{0.10}Al_{0.90}PO$-5	423	Air	39.9	–	5.1	85.0	3.5	0.7	5.8
$CoCl_{16}Pc$-Na-X	393	H_2O_2	46.5	1.5	39.8	2.2	38.8	17.2	0.6
$FeCl_{16}Pc$-Na-X	393	H_2O_2	62.7	7.6	39.0	–	26.0	25.3	2.2
$Mn_{0.04}Al_{0.98}PO$-5[b]	393	H_2O_2	22.0	10.0	15.5	45.7	14.2	9.5	5.1
$Co_{0.04}Al_{0.98}PO$-36	393	H_2O_2	28.5	17.2	24.8	15.2	25.0	17.3	0.5
$Fe_{0.04}Al_{0.98}PO$-5	393	H_2O_2	34.7	9.3	29.0	33.0	18.7	8.0	2.1

Reaction conditions: with air as oxidant: toluene = 25 g; catalyst = 0.75 g; air = 35 bar; time = 16 h; with H_2O_2 as oxidant: toluene = 15 g; catalyst = 0.5 g; substrate: oxidant = 3:1 (mole); time = 8 h.

[a] **1** = benzyl alcohol; **2** = benzaldehyde; **3** = benzoic acid; **4** = *o*-cresol; **5** = *p*-cresol; **6** = others (*m*-cresol, CO_2).

[b] The absolute values of the elemental composition have error limits of $\pm 3 \times 10^{-3}$.

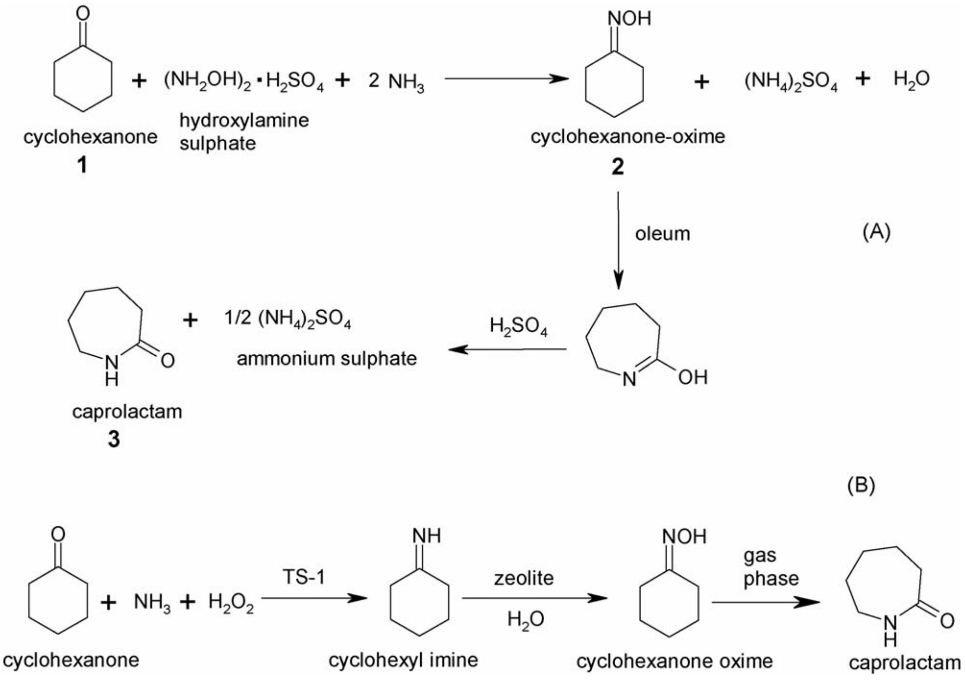
6. The "green" catalytic, single-step synthesis of ε-caprolactam (precursor of nylon-6)

Nylon-6 is of ever-increasing importance and is currently used for a wide variety of purposes: in the textile industry (lingerie, hosiery, sportswear, leisurewear, fashion wear, linings, parachutes, umbrellas, tents and sleeping bags), floor coverings (carpets and rugs), industrial yarns (tyres, conveyor belts, ropes, nets, fishing lines and tarpaulins), engineering plastics (automotive air-inlets, engine covers and aircraft windows) and in films (food and industrial packaging). It is the polymerised product of ε-caprolactam, and its worldwide production is estimated to be close to 4 billion kg. But most of the material that is produced is generated from cyclohexanone using the classic, two-step process shown in Scheme 3 [28]. Moreover the former method (Scheme 3A) generates four times the mass of ε-caprolactam as ammonium sulfate, a costly waste product to render neutral or useful. The latter method (Scheme 3B) uses a zeolite catalyst to generate the cyclohexanone oxime intermediate using ammonia and hydrogen peroxide. This is followed by a new gas-phase process to convert the intermediate oxime to ε-caprolactam.

Before we proceed to highlight the key solid-state chemical features of this new, "green" method of producing ε-caprolactam [29], we first elaborate the disadvantages of producing $(NH_4)_2SO_4$ as a by-product, and second the extra benefits that nylon-6 possesses over its equally widely used commodity, nylon-6,6. Notwithstanding the fact that ammonium sulfate is a low-value fertilizer, it is a major disadvantage in the conventional processes employed to date as it is produced in large volumes (nearly 4 kg for every kg of caprolactam produced); disposal therefore is a problem. Also, it affects the purity of caprolactam, and expensive vacuum distillation and vacuum crystallization following by treatments with ion-exchange resins are required to remove it. Even as a fertilizer, it has a lower output of nitrogen (21–22%) (hence requiring larger volumes for efficiency) and has a high acidity (requiring more lime to keep the soil neutralized). In the end, profitability for caprolactam is dependent upon the amount of ammonium sulfate produced as a by-product.

Nylon-6,6 begins as a polymer whereas nylon-6 is made from caprolactam, a monomer, where the internal (hydrogen) bonding is weak. Carpets made from nylon-6 can be depolymerized into its precursor, caprolactam, which, in turn, can be repolymerized and made again into nylon-6. The entire process recovers more than 99% of the energy and materials used to make nylon-6 carpet yarn (closed-loop recycling). In contrast, nylon-6,6 is a condensation polymer formed by combining hexamethylene diamine (HMD, the first "6") with adipic acid (the second "6"), which make separation and recycling difficult, due to a greater degree of hydrogen bonding and maximum alignment between molecular chains. Best efforts result in downcycling nylon-6,6 carpet fiber into low-performance applications, such as carpet backing. All nylon-6,6 products eventually end up at the landfill or incinerators. In Europe, recycling of fibres and plastics is of increasing importance, so that nylon-6 manufacture, on this score, is preferred over that of nylon-6,6 or other (equally recalcitrant) variants.

Our viable laboratory-scale, single-step, solvent-free method of producing ε-caprolactam (Fig. 5) employs a family of designed bifunctional, heterogeneous, nanoporous catalysts containing isolated acidic and redox sites, which smoothly convert cyclohexanone to ε-caprolactam with selectivities in the range 65–78% in air and ammonia at 80 °C [30]. The



Scheme 3.

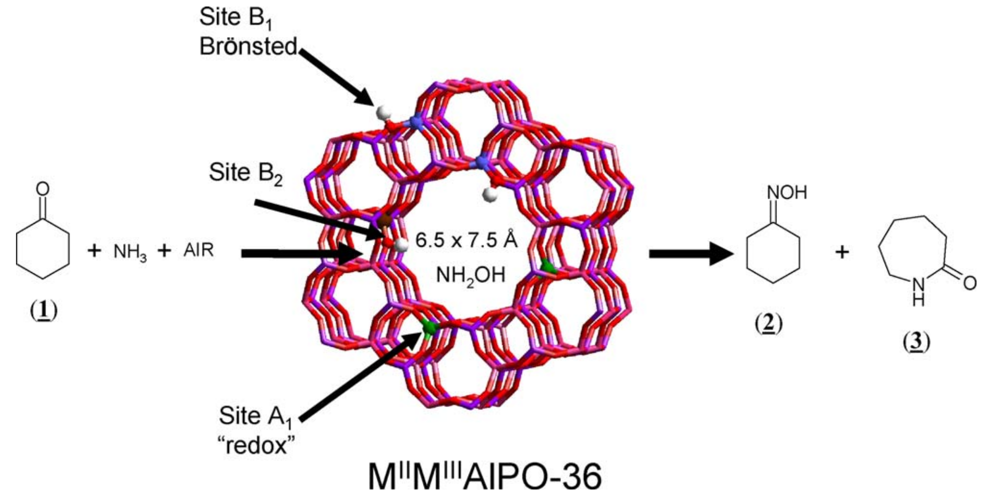


Fig. 5. At the oxidizing active center (CoIII), ammonia is converted to NH_2OH, which converts the cyclohexanone (**1**) to the oxime (**2**), which is then catalytically converted to ε-caprolactam (**3**) at the acidic active site (adjacent to the MgII).

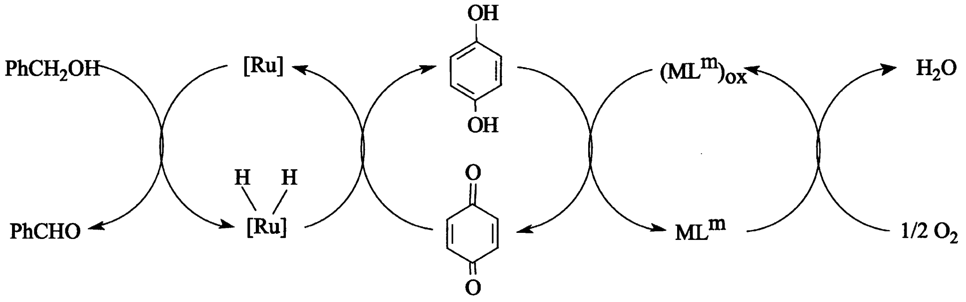


Fig. 6. Oxidation of benzyl alcohol in the triple catalytic system [16].

catalysts are microporous aluminophosphates (AlPOs) in which small fractions of the Al(III) ions are isomorphously replaced with CO(III) and Mg(II) ions, which become the loci of the redox and acidic centers, respectively. The catalysts may be further optimized, and already may be so designed as to generate selectivities of *ca*. 80% for the intermediate oxime, formed from NH_2OH which is produced *in situ* within the pore system.

7. The advantages associated with ship-in-bottle SSHC

Earlier in this article (see Sections 3 and 5) we showed that a transition-metal phthalocyanine incarcerated within a zeolite cage (as in zeolite X or Y) is particularly effective in releasing the active oxygen from APB and also in activating a hydrocarbon–oxygen (or hydrocarbon–peroxide) mixture to form desirable selective oxidation products of toluene. Several reports have shown [16,31–36] the merits of 'ship-in-bottle' type catalysts for selective oxidation. A particularly interesting example, taken from the work of Bäckvall [16] is shown in Fig. 6.

We see that this is an efficient method of selectively oxidizing alcohols. It is worth emphasizing the merits of this approach over homogeneous catalysts, as enumerated by Bäckvall [16]:

(i) the encapsulated catalyst could be removed by simple filtration from the reaction mixture and it is possible to reuse it;
(ii) the heterogenized catalyst had a higher specific rate than the homogeneous complex;
(iii) the encapsulated catalyst works without any axial ligand, whereas the homogeneous complex needs it;
(iv) the encapsulated catalyst is not dependant on any specific solvent, while under the homogeneous condition the choice of solvent is crucial;
(v) the zeolite host can serve as a water acceptor and there is no need for a separate water acceptor;
(vi) the zeolite host shows shape selectivity in the oxidation of secondary alcohols, making the sterically hindered alcohols somewhat less reactive than the others.

8. Summarizing remarks

We have focussed largely on those benign catalysts that we ourselves have developed to effect the selective oxidations that are appropriate to facilitate a sustainable overall system. Other important types of solid oxidation catalysts, some equally benign (such as nanoparticles of gold on an appropriate oxide support depending upon which reactions are to be catalyzed) – see the recent work of Hutchings et al. [37] and of Haruta et al.

[38,39] – are also likely to play an important part in the future production of fine, pharmaceutical or commodity chemicals. In addition, we have not discussed the numerous types of solid oxide catalysts (described by both Haber [40] and Baerns [41] at this issue), that operate via the Mars-van-Krevelen mechanism (of sacrificial use of lattice oxygen, as recently described by Ueda [42]). These, too, will play an increasing role in the sustainable chemistry of the future.

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