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Benign oxidants and single-site solid catalysts for the solvent-free selective oxidation of toluene

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Two types of single-site heterogeneous catalysts have been designed so as to facilitate either the side-chain oxidation or ring-hydroxylation of toluene in O_2 (solvent-free) or by employing aqueous (H_2O_2) or organic (cumene hydroperoxide) hydroperoxides in high yield. The use of H_2O_2 and cumene hydroperoxide in particular, facilitates the ring-hydroxylation of toluene when zeolite-encapsulated metal complexes, such as perhalogenated or tetra-nitro-substituted phthalocyanines, are used as catalysts. Nanoporous, redox molecular sieves, display a higher tendency for the side-chain oxidation of toluene with air as an oxidant, with benzoic acid as the predominant product.

KEY WORDS: single-site heterogeneous catalysts; toluene oxidation; benzoic acid; ring-hydroxylation; aluminophosphates; green chemistry.

As part of a general programme [1–3] 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 and ortho- and para-xylenes using either air or hydrogen peroxide as the principal oxidants. A subsidiary aim is to arrive at low-temperature single-step processes, where the production of one or other species **1** to **5** (Scheme 1) is maximized.

The two categories of solid catalysts (figure 1) that we have designed for this purpose – known from our previous work, [4–10] to be capable of activating C–H bonds in hydrocarbons in the presence of oxygen at low temperature – each consists of a family of related solids. Catalysts designated type **I** are framework-substituted transition-metal variants of microporous aluminophosphates (MAlPOs) that we previously showed are especially effective in the aerial oxyfunctionalization of a variety of aliphatic [4,5] and cyclic alkanes [6]. Catalysts of type **II** are transition-metal substituted phthalocyanines that, in their halogenated or nitrated states, are encapsulated within the cages of a faujasitic zeolite (typically Na^+-exchanged zeolite X). This category of catalyst has also been shown [7–10] to effect the selective oxidation of a range of hydrocarbons using air (or O_2), H_2O_2 and certain alkyl hydroperoxides. Full details of the preparation and characterization of these two categories of catalyst have been previously published [4–10].

Within the category **I** catalyst, two main structural forms were employed. These are M^{III}AlPO-5 and M^{III}AlPO-36, where M refers to the transition-metal ions Co^{III} or Mn^{III} or Fe^{III}, all these being in tetrahedral sites normally occupied by Al^{III} ions in the corner-sharing $Al^{III}O_4^{5-}$ tetrahedra linked to $P^{V}O_4^{3-}$ tetrahedra that constitute the three-dimensional continuous structure of the parent $AlPO_4$. The level of substitution is kept close to 4 atom percent, but in some instances a 10 percent-level was deliberately used. In each case the M^{III} ions are spatially well separated from one another, as proven by EXAFS and other methods of characterization: all the catalysts are single-site, in the sense elaborated elsewhere [11,12]. The pore diameter of the M^{III}AlPO-5 catalyst is 7.3 Å and of the M^{III}AlPO-36, where the opening is elliptical, 6.5 Å × 7. 5 Å.

Category **II** catalysts are represented by $MPc(X_n)$, where M is either Cu^{II}, Fe^{II} or Co^{II} and X either Cl or NO_2, the Pc standing for the phthalocyanine. The neat $CoCl_{16}Pc$ and $FeCl_{16}Pc$ complexes were synthesized as reported earlier [7–10] using tetrachlorophthalonitrile and 1-chloronaphthalene as solvent. An analogous procedure employing 4-nitrophthalonitrile and 1-chloronaphthalene was used to synthesize $Co(NO_2)_4Pc$ and $Fe(NO_2)_4Pc$. The *zeolite synthesis method* [7–10] was used for encapsulating the neat complexes within the supercages of zeolite Na–X. The structural integrity of the encapsulated metal complexes were confirmed with a

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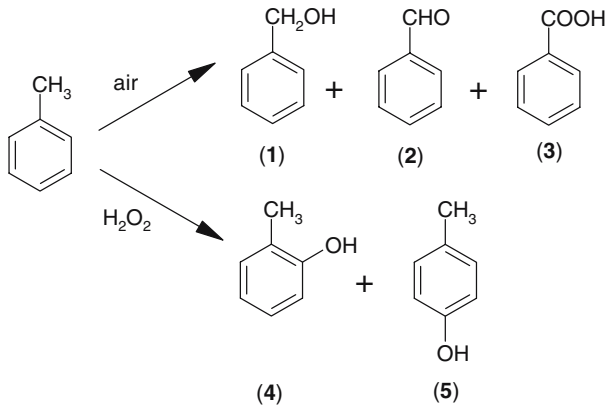

Scheme 1.

wide range of physico-chemical characterization techniques [7–10]. The diameter of the entry port into the faujasitic (α)-cage (figure 1) of these catalysts is 7.4 Å, so that molecules of toluene and the oxidant may readily reach the site-isolated active centres.

The solvent-free aerobic oxidations were carried in a high-pressure, PEEK (Poly Ether Ether Ketone)-lined, stainless steel catalytic reactor (Cambridge Reactor Design, 100 ml). About 0.75 g of the catalyst, which was stored under inert conditions (nitrogen or argon), was transferred to the catalytic reactor (using a robotically-controlled catalyst delivery unit) containing ≅25 g of toluene (Aldrich, > 99.8% pure) and 0.5 g of the internal standard (mesitylene, which did not undergo oxidation under the reaction conditions employed by us). The reactor was sealed and its contents were inertized (thrice) with dry N_2 prior to reaction. The contents of the reactor were stirred (1700 rpm) and heated to the desired temperature (from a low of 100 °C to a high of 150 °C). Dry air (dynamic pressure of 35 bar) was pressurised into the reaction vessel and, using mini-robot liquid and gas sampling valves, small aliquots (0.1 μl) of liquid and gas samples were removed to study the kinetics of the reaction (figures 2 and 3), without perturbing the pressure in the reactor. Liquid and gaseous product compositions were was continuously monitored using an on-line computer-controlled system linked to a GC and LCMS (Shimadzu QP 8000).

The products were analysed by gas chromatography (GC, Varian, Model 3400 CX) employing a HP-1 capillary column (25 m × 0.32 mm) and flame ionisation detector using a variable ramp temperature program from 80 to 240 °C. The identities of the products were first confirmed using authenticated standards and their individual response factors were determined using the calibration method. The mass of the products was further measured by LC-MS. In addition to air, some tests were also carried out using H_2O_2, cumene hydroperoxide and tert-butyl hydroperoxide, which were fed slowly (to minimize decomposition), over the course of the reaction, employing a syringe pump (Harvard "33") to the stirred contents of the reactor as this enhances the "peroxide efficiency".

Full details of the catalytic performance of the six main forms of type **I** and four forms of type **II** catalysts used in this work will be reported elsewhere. The key results, however, are summarized in Tables 1–3 and figures 2 and 3. These results compare very favourably with those of several previous [13] studies, where the catalysts were usually homogeneous and the reactions performed using a solvent such as acetic acid or acetonitrile.

It is noteworthy from Tables 1–3 that the use of H_2O_2 and cumene hydroperoxide in particular, results in ring-hydroxylation (predominantly) with type **II** 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 type **I** catalysts exhibiting a greater influence, at higher temperatures (423 K), for the formation of benzoic acid.

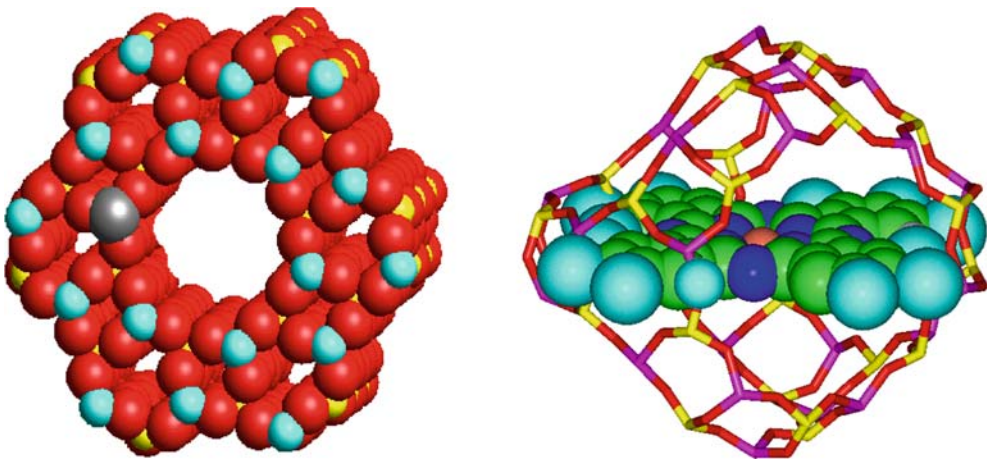

Figure 1. Graphical representation of type **I** (Fe^{III}AlPO-5 with a pore aperture of 7.3 Å) and type **II** catalysts ($CoCl_{16}Pc$ encapsulated in Na–X, where the pore diameter into the faujasitic cage is 7.4 Å).

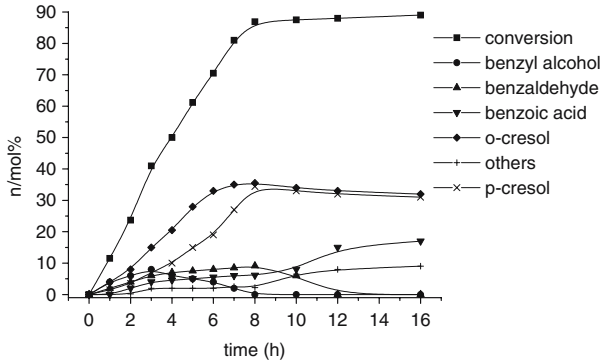

Figure 2. Typical kinetic plot for oxidation of toluene with $CoCl_{16}Pc$–Na–X at 393 K using cumene hydroperoxide as the oxidant – see Table 3 for reaction conditions.

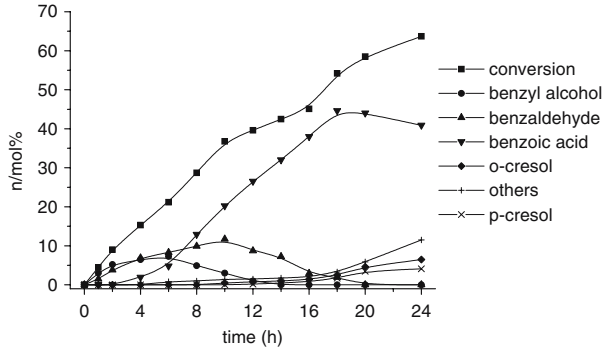

Figure 3. Typical kinetic plot for the oxidation of toluene in air at 423 K with $Mn_{0.10}Al_{0.90}PO$-5 – see Table 2 for reaction conditions.

The kinetic plots (figures 2 and 3) summarize the contrasting behaviour of the selectivity profiles of these two types of catalysts. The by-products (**6**) were mainly CO_2, though very small amounts of m-cresol were observed in a few cases – lower C_n acids were not observed.

To establish the acceptable level of stability of the catalysts in category **I** – and in particular, its lack of tendency to "lose" the active sites by leaching during the reaction – we took (figure 4) M^{III}AlPO-18 catalyst where the active sites are in exactly the same atomic environment, but where the pore diameter is so small (3.8 Å) that toluene is unable to gain access to the active sites in the interior of the high-area catalyst, but linear alkanes such as *n*-hexane are [2,3]. In the absence of a solvent such as acetic acid, the expected regioselective products from the oxidation of *n*-hexane are formed [5], but as toluene is too large to access the redox active sites in the framework it is not oxidized. However, with a solvent such as acetic acid (used in homogeneous aerial oxidations of alkanes and with *N*-hydroxyphthalimide, a popular catalyst used for a range of organic oxidations [14,15]), non-regioselective oxidation products of *n*-hexane are formed, in addition to benzaldehyde and benzoic acid, formed from toluene. Clearly, some of the active sites have been leached by the solvent. Analogous results were obtained when the above experiment was carried out employing H_2O_2 as the oxidant. Further, hot filtration experiments and ICP measurements of the resulting filtrate were also independently carried out and very small levels of cobalt (4.7 ppb parts per billion when air was used as the oxidant and 7.5 ppb when H_2O_2 was the oxidant) were observed in solution. The

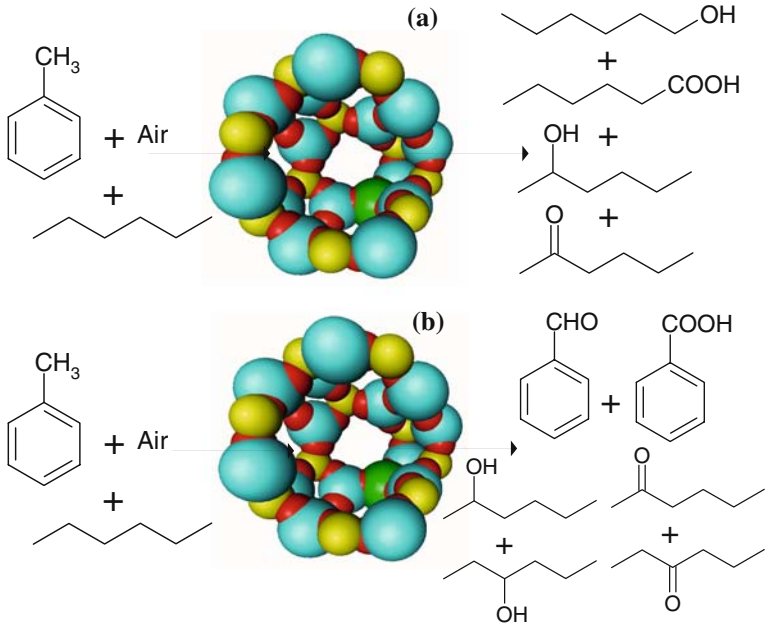

Figure 4. Competitive oxidation of toluene and *n*-hexane in air at 393 K using $Co_{0.04}Al_{0.96}PO$-18 in the presence (**B**) and absence (**A**) of acetic acid solvent.

Table 1
Oxidation of toluene[a] with H_2O_2

Catalyst	Conv. (mol %)	TOF[c]	Product selectivity (mol %)[b]					
			1	**2**	**3**	**4**	**5**	**6**
$CoCl_{16}Pc$–Na–X	46.5	230	1.5	39.8	2.2	38.8	17.2	0.6
$Co(NO_2)_4Pc$–Na–X	15.6	44	83.5	11.5	4.2	–	–	0.8
$FeCl_{16}Pc$–Na–X	62.7	259	7.6	39.0	–	26.0	25.3	2.2
$Fe(NO_2)_4Pc$–Na–X	86.8	335	51.3	29.0	18.5	–	–	1.3
$Mn_{0.04}Al_{0.96}PO$-5[d]	22.0	32	10.0	15.5	45.7	14.2	9.5	5.1
$Co_{0.04}Al_{0.96}PO$-36	28.5	45	17.2	24.8	15.2	25.0	17.3	0.5
$Fe_{0.04}Al_{0.96}PO$-5	34.7	57	9.3	29.0	33.0	18.7	8.0	2.1
$Co_{0.04}Al_{0.96}PO$-18	No Reaction							

[a] toluene ≅ 15 g; catalyst ≅ 0.5 g; substrate: oxidant ≅ 3:1 (mole); T ≅ 393 K; time ≅ 8 h.
[b] **1** ≡ benzyl alcohol; **2** ≡ benzaldehyde; **3** ≡ benzoic acid; **4** ≡ *o*-cresol; **5** ≡ *p*-cresol; **6** ≡ others (*m*-cresol, CO_2).
[c] TOF = $[(mol_{substr})(mol_{metal})^{-1}\ h^{-1}]$ where mol_{substr} = moles of toluene converted.
[d] the absolute values of the elemental composition have error limits of $\pm\ 3\ \times 10^{-3}$.

Table 2
Oxidation of toluene[a] in air

Catalyst	T (K)	Conv. (mol %)	Product selectivity (mol %)[b]					
			1	**2**	**3**	**4**	**5**	**6**
$CoCl_{16}Pc$–Na–X	393	6.7	–	63.5	16.1	15.3	4.7	0.5
$FeCl_{16}Pc$–Na–X	393	9.3	10.2	57.2	15.2	13.7	3.3	0.4
$Fe(NO_2)_4Pc$–Na–X	393	8.5	26.9	70.2	2.5	–	–	0.3
$Mn_{0.04}Al_{0.96}PO$-5	393	7.3	3.7	78.8	16.1	–	–	0.5
$Co_{0.04}Al_{0.96}PO$-36	393	4.5	–	72.9	36.2	–	–	0.8
$Fe_{0.04}Al_{0.96}PO$-5	393	8.6	3.2	41.0	54.9	–	–	0.7
$Co_{0.04}Al_{0.96}PO$-18	393	No Reaction						
$CoCl_{16}Pc$-Na-X	423	11.2	–	35.5	52.5	7.0	4.5	0.4
$FeCl_{16}Pc$-Na-X	423	13.5	–	45.0	43.9	6.3	3.6	1.0
$Mn_{0.04}Al_{0.96}PO$-5	423	16.1	–	18.2	79.8	1.1	–	0.8
$Fe_{0.04}Al_{0.96}PO$-5	423	14.9	–	13.6	83.4	1.5	0.3	1.2
$Mn_{0.10}Al_{0.90}PO$-5[c]	423	45.1	–	6.5	84.2	3.0	1.8	4.5
$Fe_{0.10}Al_{0.90}PO$-5	423	39.9	–	5.1	85.0	3.5	0.7	5.8

[a] toluene ≅ 25 g; catalyst ≅ 0.75 g; air ≅ 35 bar; time ≅ 16 h.
[b] **1** ≡ benzyl alcohol; **2** ≡ benzaldehyde; **3** ≡ benzoic acid; **4** ≡ *o*-cresol; **5** ≡ *p*-cresol; **6** ≡ others (*m*-cresol, CO_2).
[c] the absolute values of the elemental composition have error limits of $\pm\ 3 \times 10^{-3}$.

Table 3
Oxidation of toluene[a] with cumene hydroperoxide

Catalyst	T (K)	Conv. (mol %)	Product selectivity (mol %)[b]					
			1	**2**	**3**	**4**	**5**	**6**
$CoCl_{16}Pc$–Na–X	393	86.9	–	10.5	7.0	40.9	39.6	2.5
$Fe(NO_2)_4Pc$–Na–X	393	78.5	30.5	22.0	5.0	23.4	15.5	3.6
$CoCl_{16}Pc$–Na–X	413	87.5	–	–	35.0	32.3	28.5	4.3
$CoCl_{16}Pc$–Na–X	433	88.7	–	–	41.2	27.0	20.2	11.8
$Mn_{0.04}Al_{0.96}PO$-5[c]	393	67.6	–	15.5	11.3	38.9	32.0	2.4
$Fe_{0.04}Al_{0.96}PO$-5	393	68.9	–	–	35.6	33.4	26.5	4.5
$Co_{0.04}Al_{0.96}PO$-36	393	No Reaction						
$Co_{0.04}Al_{0.96}PO$-18	393	No Reaction						

[a] toluene ≅ 15 g; catalyst ≅ 0.5 g; substrate: oxidant ≅ 3:1 (mole); time ≅ 8 h.
[b] **1** ≡ benzyl alcohol; **2** ≡ benzaldehyde; **3** ≡ benzoic acid; **4** ≡ *o*-cresol; **5** ≡ *p*-cresol; **6** ≡ others (*m*-cresol, CO_2).
[c] the absolute values of the elemental composition have error limits of $\pm\ 3 \times 10^{-3}$.

same catalysts were re-used at least thrice (without significant decrease in their activities or selectivities) to check for their recyclability.

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 [16–19] using high-valent metal oxo complexes (in solution) halogens, nitric acid, chromium-based or other ecologically unacceptable catalysts.

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