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Prevention of Manganese Precipitation during the Continuous Selective Partial Oxidation of Methyl Aromatics with Molecular Oxygen in Supercritical Water

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Abstract: Presented here is an investigation of the activity and recovery of the homogeneous manganese/bromide catalyst during the continuous flow oxidation of *o*-xylene, as model substrate, with molecular oxygen (O_2) in supercritical water (scH_2O). Two strategies are discussed for preventing catalyst precipitation, mainly in the form of oxides such as manganese(IV) oxide, The first strategy involves varying the manganese:bromide ratio using either manganese(II) acetate or manganese(II) bromide in the presence of hydrobromic and other acids. The results show that the effect of acidity and bromide concentration plays an important role in preventing the manganese/bromide catalyst from precipitating. The second strategy uses aromatic carboxylic acids in combination with the manganese/bromide catalyst, particularly benzoic acid, which improves the catalyst recovery dramatically over a certain range of acid concentrations. Our studies show how the presence of an organic acid and/or its precursors is important in stabilising the catalyst. Our results are rationalised on the basis of a tentative reaction mechanism.

Keywords: aromatic acids; catalyst stability; manganese bromide; supercritical water oxidation; xylenes

Introduction

Research activity in the field of supercritical water, scH_2O ($T_c = 374\,°C$, $p_c = 221$ bar) or more generally in high-temperature water has been growing for more than 20 years because of the unusual properties of water under these conditions.[1] A wide range of chemical reactions have been studied where scH_2O plays the role of a solvent and/or reactants and/or catalyst.[2–5] The scH_2O technology is particularly well-known for efficient destruction of organic wastes by total oxidation.[6] By contrast, the homogeneously catalysed oxidation of methyl aromatics in 'hot' and scH_2O has also shown considerable potential for the selective production of carboxylic acids, provided that the reaction conditions are well controlled.[7–16,17b] One of the most studied reactions is the selective oxidation of *p*-xylene to terephthalic acid due to its importance in the chemical industry.

Our studies using continuous flow systems[9–12] have shown that scH_2O can provide: 1) an environmental advantage by eliminating the use of acetic acid as a solvent and reducing consequent waste due to unwanted by-products formation (mainly carbon dioxide, carbon monoxide, methyl bromide and organic acetates); 2) an economic advantage[16] resulting from faster reactions as well as operating at higher temperature which allows for more efficient energy recovery from these highly exothermic reactions; 3) process intensification by reducing the size of the reactor and the residence time compared to the conventional acetic acid process.

Since the 1960s, at least 251 different substrates have been aerobically oxidized using around 30 different combinations of soluble metal/bromide catalysts.[17a] The solvent typically used is acetic acid and the most common catalyst comprises a mixture of cobalt(II) and manganese(II) acetates with hydrobromic acid. One of the drawbacks, in both scH_2O and the conventional acetic acid process, is the fact that homogeneous metal catalysts, especially manganese, can hydrolyse to form insoluble metal oxides. The working oxidation states for manganese, Mn(II)–Mn(III), have been identified by UV-Vis studies in acetic acid.[18]

In a supercritical oxidation process for the production of aromatic carboxylic acids, the precipitation of manganese oxide(s) would reduce or prevent the effective and economically essential recycle of catalyst as well as reduce its activity and selectivity. In addition, the precipitation could hinder flow in a tubular reactor, which would need to be cleaned or unblocked in order to continue operation. This paper demonstrates how the formulation of the catalyst can be improved in order to maximise metal/bromide stability by largely eliminating precipitation of manganese oxides in the scH_2O reaction system.

Reaction Mechanism and Possible Cause of Catalyst Precipitation

The interpretation of the experimental data in this paper is very complex since a homogeneous aerobic oxidation will be occurring, along with precipitation of the catalyst metals. The precipitated catalyst metals themselves can then potentially act as heterogeneous oxidation catalysts. Our goal is to eliminate catalyst precipitation so that only homogeneous oxidation occurs. In our attempts to do so, we will make changes that will in most cases change the pH as well. In this section of the paper we will 1) give evidence that a free radical chain mechanism is occurring, 2) give a simplified catalyst modified chain mechanism, 3) discuss how pH affects the solubility of the metals and the free radical chain mechanism, 4) give a model which rationalises the increased solubility of the catalysts, and 5) give strategies for elimination of manganese precipitation.

In acetic acid, there is considerable evidence that the oxidation proceeds through a catalyst modified free radical chain mechanism. There are a number of phenomena in sub- and scH_2O that are the same as those observed in acetic acid suggesting a similar mechanism. Some of the similarities are: 1) the sequence of oxidation products, i.e., *p*-xylene to 4-methylbenzaldehyde, to *p*-toluic acid, to 4-carboxybenzaldehyde and finally to terephthalic acid, is the same;[7,8,12] 2) the uncatalysed oxidation in supercritical water gives low terephthalic acid yields and is very unselective producing large amounts of toluene;[19] 3) the addition of bromide to the metal-catalysed system increases the activity and yield;[15] and 4) increasing the catalyst concentration gives higher yield and selectivity.[7,8,15]

A simplified free radical chain mechanism for a manganese/bromide catalyst consists of initiation, propagation, and termination steps.[20,21] The initiation step forms the benzylic radical [Eq. (1)] where X* can be a oxidized bromide species, indicated by Br(0), or other radicals formed in the reaction such as the peroxy radical, $ArCH_2OO^*$.

$$\mathrm{ArCH_3 + X^* \longrightarrow ArCH_2^* + HX} \tag{1}$$

The propagation step [Eq. (2)] is the rapid reaction of the benzylic radical with molecular oxygen followed by the hydrogen atom abstraction of the methyl group with the peroxy radical [Eq. (3)].

$$\mathrm{ArCH_2^* + O_2 \longrightarrow ArCH_2OO^*} \tag{2}$$

$$\mathrm{ArCH_2OO^* + ArCH_3 \longrightarrow ArCH_2OOH + ArCH_2^*} \tag{3}$$

Without a metal present the peroxide will rapidly dissociate above 80 °C to the undesirable, highly energetic, unselective hydroxyl radical (OH*) [Eq. (4)].

$$\mathrm{ArCH_2OOH \longrightarrow ArCH_2O^* + OH^*} \tag{4}$$

One of the purposes of the catalyst, Mn(II), is to react selectively with the peroxides and peroxyacids,[22] generating Mn(III), thus avoiding the formation of the hydroxyl radical [Eq. (5)].

$$\mathrm{ArCH_2OOH + Mn(II) \longrightarrow ArCH_2O^* + Mn(III)OH} \tag{5}$$

In manganese/bromide-catalysed chemistry, the Mn(III) then rapidly reacts with bromide to generate an oxidised bromide species [Eq. (6)].

$$\mathrm{Mn(III) + Br^- \longrightarrow Mn(II) + Br(0)} \tag{6}$$

This species continues the reaction *via* hydrogen abstraction reactions such as in the initiation step, Eq. (1). The Br(0), as well as the peroxy radical [Eq. (3)], very selectivity reacts with the C–H bonds of the methyl group rather than those of the aromatic ring.[21]

Two types of catalyst precipitation are pertinent to oxidation in supercritical water. Firstly, the manganese(III) disproportionates to the highly insoluble, manganese(IV) dioxide. In the commercial process over-oxidation of manganese to manganese(IV) dioxide occurs when the water concentration in acetic acid is too high or the bromide/metals ratio is too low.[23,24] Black manganese(IV) dioxide co-precipitates with the terephthalic acid, not only contaminating the solids with manganese, but also changing the colour of the solids from white to grey. Secondly, a mixture of manganese(II) bromide and manganese(II) acetate in supercritical water at 400 °C precipitates as manganese(II) oxide at concentrations similar to those when these manganese compounds are used as a homogeneous catalyst.[25] Dissolving manganese(II) acetate in water and heating it to form supercritical water, is a method for generating nanoparticles of manganese oxides.[26,27]

Current evidence suggests that catalyst metal precipitation is undesirable because: 1) in acetic acid, manganese(IV) dioxide precipitation increases the rate of carbon dioxide and methyl bromide formation,[28] 2) it is known that manganese(IV) dioxide is an excellent heterogeneous catalyst in supercritical water for converting organic compounds to carbon dioxide, i.e., unselective oxidation,[7] and 3) the concentration of the homogeneous metal/bromide catalyst will decrease causing a decrease in the rate of reaction as well as a decrease in selectivity since thermal, rather than metal-catalysed, decomposition of the hydroperoxides increases. Thermal decomposition leads to such undesirable products as toluene, benzoic acid, and cresols.[28]

The pH of the solvent plays a critical role in the successful oxidation of methyl aromatic compounds and the understanding of this effect is necessary to rationalise the experimental data in this paper. pH is critical for the following reasons. 1) The strength of manganese(III) as an oxidant decreases with an increase in pH. For manganese(II)–(III) the redox potential is 1.54 V at pH 1 but decreases to 0.15 V at a pH 8.[23] In ambient water, the reason for the change in redox potential is because the structure of the manganese(II) changes. The structure at pH 1 is $[Mn(II)(H_2O)_6]^{2+}$ but with increasing hydroxide anion concentration it changes to $[Mn(II)(H_2O)_5(OH)]^+$ then to $[Mn(II)(H_2O)_4(OH)_2]$. (This is somewhat over-simplified for the sake of argument; various polynuclear compounds are known to form[29]). 2) The propensity for metal precipitation as their oxide/hydroxides will increase with increase in pH. $[Mn(II)(H_2O)_4(OH)_2]$, which occurs at high pH, being a neutral compound and containing the hydroxide anion is the precursor to metal oxide/hydroxide precipitation.[29] 3) As the pH increases, the propensity increases for O_2 to oxidise manganese(II) spontaneously. It is known that dioxygen can oxidise magnanese(II) to manganese(III) at a pH of 8.[30] Since metal oxides become more insoluble as the oxidation state of the metal increases, the degree of metal oxide/hydroxide precipitation also increases. 4) As the pH increases the disproportionation of manganese(III) will increase [Eq. (7)].

$$2\,Mn(III) + 2\,H_2O \longrightarrow Mn(II) + Mn(IV)O_2 + 4\,H^+ \qquad (7)$$

5) Maximum yield and selectivity to a given aromatic acid occur at an intermediate pH, i.e., not too low or not too high. This has been demonstrated for oxidation of *p*-xylene in acetic acid.[17a,22] For the metal to act as a catalyst, a) it must be both oxidised and reduced at equal rates and b) it must fulfil its function as a catalyst. The function of manganese is to selectively react with the hydroperoxides and oxy radicals (denoted by [O]) [Eq. (8)] and subsequently be reduced by the bromide anion [Eq. (9)].

$$Mn(II) + [O] \longrightarrow Mn(III) \qquad (8)$$

$$Mn(III) + Br^- \longrightarrow Mn(II) + Br(0) \qquad (9)$$

If the pH is too low, then the redox potential of the manganese(II)–(III) couple will be too high and Eq. (8) will not occur. If the pH is too high, then manganese(III) is too weak an oxidant for Eq. (9) to occur. Obviously, an intermediate pH where both reactions occur as rapidly as possible will provide the best catalysis.

To summarise, an increase in pH will increase the tendency for precipitation of metal oxides, will increase the propensity for dioxygen to oxidise the manganese to more insoluble oxides, will increase the tendency towards disproportionation to the highly insoluble manganese(IV) dioxide and, if the pH is too low, will decrease the rate of formation of the desired product of the oxidation reaction, i.e., the aromatic acid. The optimal state is operating at a pH to give maximum aromatic yield but which is not too high so that significant amounts of the catalyst metal precipitates.

The above discussion has been based on observations of water at ambient temperature. It is well established that the physical properties of water greatly change when the temperature is increased to supercritical temperatures, >374 °C. For example, the dielectric constant decreases from 80 to 4. As a consequence, coordination compounds do not ionise readily, i.e., they are charge-neutral, their coordination number decreases from 6 to 4, and the geometry changes from octahedral to tetrahedral. This has been demonstrated for $MnBr_2$ which exists predominately as $[Mn(H_2O)_6]^{2+}$ in ambient water, but changes to tetrahedral $[Mn(H_2O)_2Br_2]$ in scH_2O.[25] Furthermore, for

Ni, Cr and Fe, metal oxides form at lower pHs as the temperature is increased; the pH shifts from 8 in ambient water to 5 at *ca.* 300 °C. Furthermore, the strength of acids changes as the temperature of water increases. For example, hydrochloric acid is a strong acid in ambient water but becomes a weak acid at 380 °C with a dissociation constant of 2.6×10^{-4} (at 27 MPa).[39] The dissociation constant of acetic acid decreases from 1.8×10^{-5} at ambient water to 3.0×10^{-8} at 350 °C. This is the probable reason why manganese(II) acetate has been observed to precipitate as manganese(II) oxide in scH_2O. The acetate anion is a very weak base in ambient water, but is stronger in scH_2O so it hydrolyses to $Mn(II)(OH)_2$ and dehydrates to Mn(II)O.

In Figure 1, we present a model which is consistent with the discussion above as well as the experimental data that will be subsequently presented. All of the reactions shown are balanced reactions. The coordination compounds are four-coordinate tetrahedral compounds consistent to what has been found in scH_2O.[25] The initial catalyst, $[Mn(H_2O)_2Br_2]$ can be oxidised, as described above, to a manganese(III) species, Eq. (13). If the pH of the solution is increased and hydrolysis occurs, one will lose hydrobromic acid and Eq. (10) occurs. Oxidation of the product of Eq. (10), Eq. (14), will produce a dihydroxy manganese(III) compound. Oxidation of manganese(II) bromide, Eq. (13), necessitates that a monohydroxy species must form. Disproportionation occurs *via* Eq. (16) and Eq. (17) *via* species that have manganese–OH bonds which are precursors to oxide formation. The model predicts that addition of excess hydrobromic acid to manganese(II) bromide will avoid manganese(IV) dioxide formation either by Eq. (11) or by reversing Eq. (17).[31] The model also predicts that Eq. (12) will occur, if an acid, such as an aromatic acid, is added, the driving force is the reaction of the aromatic acid with the hydroxyl ligand to produce water and the aromatic acid salt of manganese(II).[32] This reaction will avoid formation of manganese(IV) dioxide since the concentration of the Mn–OH precursor has been decreased.

There are a number of strategies for preventing precipitation of manganese(IV) dioxide in scH_2O. The first involves designing a flow reactor for the best possible mixing between the methyl aromatic, dioxygen and the catalyst.[11,12] One can also apply one or more of the methods used currently in acetic acid/water solvents. 1) By increasing the bromide concentration by addition of a bromide source to manganese, i.e., increasing the ratio Br/Mn so that the rate of reduction of Mn(III) to Mn(II) by the bromide ions [Eq. (9)] is increased relative to the rate of disproportionation of Mn(III) to Mn(II) and Mn(IV), Eq. (7). 2) By finding an optimum pH, see discussion above. 3) By adding metals which have a higher Lewis acidity than manganese(IV). In the presence of a strong Lewis acid metal M (i.e., V, Ce, Zr, Fe),[19,23] the concentration of manganese hydroxides Mn–OH, formed by hydrolysis of the Mn salt and precursor of Mn oxides, is reduced:

$$\mathrm{Mn(IV)\text{-}OH} + \mathrm{M(H_2O)} \longrightarrow \mathrm{Mn(IV)\text{-}H_2O} + \mathrm{M\text{-}OH}.$$

Results and Discussion

Since several of the products from *p*-xylene oxidation, particularly terephthalic acid, are poorly soluble in cold water, it is necessary to quench the hot reaction mixture with an NaOH aqueous solution at the end of our flow reactor.[9–12] The sodium hydroxide reacts with the aromatic acids to form water-soluble sodium

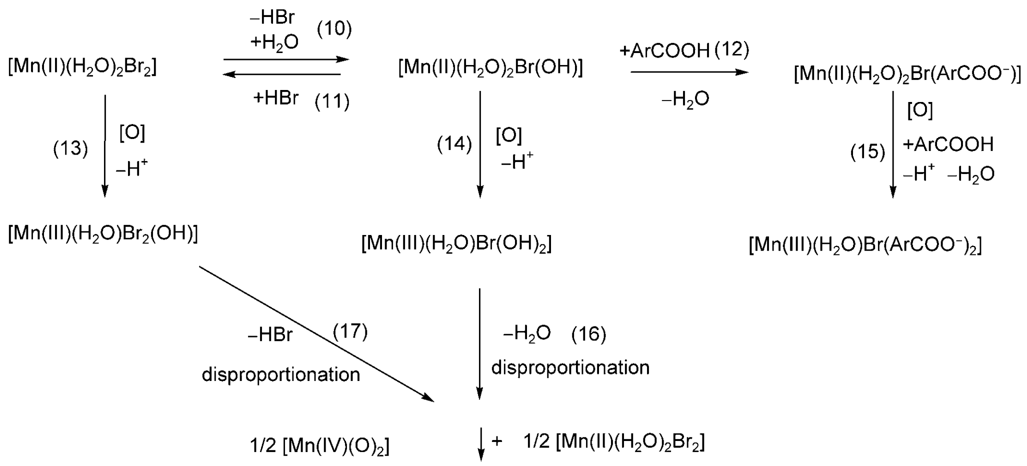

Figure 1. A model that rationalises the observed effects of bromide and aromatic acid addition to a Mn/Br catalyzed oxidation of *o*-xylene. '[O]' represents an oxidant such as a peroxy radical or a peroxide. ArCOOH is an aromatic carboxylic acid (not an aliphatic carboxylic acid such as acetic acid).

salts. However, this quench also causes any dissolved catalyst to precipitate as metal hydroxide/oxides in the heat exchanger at the end of the reactor. To avoid this problem, it was decided to study the continuous oxidation of *o*-xylene to *o*-phthalic acid (OPA),[31,32] because water-soluble products can be obtained under similar oxidation conditions without using sodium hydroxide. This switch from the *para* to the *ortho* isomer allowed a direct analysis of the metal content in the collected homogeneous samples by atomic absorption. Figure 2 gives the observed intermediates and products from *o*-xylene oxidation. *o*-Xylene is different from *p*-xylene in that the phthalide (PTL, the internal ester) can form, which can be either oxidised to *o*-phthalic acid directly or hydrolysed and oxidised to 2-CBA. *o*-Xylene is also different from *p*-xylene in that the rates of thermal decarboxylation, Eq. (18),[33] and catalytic decarboxylation[27] are both faster for *o*-phthalic acid than terephthalic acid.

Benzoic acid is the product of both Eq. (18) and Eq. (19). Benzoic acid, a product which is always seen in these oxidations, is also produced *via* the non-catalysed thermal decomposition of the hydroperoxides.[28]

To enhance our understanding of the factors that influence the stability, i.e., solubility of the manganese, we first present data in the absence of *o*-xylene, see Table 1. One is observing the intrinsic solubility of manganese(II) bromide in the absence of the reaction intermediates and products shown in Figure 2. Benzoic acid has limited solubility at room temperature,[34] so the feed mixture of manganese(II) bromide and benzoic acid was heated to 80 °C to obtain a homogeneous solution prior to its entry into the reactor. From Table 1 the following points are clear. 1) Without dioxygen present, 12% of the manganese precipitates, presumably as manganese(II) oxide/hydroxide see entry 1. So the manganese(II) bromide itself is slightly insoluble under these conditions. 2) When the

$$\mathrm{HOOCArCOOH} \longrightarrow \mathrm{HOOCArH} + \mathrm{CO_2} \qquad (18)$$

$$\mathrm{HOOCArCOOH} + \mathrm{Mn(III)} \longrightarrow \mathrm{HOOCAr^{*}} + \mathrm{CO_2} + \mathrm{Mn(II)} + \mathrm{H^{+}} \qquad (19)$$

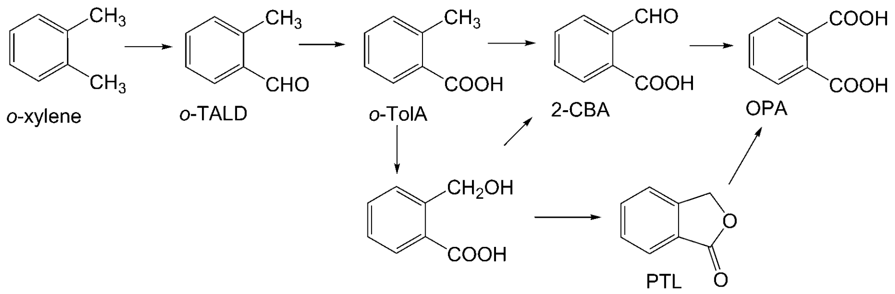

Figure 2. Oxidation pathway of *o*-xylene to *o*-phthalic acid (OPA)

Table 1. The effect of benzoic and hydrobromic acid on the stability of manganese(II) bromide under SCWO conditions in the absence of *o*-xylene. Initial concentration of Mn in reactor is 10.3 mM.

Entry	[BA], mM	O_2 (Y/N)[b]	BA/Mn [mol/mol]	Br/M [mol/mol]	BA recovery [%][c]	Mn recovery [%][d]	Colour
1	0	N	0.00	2.00	–	88	colourless
2	0[a]	N	0.00	2.40	–	99	colourless
3	0.0246	N	0.80	2.00	99	84	colourless
4	0.0409	N	1.32	2.00	99	99	colourless
5	0.0819	N	2.65	2.00	98	99	colourless
6	0	Y	0.00	2.00	–	48	yellow
7	0[a]	Y	0.00	2.40	–	66	yellow
8	0.0123[a]	Y	0.40	2.40	99	60	yellow
9	0.0409	Y	1.32	2.00	98	85	pink
10	0.0819	Y	2.65	2.00	95	90	pink

[a] Addition of 4.17 mM HBr.

[b] Oxygen feed, Y = yes, N = no.

[c] Determined by HPLC analysis.

[d] Recovered manganese as determined by atomic absorption.

experiment is repeated with O_2 present, entry 6, then 52% of the manganese precipitates. So about $52-12=40\%$ of manganese has been oxidised to either manganese(III) or manganese(IV). We conclude that the pH is sufficiently high that spontaneous oxidation of manganese(II) can occur. Evidence that oxidation has occurred is also indicated by the change in colour of the effluent from colourless to yellow. This colour could be from the oxidation of manganese or bromide or both. The dioxygen to manganese molar ratio is 3 under these conditions. 3) Addition of hydrobromic acid to the manganese(II) bromide, in a molar ratio of 0.4 HBr:$MnBr_2$, significantly increases the recovery of the manganese(II) bromide, from 88% to 99% in the absence of dioxygen (entries 1 and 2), and from 48% to 66% under dioxygen (entries 6 and 7). So a decrease in pH does indeed enhance the solubility suggesting the formation of Mn(II) hydroxides does occur, see Eq. (11) of Figure 1. It should be noted that the acid strength of hydrobromic acid is probably substantially diminished at these high temperatures similar to what has been observed for hydrochloric acid.[39] 4) Similarly, addition of benzoic acid either in N_2 or O_2, enhances the solubility of the $MnBr_2$, compare entries 1 with 3, 4 and 5 and entry 6 with 9 and 10. This change in recovery suggests the incorporation of the benzoic acid into the coordination sphere of manganese(II), see Eq. (12) of Figure 1. There will be a increase in pH as well since aromatic acids still have measurable acid character at high water temperatures.[39] Under dioxygen, the colour also changes from yellow to pink with increasing benzoic acid content consistent with less oxidation of manganese(II) to manganese(III). 5) The recovery of the benzoic acid after the experiment is close to quantitative. This suggests that thermal or catalytic decarboxylation of benzoic acid is not occurring under these experimental conditions.

In Table 1, it was demonstrated that the addition of benzoic acid to manganese(II) bromide enhanced the manganese recovery and hence its solubility.[32] In Table 2, the same experiment is performed but now during the oxidation of *o*-xylene. The same phenomenon is seen – manganese recovery increases with increasing benzoic acid concentration from 76% without benzoic acid monotonically increasing to 97% with benzoic acid present, see entries 1–4 in Table 2. Table 2 also illustrates that a number of different aromatics have an identical effect on solubility – *o*-phthalic acid (OPA) (entries 5 and 6), trimellitic acid (TMA) (entry 7), mellitic acid (MLA) (entry 8). The non-aromatic acid, acetic acid (AA) (entry 9), decreases the solubility. Along with the increase in manganese solubility, a modest increase in *o*-phthalic acid (OPA) yield and selectivity is observed when an aromatic acid is present, while the presence of acetic acid significantly decreases the yield.

One would anticipate that the solubility of manganese during *o*-xylene oxidation to be higher because *o*-toluic acid and *o*-phthalic acid are forming as one proceeds down the tubular reactor. As confirmation of this, the solubility of manganese is 76% during the oxidation of *o*-xylene (entry 1, Table 2) while it is only 48% in its absence (entry 6, Table 1).

Addition of benzoic acid and the other aromatic acids further enhanced the solubility because the Mn-aromatic acid interaction occurs when the reagents are mixed together at the beginning of the reactor before oxidation has formed significant amounts of aromatic acids. The enhanced yield to *o*-phthalic acid seen in Table 2 may be due to three effects – the decreased amount of catalyst precipitation will provide

Table 2. The effect of selected carboxylic acids on the oxidation of *o*-xylene and manganese recovery in scH_2O. Catalyst was manganese(II) bromide at an initial concentration of 10.3 mM.

					Selectivity [%][a]						Mn [%][b]
Entry	Acid[c]	[Acid], mM	Acid/Mn [mol/mol]	OPA Yield [%]	OPA	2-CBA	PTL	BA	*o*-TolA	TALD	
1	None	0.0	0.0	62	91.8	1.0	0.8	6.2	–	0.0	76
2	BA	8.2	0.8	73	92.0	1.0	2.1	3.4	1.3	0.0	78
3	BA	13.6	1.3	70	94.0	0.8	1.3	2.9	0.7	0.2	94
4	BA	27.3	2.7	72	92.4	0.5	0.8	6.2	0.0	0.0	97
5	OPA	14.1	1.4	74	93.7	0.6	3.4	3.4	0.8	0.0	88
6	OPA	23.3	2.3	78	96.5	0.5	1.3	1.2	0.4	0.0	91
7	TMA	13.7	1.3	73	94.3	0.3	1.1	3.8	0.5	0.0	94
8	MLA	2.3	0.2	70	94.4	0.4	1.0	3.7	0.3	0.0	92
9	AA	55.6	5.4	43	95.8	0.4	2.7	1.0	1.0	0.0	64

[a] Selectivity for the identified aromatic compound calculated as the molar concentration of that compound relative to the total molar concentration of all identified aromatic compounds.

[b] Recovered manganese as determined by atomic absorption.

[c] BA = benzoic, OPA = *o*-phthalic, TMA = trimellitic (1,2,4-tricarboxybenzene), MLA = hexacarboxybenzene, AA = acetic acid.

a more active catalyst (due to its higher concentration), decreased unselective oxidation due to the precipitated Mn oxide solids, and a change in structure of the catalyst that could be more active and/or selective. In the model given in Figure 1, this could occur *via* Eq. (12). There are other possibilities such as the reaction given in Figure 3 where hydrobromic acid is released which could further enhance the solubility of the Mn.

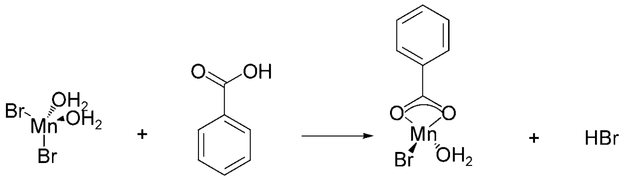

Figure 3. The possible reaction of benzoic acid with the Mn^{n+} centre in scH_2O.

The equilibrium constants for the formation of metal-carboxylate complexes in ambient water are small but are much higher in non-aqueous solvents such as acetone.[35] This suggests that the formation of metal-carboxylate complexes in scH_2O could be quite favourable.

Significantly higher manganese precipitation and lower yields are observed in the presence of acetic acid. It is not obvious to us why this should be so, since the opposite effect is seen with aromatic acids. The acidity of benzoic acid ($K_d = 6.5 \times 10^{-5}$) is somewhat higher than acetic acid ($K_d = 1.8 \times 10^{-5}$) in ambient water, but both are weak acids.[35] The acidity of acetic acid is reduced as the temperature of water increases hence may be substantially different from that of benzoic acid at the temperatures used in these experiments.[39] More subtle structural differences in the coordination chemistry, for example, the steric bulk of the aromatic ring, which affect the precipitation of the metal, may also be present.

The data in Table 2 are consistent with an insignificant amount of thermal decarboxylation occurring during the reaction. The relative degrees of thermal decarboxylation are trimellitic acid $\gg$ *o*-phthalic acid $>$ benzoic acid.[33] The product of thermal decarboxylation of *o*-phthalic acid is benzoic acid. Addition of *o*-phthalic acid to the oxidation of *o*-xylene did not increase the selectivity to benzoic acid, as can be seen by comparing entry 1 with entries 5 and 6 in Table 2. The data are also consistent with the fact that catalytic decarboxylation, although it is almost certainly occurring, is not a dominant reaction. Catalytic decarboxylation causes a decrease in rate of reaction because Eq. (9), which propagates the reaction, is in competition with the manganese(III) in the catalytic decarboxylation, see Eq. (19). It is established that, during the Co/Mn/Br-catalysed oxidation in acetic acid, the addition of aromatic acids decreases the relative rate of reaction in the order: benzoic acid (1.0) $<$ *o*-phthalic acid (2.2) $<$ trimellitic acid (3.8) $<$ hemimellitic acid (1,2,3-tricarboxybenzene; 16). Thus one might expect to see lower yields in the presence of *o*-phthalic acid, trimellitic acid, and mellitic than when benzoic acid is present. This was not observed. The effect of addition of aromatic carboxylic acids, $ArCO_2H$, has also recently proved to be beneficial for improving the activity of the Mn/Co-catalysed air oxidation of cyclohexane to adipic acid.[36]

In Table 1, we found that both benzoic acid and hydrobromic acid increased the solubility of manganese(II) bromide in the presence of air even without *o*-xylene present. In Table 3, we confirmed that addition of hydrobromic acid also increased its solubility during the oxidation of *o*-xylene with a resulting increase in *o*-phthalic acid yield and selectivity, compare entry 1 with entries 2 and 3. The yield is lower at a Br:Mn ratio of 4.0 than at 2.4 (entries 3 and 2, respectively) possibly because the pH is too low and too far from its optimum value (see discussion above). Other interpretations are also possible. The recation of thermal decarboxylation is acid catalysed,[33] so this rate

Table 3. Oxidation of *o*-xylene with different catalytic mixtures. Initial concentration of manganese in reactor is 10.3 mM.

Entry	Catalyst	Br/Mn [mol/mol]	Yield [%]	Selectivity [%][a]					Mn [%][b]
				OPA	2-CBA	PLT	BA	*o*-TALD	
1	$MnBr_2$	2.0	62.4	91.8	1.0	0.8	6.2	0.0	76
2	$MnBr_2$+HBr (4.17 mM HBr)	2.4	66.0	93.4	0.2	0.8	5.6	0.0	88
3	$MnBr_2$+HBr (20.8 mM HBr)	4.0	64.5	91.5	0.7	0.7	7.1	0.0	99
4	$MnBr_2$+HCl (20.8 mM HCl)	2.0	63.9	94.4	0.5	0.4	4.6	0.0	85
5	$MnBr_2$+NaBr (4.17 mM NaBr)	2.4	58.3	73.3	0.8	3.9	21.9	0.0	61
6	$Mn(OAc)_2$	0.0	8.0	21.3	5.7	61.2	7.6	4.1	14
7	$Mn(OAc)_2$+HCl (20.8 mM)	0.0	16.8	28.2	14.4	53.4	1.8	2.2	49
8	$Mn(OAc)_2$+HBr (20.8 mM)	2.0	63.4	80.4	0.2	1.0	18.3	0.0	89

[a] Selectivity for the identified aromatic compound calculated as the molar concentration of that compound relative to the total molar concentration of all identified aromatic compounds.

[b] Recovered manganese as determined by atomic absorption.

could be increasing, which is consistent with the higher observed benzoic acid selectivity. Also the HPLC analysis suggests that brominated by-products may have also formed, accounting for the lower yield. A non-bromide-containing mineral acid, hydrochloric acid, also increases the manganese recovery and increases the yield, compare entries 1 and 4. Sulfuric acid, H_2SO_4, was also tried, but the reactor tubing rapidly become plugged due to formation of insoluble manganese(II) sulfate. Addition of sulfuric acid to a Co/Mn/Br catalyst in acetic acid also causes precipitation of the metals as their sulfates. The replacement of hydrobromic acid by sodium bromide results in a dramatic decrease in Mn solubility as well as lower *o*-phthalic acid yield and selectivity, see entries 2 and 5. This clearly demonstrates that there is a pH effect present in these reactions. At 380 °C, sodium chloride increases the pH of water because one is adding chloride,[39] which is the anion of a weak acid, hydrochloric acid. A similar increase in pH is probably also occurring when sodium bromide is being added in these experiments. The unusually high selectivity to benzoic acid in entry 5 may be due to the large decrease in catalytic activity which leads to the unselective formation of toluene, and its subsequent oxidation to benzoic acid.[28]

In acetic acid, the manganese(II) acetate catalyst has very weak activity, while manganese(II) bromide is much more active.[17a,37] The same is true in scH_2O, see entries 1 and 6 in Table 3. However, in acetic acid, both manganese(II) acetate and bromide are completely soluble at these concentrations and one is observing the intrinsic activity of these catalysts. This is NOT true in scH_2O because the solubility of the catalyst is increasing as the yield increases, i.e., in entry 1 we have a yield of 62% with a manganese recovery of 76% and in entry 6 we have a yield of 8% with only 14% manganese recovery. Since yield generally increases with catalyst concentration, one cannot tell whether this reflects the intrinsic catalytic activity or merely the change in catalyst concentration. (We are assuming that the precipitated catalyst does not have significant activity). Thus the relative activities of catalysts in acetic acid and scH_2O are in the same order. However in acetic acid, one is comparing the intrinsic activities of the homogeneous catalysts because they are 100% soluble. But in scH_2O they are not completely soluble and the relative activities of the catalysts and their relative solubilities are the same. So one cannot deduce the intrinsic activities of the catalysts in scH_2O.

Another example can be seen in entries 6–8 in Table 3 where one compares the addition of hydrochloric acid and hydrobromic acid to a manganese(II) acetate catalyst. The relative activity of the catalysts, based either on the yields or selectivities, is Mn/Br > Mn/Cl > Mn. This is the same as is found in acetic acid.[17a,37] But a confounding factor in scH_2O is that solubility of the catalyst occurs in the same order: Mn/Br > Mn/Cl > Mn. So we cannot assign an intrinsic activity to these catalysts in scH_2O because of the concentration differences of the homogeneous catalyst. In acetic acid, the Mn/Cl catalyst is less active than the Mn/Br because the reaction of manganese(III) with chloride is much slower than with bromide and because the Cl(0) species is much less selective than Br(0).[17a,37]

Table 4 demonstrates that, using manganese(II) acetate/hydrobromic acid mixtures, increasing the Br:Mn ratio up to a value of 1.6 increases the yield but the selectivity continues to increase up to a Br:Mn value of 2.4. The solubility of the Mn also increases in this order. Changing the bromide:metal ratio is a common method for optimising metal/bromide catalysts and many studies have been reported for different methyl aromatic compounds.[17] Generally one finds that increasing the bromide:metal ratio increases the activity and selectivity up to some maximum value and beyond that maximum the activity either remains constant or decreases. This is also what is seen in Table 4, but again we have the problem that the solubility of the catalysts is in the same order as

Table 4. Oxidation of *o*-xylene with catalytic mixtures of manganese(II) acetate and hydrobromic acid.

Entry	% Org.w/w	[Br] mM	[Mn] mM	Br/Mn [mol/mol]	OPA Yield [%]	Selectivity [%][a]					Mn [%][b]
						OPA	2-CBA	PTL	BA	*o*-TALD	
1	0.44	0.0	10.3	0.0	8.0	21.3	5.7	61.2	7.6	4.1	14
2	0.44	4.2	10.3	0.4	39.1	54.5	4.5	27.2	13.8	0.0	11
3	0.44	12.5	10.3	1.2	60.0	64.6	2.7	17.2	15.4	0.1	64
4	0.44	16.7	10.3	1.6	64.9	73.6	1.6	7.0	17.8	0.0	70
5	0.44	20.9	10.3	2.0	63.4	80.4	0.2	1.0	18.4	0.0	89
6	0.44	25.0	10.3	2.4	63.6	87.8	< 0.1	0.2	11.9	0.0	87
7	0.44	20.9	7.3	2.8	56.8	73.3	2.4	7.9	16.4	0.0	93
8	0.26	20.9	7.3	2.8	57.9	84.2	0.5	0.0	13.1	2.2	69

[a] Selectivity for the identified aromatic compound calculated as the molar concentration of that compound relative to the total molar concentration of all identified aromatic compounds.

[b] Recovered manganese as determined by atomic absorption.

the observed activity in acetic acid, making any definitive conclusion regarding the intrinsic activity of the catalyst impossible.

One can say that increasing the bromide concentration in the coordination sphere of the Mn does increase the solubility of the catalyst. As increasing amounts of hydrobromic acid are added to manganese(II) acetate, the reactions shown in Figure 4 probably occur. So one is dealing with at least three different catalyst species - with each probably having a different intrinsic activity/selectivity. Apparently one undesirable characteristic of starting with a manganese(II) acetate catalyst is that, at high conversion of the *o*-xylene, the yield and selectivity to benzoic acid is unusually high. This can be seen from entries 2–8 in Table 4; an even clearer example is entry 1 in Table 3 where one initially starts with a manganese(II) bromide catalyst and obtains an *o*-phthalic acid yield of 62% with a benzoic acid selectivity of 6% while, in entry 5 in Table 4 with a $Mn(OAc)_2/2HBr$ mixture, one obtains an *o*-phthalic acid yield of 63% but the a much higher benzoic acid selectivity at 18%. As previously discussed, benzoic acid can arise from three sources, see Eqs. (18) and (19). Why the rates of one or more of these reactions should be changed when one starts with manganese(II) acetate awaits further understanding of the chemistry and catalytic behaviour of the different catalytic species.

A further run was conducted using sodium bromide as co-catalyst with manganese(II) acetate but the reactor blocked very quickly due to the precipitation of the catalyst and also perhaps because of the insolubility of sodium bromide in scH_2O, demonstrating that both acidity and a high bromide content are required to avoid precipitation of the catalyst.

Table 5, entries 1–3 illustrate the effect on manganese solubility when *o*-xylene, dioxygen and catalyst are passed into the continuous reactor, the reaction is allowed to come to steady state, but then the *o*-xylene feed is turned off. An abrupt decrease in the manganese recovery, i.e., an increase in precipitation of the manganese, is observed in the absence of *o*-xylene. Comparison of entries 1 with 4 or 2 with 5 illustrates that the effect is reversible. Based on the discussion above, the results are unsurprising since aromatic acids are being generated in increasing concentration as one moves down the tubular reactor and we have already shown that the aromatic acids help to keep the manganese in solution, see Table 2. Another factor which helps to keep the manganese soluble is that the manganese(III)–(IV) species in solution are constantly being reduced to manganese(II) by their reaction with bromide, see Eq. (9). With metal/bromide catalysts in acetic acid, the steady-state concentration of the metals in the higher oxidation states is virtually zero; during Mn/Br-catalysed autoxidation of methyl aromatics in acetic acid, the solution is colourless, i.e., the steady state concentration of manganese is essentially 100% manganese(II). Without bromide, a manganese(II)-catalysed autoxidation reaction appears brown, i.e., contains a mixture of manganese(II), manganese(III), and manganese(IV). The same is probably occurring in scH_2O, which accounts for the increased solubility of the manganese when *o*-xylene is being oxidized.

Table 5. Effect of switching the *o*-xylene feed on or off on the manganese recovery. The initial concentration of manganese in reactor is 10.3 mM.

Entry	Catalyst	*o*-Xylene stream (On/Off)	Mn [%][a]
1	$MnBr_2$	On	75
		Off	18
2	$MnBr_2$+HBr (4.17 mM)	On	90
		Off	52
3	$MnBr_2$+HCl (4.17 mM)	On	84
		Off	47
4	$MnBr_2$	Off	20
		On	75
5	$MnBr_2$+HBr (4.17 mM)	Off	25
		On	92

[a] Recovered manganese as determined by atomic absorption. After 20 min equilibration time, 5 samples were taken, one every 10 min, and the results averaged.

Conclusions

This study has shown that the activity and the recovery of a manganese(II) bromide catalyst can be improved by addition of aromatic acids, by mineral acids (HCl, HBr), and by increasing the Br:Mn ratio during the Mn/Br-catalysed oxidation of *o*-xylene in scH_2O. This result can probably be extrapolated to different kinds of metal/bromide-catalysed oxidation of methyl aromatics in scH_2O, particularly, the commercially more interesting oxidation of *p*-xylene to terephthalic acid.

$$[Mn(H_2O)_2(OAc)_2] \xrightarrow[-HOAc]{HBr} [Mn(H_2O)_2(OAc)(Br)] \xrightarrow[-HOAc]{HBr} [Mn(H_2O)_2(Br)_2]$$

Figure 4. Proposed reactions occurring when increasing the amount of HBr added to Mn/Br catalyst.

In this study, hydrobromic acid proved to be the most effective acidic co-catalyst because it is a source of both bromide and acidity. The bromide provides activity and selectivity to the reaction; the acidity plays a more complex role because there is an optimal pH for maximum catalyst activity and selectivity, and because a low pH increases the solubility of the catalyst.

Aromatic acids also increase the solubility of the manganese catalyst not only because they are acids but also because they probably enter the coordination sphere of the metal. Benzoic acid is particularly favoured because it is produced in the reaction as a by-product and eventually must be separated from the terephthalic acid.

This discovery offers the opportunity of using benzoic acid to limit the use of high bromide concentrations that could accelerate the rate of corrosion of the reactor tubing in scH_2O.[38] Three examples are given where the activity of different catalysts in scH_2O are in the same order as those in acetic acid. One important difference however, is that in acetic acid the catalysts are 100% soluble, while in scH_2O the trend of increased activity has the same trend as increased catalyst solubility. So the trend of increased activity in supercritical water coincides with an increased concentration of homogeneous catalyst as well.

Experimental Section

Caution: High pressure oxidation experiments are potentially hazardous. It is the responsibility of individual researchers to ensure that their equipment is suitable and safe to operate under these conditions.

All chemicals (Sigma–Aldrich UK Ltd.) were used without further purification. All the experiments were conducted using a tubular continuous flow reactor, similar to the one that has been previously described.[11,12] Experimental work was carried out on the continuous oxidation of *o*-xylene by O_2 in scH_2O at about 380 °C and 230 to 240 bar with a combined catalyst and acid solution. In a typical experiment, 56 mL of 100 volume H_2O_2 solution (>30% w/v) commercially available from Fisher Scientific UK Ltd. was mixed with 760 mL deionised H_2O. The H_2O_2 solution was pumped into the system and decomposed in a pre-heater under the required experimental conditions to generate a homogeneous mixture of O_2 and scH_2O. This corresponds to an O_2 concentration of 0.276 mol/L (1.5 molar equivalents of the stoichiometry required for oxidation of the *o*-xylene to *o*-phthalic acid, i.e., 3 O_2/*o*-xylene). The full decomposition of H_2O_2 to O_2 was demonstrated by measuring the volume of gas and liquid exiting the reactor. Individual flow rates were: H_2O (or H_2O_2), 8 $mL\,min^{-1}$; Mn/Br solution (containing either mineral or organic acids), 4 $mL\,min^{-1}$; pure organic, 0.06 $mL\,min^{-1}$ which gave 0.5% v/v organic/H_2O at the mixing point. The total volumetric flow rate (total FR) after mixing was about 12 $mL\,min^{-1}$. A hot-catalyst feed system was used when aromatic carboxylic acids were used (typically for acid concentrations greater than 1500 ppm in the catalyst feed solution). A 100 W band heater was placed around the catalyst feed pipe (1/8 inch), controlled by a VARIAC® (100 V needed to reach 80 °C). Hot water (80 °C) was circulated around the catalyst pump head to prevent any crystallisation of the acids used.

Before each run, the apparatus was hydrostatically pressure-tested when cold, and was then heated with a flow of pure water (5–10 $mL\,min^{-1}$). Once the operating temperature had been reached, H_2O_2/H_2O was fed into the reactor and the pumps for *o*-xylene and acid/catalyst were started, typically in that order. The residence time for each run remained constant, typically up to 1 min, but in most cases 5–10 seconds.

Precipitated species (mainly in the form of manganese oxides) were continuously filtered during the reaction *via* an on-line filter placed after the cooler.[11,12] The resulting aqueous solution of products exiting the reactor *via* the back pressure regulator was then sampled for periods of 2 min every 10 min and analysed by HPLC and atomic absorption.

HPLC analysis was carried out on a Hewlett Packard 1050 Series HPLC apparatus from Agilent Technologies UK Ltd. equipped with an XTerra® RP18 3.5 μm, 30 × 150 mm column and an oven at a temperature of 40 °C; detection was at 254 and 230 nm. Every compound (acid and intermediates) was calibrated by HPLC prior to analysis of the samples. The actual yield was calculated by HPLC as a percentage of the expected yield based on the measured amount of organic and water pumped into the apparatus. Selectivity is defined as the molar amounts of each aromatic compound as measured by HPLC given on a percentage basis.

For the atomic absorption analysis, the aqueous samples were filtered using disposable membrane syringe filters and appropriately diluted with water to suit the operating conditions of the atomic absorption apparatus, which was calibrated with freshly prepared Mn standards (5, 10, 15 ppm Mn in water) from commercially available Mn aqueous solutions. Mn concentrations were then measured based on this calibration. The yields of Mn were calculated from the flow-out of Mn divided by the flow-in of Mn where the concentration of Mn was measured by atomic absorption. The average yields and selectivities of the samples collected during each run are quoted in the tables.

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